Eutrophication from Agriculture Sources 2000-LS-2-M2

FINAL REPORT

Nitrate Leaching – Groundwater
(2000- L S 2.3.1.3-M2)

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Prepared for the Environmental Protection Agency

by

Department of Civil, Structural and Environmental Engineering, Trinity College Dublin (TCD)

Authors:

Pamela Bartley and Paul Johnston

ENVIRONMENTAL PROTECTION AGENCY

An Ghníomhaireacht um Chaomhnú Comhshaoil

PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353-53-60600 Fax: +353-53-60699

Email: info@epa.ie Website: www.epa.ie

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Project Structure

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, focussed on different subsurface zones, at a fully productive 50ha dairy farm called Curtin's farm, which is situated in an intrinsically vulnerable area. This project [Project reference: M1-LS-2.3.1] was envisaged as part of a first-step towards systems-scale research appropriate to the Nitrates Directive. Work commenced in November 2000 for three years. Firstly, a farm-scale soil-drainage-water study, led by 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. A team from National University of Ireland, Galway (NUIG), led by 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. It is that groundwater component of the nitrogen research project that is presented, in summary format, in this report.

The integrated project was overseen by a representative of the EPA, co-ordinated by Owen Carton and reviewed by an international steering committee with expertise in agronomic research and nitrogen efficiency. In 2006 the integrated results from the three concurrent projects will be reported and published by the EPA.

Details of Project Partners (LS 2.3.1.3–M2)

Pamela Bartley
Department of Civil, Structural and
Environmental Engineering
Trinity College
Dublin 2.
Tel: +353-87-8072744
Email: pamela@bosenvironmental.com

Paul Johnston
Department of Civil, Structural and
Environmental Engineering
Trinity College
Dublin 2.
Tel: +353-1-6081372
Email: pjhnston@tcd.ie

Details of Project Team (LS 2.3.1–M2)
Co-ordinator:

Owen Carton
Teagasc
Johnstown Castle

Wexford
Tel: +353-1-53-71260
Email: ocarton@johnstown.teagasc.ie

LS 2.3.1.1 Group Contact
Michael Ryan
Teagasc
Johnstown Castle
Wexford
Tel: +353-1-53-71256
Email: mryan@johnstown.teagasc.ie

LS 2.3.1.2 Group Contact
Michael Rodgers
Department of Civil Engineering
National University of Ireland
Galway
Tel: +353-91-492219
Email: michael.Rodgers@nuigalway.ie

Summary

A considerable body of research already exists on establishing nitrate dynamics in agricultural systems' subsoils. However, the capacity to predict rates of nitrogen (N) arrival at the receiving environment, namely surface or groundwaters, has been elusive in an Irish context. A farm-scale (50 ha) 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 2.5 m, on average, but undulates in depth from 0-4.5 m, consistent with the karst terrain. Part of the farm is located within a source protection zone delineated for a public supply borehole located 1.5 km to the northeast, in the direction of groundwater flow. This public supply borehole has demonstrated an upward trend in nitrate-nitrogen (NO_3-N) concentrations over the last twenty years, with periodic breaches, in the last decade, of the EU parametric limit of 11.3 mg/l for potable water (EC, 1998). However, this research was commissioned by the EPA with regard to the contribution of dairy farming agriculture to eutrophication of water resources and not with regard drinking water legislation. The appreciably lower 2.6 mg/l N eutrophication criteria for tidal freshwaters (EPA, 2001) must be acknowledged when evaluating groundwater nitrate (NO_3) concentrations beneath agricultural lands. Ireland has yet to define hydrochemical criteria for definition of groundwater 'good status', with respect to the Water Framework Directive (EC, 2000). However, the EPA has set 25mg/l NO_3 (equivalent to 5.6mg/l NO_3-N) as the Interim Guideline Value (IGV) towards protection of groundwater.

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, 27-30 m below ground level (bgl), that was isolated from contamination from the ground surface using bentonite and cement grout seals. The water table is 25 m bgl, on average, and has a maximum annual range of 15 m. 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 farm stocking density was ~2.4 Livestock Units (LU)/ha and all plots on the farm received 290 kg /ha, on average, as inorganic N fertiliser. There was large spatial variation in the organic N loading rates in each of the four management zones mentioned.

For the 2001-2002 hydrological year NO_3-N concentrations in groundwater ranged from 3-31 mg/l, depending on the location of the borehole within the 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 (R_{eff})fell in the winter of the second year, as compared to the first winter. Averaging all piezometer groundwater NO_3-N concentrations over the entire farm showed that the means were 16.5 mg/l in the first year and 12.6 mg/l in the second year. Groundwater levels rise by up to 8 m within one month of the heavy block of winter recharge, observed to be 200 mm in the wettest winter month in both years. Spring and summer recharge events also increased groundwater levels. The observed groundwater nitrate response at Curtin's farm has a clear temporal dimension. Groundwater NO_3-N 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 the NO_3-N concentrations caused by winter recharges, they were observed to increase again later. There was a rapid response to groundwater loadings. Moreover, the groundwater NO_3-N response was discernible in correspondence to differing agricultural practices – being highest in the areas of highest organic N loading. At the field scale there was a strong relationship between grazing intensity and the following year's average NO_3-N

concentration. An agricultural signature in the groundwater is evident at some locations. In addition to high NO_3-N concentrations, spikes in groundwater concentrations of phosphorus (P), potassium (K), ammonium (NH_4) and nitrite (NO_2) were observed in response to recharge events, which again suggests a highly vulnerable hydrogeological setting.

A tracer study indicated dual flow mechanisms in the subsoil: preferential flow and flow through the soil matrix. The tracing investigation also proved connectivity between some piezometers and horizontal groundwater velocity was measured to be ~8 m/day. In these conditions, the NO_3-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 NO_3-N concentrations found in the groundwater indicate that farming practices as conducted in 2001 and 2002 in vulnerable environments, such as Curtin's farm, need to be modified in order to ensure future compliance with the Nitrates Directive (EEC, 1991a). With respect to identification of the loadings that most significantly influenced groundwater NO_3-N concentrations – R_{eff}, or hydraulic loading, and the intensity of animal grazing were identified as the main drivers in the system. The organic N-loading rate is a crucial manageable factor in controlling N loss to groundwater. This finding supports the aim of the Nitrates Directive (EC, 1991a) to restrict grazing intensity in vulnerable areas. The importance of the N contributions and hydraulic loadings by grazing animals should not be ignored in future.

The risk assessment concept was progressed by successful testing of the RAM model (ESI, 2000) for the karstified hydrogeological system at Curtin's farm. The agronomic NCYCLE model (Scholefield et al., 1991) was validated as an adequate source term model for definition of peak porewater nitrate concentrations in the root zone.

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Units and Abbreviations

Metric units are used throughout this report.

AOD	Above Ordinance Datum
bgl	Below ground level
BHC.	Bore Hole at Curtins Farm
Br	Bromide
d	day
DAF	Department of Agriculture and Forestry
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
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
EQS	Environmental Quality Standard
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)
m^2	area, metres squared
mg	milligram
N	Nitrogen
NFGWS	National Federation of Group Water Schemes
NGQMP	EPAs' national groundwater-monitoring programme
NH_4-N	Ammonium-Nitrogen
NO_2-N	Nitrite-Nitrogen
NO_3-N	Nitrate-Nitrogen
NRC	National Research Council
NUIG	National University of Ireland Galway
NVZs	Nitrate Vulnerable Zones
OPW	Office of Public Works
P	Phosphorus
REPS	Rural Environmental Protection Scheme
R_{eff}	Effective Rainfall
SMD	Soil Moisture Deficit
SPZ	Source Protection Zone
TD	Total Depth
µg	microgram
USDA	Unites States Department of Agriculture
yr	year

NOTE

Data pertaining to BHC.10 is included in the appendices to this report but was not considered in the final analyses because of a structural failure in the borehole that occurred mid-way through the experiment (see Bartley, 2003).

1. Introduction

Groundwater is an important national resource, supplying Irish local authorities and private rural dwellers with drinking water and providing industry with a 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, 2003).

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. In 2002, Ireland produced eight times more beef and ten times more milk, than was required to meet national needs (DAF, 2003). Of all industries in Ireland, agriculture produces the largest quantity of waste. 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).

Farmers apply nitrogen (N) to enhance plant growth. 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 and Horton, 2000). Nitrate (NO_3) leaching is now believed by many (Spalding and Exner, 1993; Heathwaite *et al.*, 1996; Zhang, *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). Excess NO_3 can easily be washed out of the root zone and displaced into the groundwater with percolating water (Wendland *et al.*, 1998) because the negatively charged clay ion repels the similarly negatively charged NO_3 ion, which is soluble in water and highly mobile (Kolenbrander, 1981). Groundwater is the usual receiving environment for NO_3 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 NO_3 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 N and/or phosphorus (P) (EPA, 2001).

Groundwater and agriculture are 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 and 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, 2003). This 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).

Scientists commonly categorise water contamination according to the source of the contaminating nutrient, being a specific location (point) or an extended spatial area (diffuse). Point sources can be identified as a specific point of discharge to the environment, *e.g.* from wastewater treatment plants (House and 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 N from agricultural activities include fertilisers, manure application, and leguminous crops (Almasri and Kaluarachchi, 2003). Diffuse source pollution resulting from agricultural activities, and affecting surface- and groundwaters, has received considerable attention during recent years (Dillon and 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 NO_3 from diffuse sources. Appropriate consideration was given to potential point sources of contamination on the study farm.

1.1. Reasons for Concern about Nitrate

Traditional reasons (*e.g.* WHO, 1984) for limiting NO_3 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-lymphoma in the general population (Ward, *et al.*, 1996). Some (*e.g.* Addiscott, 1999; Mulqueen, 2004) debate the issue of whether NO_3 is indeed a health hazard. However, the real focus and drive of measures to curtail NO_3 loss to the environment are based on the issue of sustainability of natural resources (McGarrigle *et al.*, 2002). This 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).

Groundwater containing high NO_3 concentrations is unfit for human consumption and, if discharging to freshwater or marine habitats, can contribute to algal blooms and eutrophication (Thorburn *et al.*, 2003). 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. 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). Nitrogen and P concentrations in water are factors determining the risk of eutrophication occurring (Archer and Thompson, 1993). Phosphorus is most commonly the key nutrient most limiting and responsible for eutrophication in freshwater bodies (Massik and Costello, 1995). Nitrogen is the element more likely to cause eutrophication in estuaries, coastal ecosystems and marine waters (Howarth, 1988; Brennan *et al.*, 1998; Service *et al.*, 1998; EEA, 2000; McGarrigle *et al.*, 2002).

1.2. 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, 2003).

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, 2003). 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 localised contamination sources. Previous review articles regarding groundwater quality have concluded that NO_3 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, NO_3 contamination problems have been identified, for example in Kildare and Carlow (Thorn and Coxon, 1991), Cork county (Cork County Council, 1998; 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 NO_3 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 and DAF, 2003) under the Nitrates Directive (EEC, 1991a).

1.3. Legislation Protecting Water

Numerous EU Directives impose standards for NO_3 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 aforementioned Directives is that for NO_3, in particular, the parametric value must not exceed 50 mg/l (equivalent to 11.3mg/l as NO_3-N)[1]. A guide level (GL) of 25 mg/l NO_3 (equivalent to 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 EU created another type of Directive to deal with controlling the sources of contamination based on the quality of a receiving environment. The Nitrates Directive (EEC, 1991a) concerns pollution by NO_3 from agricultural sources and the Urban Wastewater Directive (EEC, 1991b) concerns discharges from urban wastewater treatment

[1] The Nitrates 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.

plants. Both of these Directives concern nutrient impact on groundwaters and surface waters with regard to controlling eutrophication.

It is the Nitrates Directive (EEC, 1991a) that most directly relates to the study in hand. The objectives of the Directive are to reduce water pollution caused or induced by NO_3 from agricultural sources and prevent further incidences. Where water bodies have been identified as having breached the 11.3mg/l as NO_3-N limit, or are likely to do so in the absence of pollution controls, and in situations where there is a risk of N contributing to eutrophication, the Directive requires that legally binding measures be taken in respect of farming practices so as to reduce NO_3 loss to waters (DELG and DAFF, 1996). Interestingly, the Nitrates 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 P, rather than NO_3, 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 Nitrates Directive (DEHLG and DAF, 2003). The results of this research are also of relevance to Irish implementation of the Water Framework Directive (EC, 2000). Ireland has yet to define hydrochemical criteria for definition of groundwater ‘good status’, with respect to the Water Framework Directive (EC, 2000). However, the EPA has set 5.6mg/l NO_3-N as the Interim Guideline Value (IGV) towards protection of groundwater.

1.4. Irish Implementation of the Nitrates Directive

It is 13 years since the Nitrates Directive (EEC, 1991a), concerning the protection of waters against pollution caused by nitrates from agriculture, was adopted at European Union level. The Nitrates 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 N application restrictions would apply to specific vulnerable areas only. Ireland was slow to act in either regard. However, Regulations (DEHLG, 2003) 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 Nitrates Directive will be applied. However, in March 2004, the European Court of Justice (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 and DAF, 2004).

Ireland’s ‘Draft Action Programme under the Nitrates Directive’ (DEHLG and DAF, 2003), released for consultation in December 2003, detailed the background to the implementation of the Directive in Ireland, the rationale for the whole country designation and the proposed National Action Programme. Following submissions from interested parties and ECJ rulings, a revised consultation document concerning Ireland’s ‘Action Programme under the Nitrates Directive’ (DEHLG and DAF, 2004) was issued. This later document provides more detail on how and when the actual Action Programme is to be adopted, the proposed schedule of implementation, and details regarding the planned derogation application[2]. The Statutory Instrument (SI 788 of 2005) implementing the Action Programme was signed into law in December 2005.

[2] 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 and DAF, 2004).

It is estimated that some 90% (120,000) of farms in Ireland operate within the organic N limit of 170 kg /ha (DEHLG and DAF, 2003). Regardless of this, Irish farming lobbying groups 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 N limits of up to 250 kg/ha (DEHLG and DAF, 2004). The Directive, when enacted in 1991, also made provision for a transitional limit up to 210 kg /ha organic N during their first four-year action programme. Some 130,000 Irish farms (over 95%) operate within this limit (DEHLG and 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 and DAF, 2004). Measures already taken towards implementation of the Nitrates Directive include the development of the 'Code of Good Agricultural Practice to protect Waters from Pollution by Nitrates' (DELG and 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. All farmers receiving payments under various direct payment schemes must practice farming in accordance with certain environmental requirements under the Agenda 2000 agreement (EC, 1999). Protection of the direct payments Ireland receives from the EU annually (€1.6 billion) is vital to the agricultural community (Walsh, 2004). 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.

1.5. Appropriate Reference Concentration

Previous discussion has referred to EU legislation that regulates NO_3 concentrations in water by defining a concentration of 11.3 mg/l NO_3-N, in the Drinking Water Directive (EC, 1998), and a similar threshold in the Nitrates Directive (EEC, 1991a). The issue of eutrophication of water bodies has also been discussed. Water bodies that fall under the remit of the Nitrates Directive (EEC, 1991a) include estuaries. The N criterion for eutrophication in Irish estuaries and coastal waters is defined as 2.6 mg/l NO_{3-}N for tidal freshwaters (EPA, 2001). The issue, of which NO_3-N limit (11.3 mg/l or 2.6 mg/l) 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 still under discussion in Ireland.

1.6. Learned Concepts Informing this Investigation

So much is now known about the complex dynamics of the N cycle in the soil that many recent publications are review articles on the extensive available knowledge on NO_3 loss from the subsoil (Addiscott, 1996; MAFF, 1999; Wilson *et al.*, 1999; Jarvis, 2000; Follet and Hatfield, 2001). The focus of the present work concerns the loss of NO_3 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:

1.6.1.Application rates not considered to be excessive under current agricultural practices can lead to groundwater NO_3-N 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).

1.6.2.Given constant fertilisation, the variance in the yearly NO_3 concentration in the groundwater recharge (percolating water) is mainly a function of the weather (CEC, 1991). For any given soil type, the quantity of annual N fertilisation and precipitation are the main readily quantifiable factors influencing groundwater recharge NO_3 concentrations (Mull and Pfingsten, 1991).

1.6.3.Detailed characterisation of topsoil properties that may govern NO_3 production, such as carbon (C) and N content, mineralisable N and denitrifying enzyme activity, were found to have limited use on their own for predicting groundwater NO_3 status (McLay *et al.*, 2001). The same study found a better relationship between the proportion of dairy farming in a district and regional groundwater NO_3 concentrations, than subsoil characterisation with respect to NO_3 production. MAFF (1999) concluded that the underlying assumption is that the number of livestock determines the quantity of N returned in excretions, as well as indirectly dictating the N fertiliser input: their national-scale investigations found that the potential loss of NO_3 from grassland was greatest in areas of intensive livestock.

1.6.4.The timing of percolating water, governed by the hydraulic parameters, is more important for the release of NO_3 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 N present in the soil at the end of the growing season, when recharge is initiated, is the major factor influencing N loss from the root-zone in northern temperate climates.

1.6.5.Water recharge to groundwater can be by ‘by-pass’ (preferential) flow. 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 and Whitmore, 1991).

1.6.6.The NO_3 concentration in groundwater reflects both the total amount of NO_3 leached per year and the excess winter rainfall. With increasing excess rainfall, there is an increase in the N load that can be leached before the concentration will cause breaching of the parametric limits defined in EU Directives (Whitehead, 1995). Excessive N application increases the risk of NO_3 leaching but weather controls leaching loss.

1.7 Overview of Project Objectives

Objective 1: To measure and evaluate the attenuation of NO_3 migrating through soils and subsoils to groundwater, under an intensively managed dairy farm on a free-draining soil, which is typical of a nitrate vulnerable zone.

This objective was set under the remit of meeting this country’s obligations under the Nitrates Directive (EEC, 1991a). The investigative approach involved quantification of all loadings, both meteorological and agronomic, monitoring of the response of the groundwater system at numerous locations on the farm, and carrying out tracing experiments. Results analysis identified drivers of groundwater NO_3 response.

Objective 2: Assess GSI groundwater vulnerability assessment methodology.
Groundwater NO_3 concentrations were evaluated in the context of the GSI groundwater vulnerability classification.

Objective 3: Review methods for modelling NO_3 leaching from dairy farming.
Models and methodologies were reviewed (Bartley, 2003) and a hydrogeological modelling strategy was tested for Curtin's farm.

2. The Study Area: Curtin's Farm

2.1 Introduction

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 Livestock Units (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 and 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 and 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 and Williams, 1989).

The farm chosen is situated in an area with potential for NO_3 loss to the environment because of the practice of intensive agriculture in an intrinsically vulnerable area. A substantial area of Curtin's farm is located within a source protection zone delineated for a public supply borehole located 1.5 km to the northeast, in the direction of groundwater flow (see Chapter 4 for further details). This public supply borehole has demonstrated an upward trend in NO_3-N concentrations over the last twenty years, with periodic breaches in the last decade (Cork County Council, 1998, 2003), of the 11.3 mg/l parametric limit specified in the Drinking Water Directive (EC, 1998). Available background groundwater NO_3-N concentrations in north Cork indicate an average of <5 mg/l (Cork County Council, 1998, 2003; O'Connell, 2003).

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 and Trudgill, 1993). The groundwater coming from up gradient may have higher or lower NO_3 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 NO_3 concentrations, in the underlying groundwater, mostly reflect the influence of recharge percolating vertically through the subsoils of Curtin's farm.

Figure 2.1 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 2.1 Study farm location, Curtin's Farm, within the region and also its position nationally.

2.2 Subsoils Overview

Curtin's farm's subsoils comprise a mixture of coarse and fine-grained materials. Limestone fragments tend to dominate the subsoil, which varies from silty sand with frequent/abundant gravels to angular sandy gravels with clay (Kelly and Motherway, 2000). Generally, over the entire farm the overburden stratigraphy is as follows: 0.3-0.4 m of rich brown topsoil in the upper layer that contains many rounded pebbles; then 0.4 m 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.

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 freely draining, which is borne out by the excellent trafficability of the land on this farm, which makes it successful dairy grazing pasture. On a textural basis the high sand content of the subsoils suggests high permeability. However, sandy soils can be quite compacted in the upper layers. Hydraulic conductivity was investigated at 0.5 m intervals in the subsoil profile.

2.3 Geology Overview

The farm lies on the top of a gently sloping ridge of Waulsortian reef limestone having a ground-surface elevation of approximately 50 m AOD and some 25 m above the adjacent River Funshion. The Waulsortian Limestone has been described as a massive unbedded lime-mudstone (Sleeman and 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 2 km east of the farm. Only one type of bedrock was encountered during drilling, as was expected, given that Shearley (1988) suggests a thickness of 500-700 m below ground level (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 1 m and 4.5 m bgl. The upper bedrock surface was usually soft weathered rock for the first 1-2 m as is expected in the epikarst region.

The only discernable difference between project boreholes is the degree of fracturing (*i.e.* the secondary permeability that governs water flow in limestone aquifers). A topographic survey in conjunction with vertical sections, constructed from numerous borehole-logs, 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.

2.4 Hydrogeology Overview

The returns from bedrock drilling to the water-strike zone mostly indicated solid rock. In general, water was only encountered in sand-filled cavities, or in slight bedrock anomalies/cracks, all in the region 30-35 m bgl. These water-bearing fractures have elevations in the range of 20-25 m above ordinance datum (AOD). At many locations cavities were encountered through the drilling profile, which were not water bearing. 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. The average groundwater table elevation beneath the Curtin's farm area throughout the two-year monitoring period was 30 m AOD (25 m bgl). The River Funshion, at the Downing's Bridge OPW gauging station, had a lower water-surface elevation (river-bed elevation being ~20 m AOD at Downing's Bridge). 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.

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 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 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 (approximately 20 m bgl in winter and 30 m bgl in summer) draining northwards to the River Funshion. The predominant sand content of the subsoil aids rapid infiltration to bedrock. 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. Groundwater travel velocity calculations suggest a turnover rate of four to six per year.

2.5 Nutrient Status of Curtin's Farm's Topsoil

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 (Figure A.1, Appendix A).

In the course of soil fertility investigations for agronomic purposes a technician sampled the topsoil 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 land surface for at least four months. Results from the standard soil P test (Morgans extractable P) by the soils laboratory in Johnstown Castle revealed high concentrations in the dirty water treatment area (Figure A2, Appendix A). Soil P concentrations of 20mg /l were observed in the topsoil of the dirty water area. Values greater than 10 mg/l for grassland are not necessary to achieve agronomic production targets. Teagasc recommends that no P fertiliser be applied to grassland soils with soil test P values greater than 10. Soil test P values in the grazing and silage areas were 12 mg/l, on average, with values of 14mg/l observed in the two-cut silage area.

Potassium (K) levels in the topsoil of Curtin's farm were approximately 80 mg/l in the grazing and silage areas. In the dirty water disposal area soil test K levels were 200-300 mg/l (Figure A3, Appendix A). Teagasc does not routinely test soils for N levels as part of soil fertility assessment. However, the variance in soil P and K levels is a measure of relative agricultural impact on different areas of Curtin's farm.

3. Methodologies

3.1 Borehole Locations

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. All drilling locations are shown in Figure B.1, Appendix B.

3.2 Piezometer Installations

This project installed nine groundwater piezometers at farm scale, 50 ha area, on an intensive dairy farm. The piezometers are labelled BHC.1-BHC.10 (Figure B.1, Appendix B). The schematic detail of piezometer installations is presented in Figure B.2, Appendix B. 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 NO_3 concentrations) hydrogeological testing and analysis of flow directions. Holes were drilled using compressed air boring methods: the drilling rig created a 150 mm diameter borehole to house a 50 mm diameter piezometer. 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.

Each piezometer had a 3 m sump and a fixed bottom cap at its base, then a 3 m-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 1 m 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. In the cases of BHC.3 and BHC.8, these bores were drilled by a mineral exploration company whose drilling rig created only a 50 mm diameter annulus. It was not possible to install a piezometer in the 50 mm bores. The installation of a grouted protective sleeve prevented possible contamination of the groundwater from the subsoil at BHC.3 and BHC.8. At BHC.4 water-strike was within a subsurface cavern, which prevented fixing of a piezometer and so access to groundwater here was by open 150 mm bore.

3.3 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. 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. These maps allowed the direction of groundwater flow to be determined.

3.4 Groundwater Sampling

Groundwater samples were collected using a 50 mm diameter Grundfoss submersible pump powered by a generator (Figure B3, Appendix B for sampling instrumentation). 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 (EC) were measured in-situ. Duplicate samples were collected from each piezometer.

3.5 Groundwater Sample Analysis

Samples were transported, under refrigeration, to the Johnstown Castle water analysis laboratory, Wexford, where they were analysed. Samples were not preserved in the field because they were analysed within 24 hours of collection. In addition to the suite of nutrients (Total Oxidised Nitrogen, NO_3-N, Nitrite-Nitrogen (NO_2-N), Ammonium-Nitrogen (NH_4-N) and P) the water samples were analysed for the following ions, K, sodium (Na), calcium (Ca), sulphate (SO_4), chloride (Cl) and magnesium (Mg). These data were used in an attempt to define the hydrochemistry and the agricultural signal in the groundwater.

Nutrient analysis was carried out using the KONELAB auto analyser. The water analyst ensured that analysers operated within the defined quality control procedures. The two groundwater samples collected from each piezometer were analysed in duplicate. Results from the KONELAB were checked 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.

3.6 Investigating Mechanisms of Solute Leaching – Tracing Study

A bromide (Br) -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 (as indicated in Figure A.1, Appendix A). This area of the farm was chosen, as the onus was on this research effort to explain the monitored rapid-reaction of the groundwater table to recharge events.

The Br ion has been widely used as a tracer to investigate water and contaminant transport in agricultural research (Smith and Davis, 1974; Jabro *et al.*, 1994; Kessavalou *et al.*, 1996; Schuh *et al.*, 1997; Kelly and 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 NO_3 in the subsoil (Flury and Papritz, 1993; Schuh *et al.*, 1997). Background soil Br concentrations are generally low at ~1.0 mg/kg (Flury and Papritz, 1993). The toxicity of Br 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 and Papritz, 1993; Bowman *et al.*, 1997). Richards (1999) conducted a successful Br-tracing experiment on another Moorepark dairy farm, Ballyderown, with no ill effects to vegetation or animals on the farm.

3.6.1 Tracing Site Details

One field on the farm, containing one groundwater-piezometer (BHC.7) and eight subsoil-pore-water ceramic cups, was selected for ground-surface irrigation with a potassium bromide (KBr) solution. The depth of subsoil cover at BHC.7 is 2 m to the top surface of the bedrock, which is soft and weathered for the upper 1 m (epikarst). Particle size analysis describes the subsoil to be a gravely, silty SAND at 1 m bgl, as it is at most locations on the farm, and at 2 m is described as a brown silty very gravely SAND (BS 1377, 1990). The Waulsortian limestone bedrock is solid until 30 m bgl where a 0.5 m deep cavity and water strike were encountered. Drilling continued to 35 m.

3.6.2 Instrumentation

The ceramic cups used in the farm scale study (Ryan et al, 2006) were also used for the Br tracing study. Each of the eight subsoil-pore-water ceramic cups in the plot were installed in 2001, at 1 m bgl. The cups were staggered (Figure B.4, Appendix B) at either 6 m or 8 m from the electric fence. Tubing connected the cup at 1 m depth to a Buchner vacuum flask on the soil surface which was protected by temporary fencing.

The groundwater-piezometer (BHC.7) was installed with a screened interval at 29-32 m bgl. Piezometric water level at the time of the experiment was 19.84 m bgl.

In the month prior to the experiment samples were collected and analysed to determine the background Br concentrations in both the subsoil pore-water and groundwater, each of which were below the detection limit of the analyser.

3.6.3 Methodology

The Br solution was applied on the 28th January 2003 at a rate of 732 kg/ha in the chemical stock form of KBr using a watering can fitted with a perforated T-bar. A total of nine grids were marked out each one centering on a single monitoring instrument (eight ceramic cups and one piezometer). It was financially prohibitive and deemed environmentally wasteful to dose the entire 0.86 ha plot.

The dosing grid around the groundwater piezometer had overall external dimensions of 10 m by 15 m, with a total dosed area of 110 m^2 (40 m^2 around the piezometer was not dosed in part to ensure no preferential movement of Br in the immediate vicinity of the piezometer and also because of a farm road, 3 m wide, adjacent to the piezometer (Figure B.5, Appendix B). The concentration applied was 67,000 mg/l Br. The irrigation was equivalent to a recharge depth of 1 mm.

In the case of each of the ceramic cups a 3 x 3 m square, with the cup as centre, was marked out on the ground surface. For each of the eight cups, 1 kg of KBr was dissolved in 10 l of water and the area was evenly applied using the watering can. 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 plot under investigation was part of the 7 ha of the farm devoted to the treatment of dirty-water generated from yard and milking parlour washings. Therefore, in addition to natural recharge the plot received an additional artificial recharge of dirty water. The irrigator was moved into the plot two days after the Br solution was applied. The movement of the irrigator in the plot was recorded and the depth of irrigation was determined to be 16mm. It took twenty-six days for the irrigator to pass through the entire plot, which covered an area of 0.86 ha (8600 m^2).

3.6.4 Monitoring

The ceramic cups were sampled once every week by a field technician to establish the travel time of the Br tracer, and hence solutes, to the 1 m depth in the subsoil. Each week a negative pressure of 50 kpa 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.

Disposable bailers, of 1 l 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 Br pulse passed. The other piezometers on the farm were bail-sampled twice weekly. Duplicate samples were collected from the screened-interval depth.

3.6.5 Sample Analysis

All samples were analysed, in batches, within one-month of collection. Samples were refrigerated while stored. Groundwater samples were selected for analysis after consideration of effective rainfall (R_{eff}) calculations and observed top-water levels in the piezometers. The Centre for the Environment, University of Dublin, Trinity College, determined the Br concentration using a DIONEX ion chromatograph. The limit of detection for Br was 0.25 mg/l.

3.7 Loadings Determinations

Project objectives were to quantify loadings and measure the response of the groundwater system at the farm-scale. Meteorological modelling allowed determination of recharge (R_{eff} loading) and daily N applications and grazing activity data were collected and used to determine agronomic N loadings.

A farm gate balance is presented for both hydrological years monitored in this study, 2001-2002 and 2002-2003 (Table B.1, Appendix B). The method follows the agronomic methodology suggested for Irish dairy farms (Humphreys *et al.*, 2003). Raw data used to generate the farm gate balance were supplied by the Curtin's farm-manager. These data were supplied as volumes of milk sold each month together with the measured protein content of that milk, and recorded animal liveweight gains. The N concentration was determined using information published by Kemp *et al.* (1979). The balance suggests a 25% efficiency rate of imported N on Curtin's farm. This efficiency rate concurs with balances determined by others (Sherwood and Tunney, 1991; Watson *et al.*, 1992; Jarvis 1993; Richards, 1999; Humphreys *et al.*, 2003). Given that only 25% of the N added to the system is removed in product, there is a large proportion potentially available for loss to the environment.

3.7.1 Meteorological Modelling

A full daily-meteorological water balance for the study farm was completed, within the MS EXCEL spreadsheet programme, using data from the Moorepark weather station to determine daily R_{eff}. Firstly, daily evapotranspiration (ET_o) was determined employing the FAO Penman-Monteith method (FAO, 1998). Observed daily rainfall and calculated evapotranspiration, ET_o, details were then used to determine daily soil moisture deficit values (SMD). Daily SMD information was used to modify potentially overestimated evapotranspiration data using the Aslyng scale (Aslyng, 1965). Daily R_{eff} (recharge) was the balance of the rainfall addition to the system and SMD and ET losses from the system. 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. Effective rainfall data were used for weekly and annual timescale groundwater response analyses.

The recharge and non-recharge seasons were clearly defined by cumulatively plotting RF_{eff} over the time period of the study (Bartley, 2003). 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.

It is interesting to observe the differences in seasonal R_{eff} totals for the duration of the experiment. The season in which the recharge occurs is of critical importance with respect to NO_3 leaching. Seasonal totals are presented in Table 5.1, 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 NO_3 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.

Table 5.1 Seasonal effective rainfall (mm) for Curtin's Farm for 2000 - 2001, 2001 - 2002 and 2002 -2003.

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

3.7.2 Nitrogen Loadings

All agronomic loadings on the farm area were recorded. Nitrogen is added to dairy farming systems, and the Curtin's farm system, from the following sources:

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

An additional N source is that deposited in rainfall. Atmospheric N depositions were monitored by analysing rainfall samples collected on site. An annual rate of 9 kg/ha N was recorded in one study year, 2002-2003, (Ryan, pers. comm., 2003), which is small compared to the magnitude of the agronomic N loading rates.

Data for each of the above N sources was collected, on a daily basis, by farm technical staff. These data were supplied to the TCD team where they were collated to create weekly loading rate diaries for each farm field. A separate diary was created for each of the nineteen farm fields. Essentially, the approach taken was to convert all N loadings (kg) to rate values (kg/ha). In that way individual N sources loading rates could be compared and also combined, where appropriate, to give a total organic N loading rate to each farm field. The field-scale N loadings were then used in analysis of each individual piezometer's temporal groundwater NO_3 response (Bartley, 2003). In addition, the field-scale loadings data were analysed further to generate agricultural management-scale N loading rates data sets on an annual time-scale (Tables B.2 and B.3, Appendix B). Inorganic N fertiliser rates did not vary greatly in each of the four different management areas or zones. Differences thus observed in groundwater NO_3 concentrations in different management zones were therefore not related to inorganic N fertiliser application rates.

The total organic N loading rates varied considerably between management areas. In each year, the average total organic N loading rate was highest in the area dedicated to dirty water treatment relative to the other three zones (Tables B.2 and B.3, Appendix B). The average organic N load contributed by grazing animals was calculated to be 179 kg/ha and 198 kg/ha in the grazing only and dirty water treatment areas, respectively, in the first year (2001 –

2002). However, the additional organic N load contributed by dirty water irrigation results in almost a doubling of the load to 378 kg/ha N in the dirty water treatment area. 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 N loading from slurry application and half from grazing animal's depositions. In the first year the average total organic N loadings were 230 kg/ha and 194 kg/ha for the one-cut and two-cut silage areas, respectively. These data again reinforce the significantly higher organic N loading rate over the 7 ha devoted to dirty water irrigation.

In the second monitoring year (2002-2003) the pattern of total organic N loading over management areas was similar. The dirty water area received the highest N loading (471 kg/ha) and the grazing area received the lowest (165 kg/ha). The one- and two-cut silage areas received organic N loadings of 256 kg/ha and 263 kg/ha, respectively. These values for the two different silage management zones were similar when totals were compared, but it is the nature of the components that is important. The two-cut silage zone received 71% of its total organic N loading as slurry, which was 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 N load was applied as slurry and the remainder was deposited by grazing animals.

Farm-area weighted average organic N application rates were 216 kg/ha and 248 kg/ha in the first and second years, respectively. These area weighted values mask the impact of the dirty water zone organic N loading rates because the dirty water area represents only 14% of the total farm area. In the context of the Nitrates Directive (EEC, 1991a) with an organic nitrogen loading rate limit of 170 kg/ha, the dirty water area is a big pressure point. It is acknowledged that the limit in the Directive concerns a farm's average loading rate. However, the environmental significance of a small area of the farm receiving double the organic N than other areas should not be ignored.

3.7.3 Combining Meteorological and Nitrogen Loading Calculations

Inorganic N is applied for grass growth. Animals consume grass and retain a proportion of its N content but they excrete most of it. Selecting the correct component of the N sources that should be considered for the purposes of defining response relationships and modelling NO_3 loss to the groundwater body was difficult. Given that organic N is derived from the inorganic N source, to sum both to give a total N input would amount to double accounting because dirty water, slurry and grazing animal loads are all recycled N that was originally sourced in the fertiliser applied to the grass. If only one N source was to be considered it was decided that, for this work, the organic N 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 and Dampney, 1993; Whitehead, 1995) suggests that N fertiliser that is applied at incrementally low rates, as it is on Curtin's farm, matches grass growth requirements well and therefore is not available to direct loss in leachate.
- The special significance of grazing N loads, in terms of the N applied and the hydraulic load that accompanies urinations, has been outlined in the literature (Cuttle

et al., 1992; Cuttle and Scholefield, 1995; Loiseau *et al.*, 2001; McGechan and Topp, 2004; Decau *et al.*, 2004). This issue is discussed more fully in section 7.8.

- Others have used organic N loading as a key component of N available for loss to water resources at a national scale for Scotland's obligations under the Water Framework Directive (e.g. Dunn *et al.*, 2004).
- The whole tenet of the Nitrates Directive (EEC, 1991a) is the organic N loading rate.
- Inorganic N fertiliser rates did not vary greatly in each of the four different management zones, yet large differences in groundwater NO_3 concentrations were observed between piezometers in different farm zones.

An estimate of recharge N concentration for Curtin's farm was made on an annual basis using calculated R_{eff} and area weighted average organic N application rates (Tables B.2 and B.3, Appendix B). For the 2001-2002 hydrological year, R_{eff} was calculated to be 464 mm and the area weighted organic N loading rate was determined to be 216 kg/ha (Table B.2), which provides an indicative recharge N concentration of **46.6 mg/l N** in the first year. For the 2002-2003 hydrological year R_{eff} was calculated to be 537 mm (Table B.3) and the area weighted organic N loading rate was determined to be 248 kg/ha (Table B.3), which provides an indicative recharge concentration of **46.2 mg/l N** the second year. However, the total organic N load is not necessarily available for leaching as NO_3. The various processes in the N cycle will reduce the recharge concentration. These calculations presented do not consider plant uptake, volatilisation, denitrification or immobilisation. While denitrification is unlikely to reduce the N content in the sandy, freely draining soils of Curtin's farm, volatilisation losses of 9% of N have been measured from grazing animals (Hutchings *et al.*, 1996). Organic N applied as slurry and irrigated as dirty water will also incur NH_3 volatilisation losses. 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.

4. Results

A representative water table map for Curtin's farm is shown for December 2002 (Figure C1, Appendix C). Groundwater piezometer locations are identified on this map for use with the summary results tables presented (also in Appendix C) and referred to in sections 4.1.2 and 4.1.3, below.

4.1 Groundwater Quality beneath Curtin's Farm

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.

4.1.1 Physiochemical Characteristics

4.1.1.1 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. Minimum groundwater temperatures were approximately 11 ^{o}C and were recorded in February and March each year, during the recharge season. Maximum observed groundwater temperatures were approximately 13 ^{o}C, which occurred in summer and autumn each year, during the non-recharge period. Groundwater did not exhibit unexpected variations in temperature at any location on the farm at any time.

4.1.1.2 Electrical Conductivity (EC)

In-situ groundwater EC varied greatly throughout the monitoring period in each piezometer (Table C.1, Appendix C). Variation in EC is directly related to variation in ion concentration: the greater the number of ions the higher the value (Dojlido and 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 380 μS/cm. Most piezometers had EC values of between 800 and 900 μS/cm, which are within the EPA IGV (EPA, 2003). However, one piezometer, BHC.4, sited in the dirty water irrigation area, consistently breached the EC IGV of 1000 μS/cm during the monitoring period. The EC of the water from the River Funshion was also monitored throughout the study period and was within the range of 354 to 630 μS/cm.

4.1.1.3 Groundwater pH

The pH of the all groundwater samples for the monitoring period was between 6.9 and 7.2 which complied with the EPA IGV pH range of 6.5 to 9.5.

4.1.2 Hydrochemical Quality

The general hydrochemistry of the groundwater was assessed using the following parameters – K, Na, Cl and the K:Na ratio. Other parameters analysed were Ca and SO_4.

4.1.2.1 Groundwater Potassium (K) Concentrations

Generally the K concentrations in groundwater beneath Curtin's farm conformed to the Drinking Water Standards limit of 12 mg/l and the IGV of 5 mg/l (Table C.2, Appendix C). However, the K concentrations for samples from BHC.3 and BHC.4 consistently breached the 12 mg/l. A GSI survey of principal springs in Ireland found mean K concentrations 2.9 mg/l (Daly, *et al.*, 1989). The overall median K concentration observed in the groundwater beneath Curtin's farm was 4.7mg/l, which is close to the IGV. However, groundwater K concentrations ranged from 1-215 mg/l 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 high autumn values are probably due to contamination caused by dirty water irrigation.

4.1.2.2 Groundwater Sodium (Na) Concentrations

A typical Irish Carboniferous limestone aquifer might have Na concentrations of approximately 9 mg/l (EPA, 2003). Sodium is always present in natural waters (Flanagan, 1992). It is not a harmful constituent but is used as an indicator of impact on groundwater quality (GSI, 1999). The Irish Drinking Water Standards set a Na limit of 150 mg/l and this was never breached on Curtin's farm. There is no GSI trigger value. Observed groundwater Na concentrations ranged between 5-29 mg/l (Table C.3, Appendix C). Slightly elevated Na concentrations were persistently identified in the first year at BHC.3 (mean 2002 Na concentration was 11mg/l) and in both years at BHC.4 and BHC.7. These latter piezometers are located in the dirty water irrigation area.

4.1.2.3 Groundwater Chloride (Cl) Concentrations

The dominant ion in rainwater is Cl 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. Natural Cl concentration in Carboniferous limestone aquifers would be approximately 26 mg/l (Kiely, 1997 adapted from Daly, 1994). The GSI trigger value and EPA IGV (EPA, 2003) for Cl is 30 mg/l Cl. On average, all monitoring locations returned groundwater samples with Cl concentrations less than the IGV. Mean and median Cl concentrations from BHC.4 and BHC.5 breached the IGV (Table C.4, Appendix C). Richards (1999) found that high Cl concentrations were associated with dirty water irrigation. The high Cl concentrations observed in BHC.5 are not supported by elevated concentrations of any other constituents in any of the groundwater samples from this location.

4.1.2.4 Groundwater potassium to sodium (K:Na) ratios

Daly and 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 from plant material. 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). Summary data for K:Na ratios for each piezometer at Curtin's farm is presented in Table C.5, Appendix C. 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 greater than 0.4, but mostly in the first year. The 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 less than 0.4, indicating the responsiveness of the system to changes in loadings.

4.1.2.5 Groundwater Sulphate (SO_4) Concentrations

The EPA (2003) acknowledges SO_4 as a significant indicator of groundwater contamination and labels its sources as agriculture, acid rain and urban. Bohlke (2002) suggests that SO_4 is a useful tracer of agriculturally impacted groundwater. The Environmental Quality Standard (EQS) for SO_4 is 200 mg/l and the EPA has adopted this value as the IGV for groundwater (EPA, 2003). There were no breaches of the SO_4 IGV at Curtin's farm (Table C.6, Appendix C). Most piezometers returned groundwater samples with similar SO_4 values and ranges.

4.1.2.6 Groundwater Calcium (Ca) Concentrations

Calcium concentrations did not vary significantly, spatially throughout the farm and the average Ca concentration observed was 125 mg/l, which is below the 200 mg/l IGV set by the EPA (EPA, 2003).

4.1.3 Groundwater Nitrogen Concentrations

All groundwater samples were subjected to analysis for ammonium (NH_4-N), nitrite (NO_2-N), and the NO_3 ion. In addition, groundwater P concentrations were also investigated. Summary tables for each nutrient are presented in Appendix C and are referenced in the following sections. In addition, groundwater NO_3 and P trend graphs are also presented in Appendix C.

4.1.3.1 Groundwater Nitrate (NO_3) Concentrations

Average groundwater NO_3-N concentrations beneath Curtin's farm were elevated with respect to regional groundwater status (Bartley, 2003). The EPA IGV for NO_3-N (EPA, 2003) of 5.6 mg/l was generally exceeded at each piezometer, except at the upper fringe of the farm. A typical example of differences between groundwater NO_3 -N concentrations at different locations on Curtin's farm is shown in map format in Figure C.1, Appendix C which also shows associated groundwater elevations and the localised flow directions.

The NO_3-N concentrations in groundwater ranged from 3 to 31 mg/l and from 4 to 23 mg/l for the first (2001-2002) and second (2002-2003) monitoring years, respectively. Summary groundwater NO_3-N concentration data is presented in Table C.7, Appendix C.

There were significant differences in the piezometer groundwater NO_3-N concentrations that were related to their location in management zones. The average groundwater NO_3-N concentrations for each piezometer, in both monitoring years, are shown in Figure C.2, Appendix C. However, not all piezometers had excessive NO_3 -N concentrations. The NO_3 -N concentration of the inflowing groundwater, the N loading above the piezometer and most importantly, the hydrogeological controls on NO_3 leaching directly above each monitoring location all influenced observed groundwater NO_3 -N. The outlying piezometer, BHC.1, demonstrated the lowest NO_3 -N concentrations in both years monitored (Figure C.2, Appendix C).

4.1.3.2 Groundwater Ammonium (NH_4) Concentrations

The NH_4 ion can enter water systems on occasion even though the ion has a low mobility because it is usually tightly bound to soil particles (Jarvis, 1999). It is not often subject to investigation because it is a transitory constituent in the N cycle. Some suggest that the presence of NH_4-N in water at concentrations much above 0.1 mg/l indicates point source contamination (e.g. Flanagan, 1992; Jarvis, 1999). However, others acknowledge that vulnerable conditions may also be the cause of elevated in NH_4 groundwater (Kiely, 1997). The EPA IGV for NH_4 expressed as NH_4-N is 0.12 mg/l (EPA, 2003) which is also the GSI trigger value. A range of 0.05 to 3.98 mg/l NH_4-N was observed in the groundwater beneath Curtin's farm (Table C.8, Appendix C). Average observed groundwater NH_4-N concentrations conform to the IGV in most boreholes. However, BHC.2 and BHC.10 showed occasional breaches and BHC.4 persistently breached the IGV over the two year monitoring period. The farmyard and dirty water irrigation are implicated in the contamination of BHC.4. The observed maximum concentrations at 77% of the monitoring locations have peak NH_4-N concentrations that breach the IGV. These results highlight a significantly vulnerable groundwater. A concurrent leaching investigation at Curtin's farm, which targeted 1 m depth in the subsoil, revealed NH_4-N concentrations that consistently breached the Drinking Water Regulations parametric limit of 0.23mg/l NH_4-N (DELG, 2000) during the winter monitoring period (Ryan, *et al.,* 2005).

4.1.3.3 Groundwater Nitrite (NO_2) Concentrations

Nitrite is an intermediary in the oxidisation of NH_4 to NO_3 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 NH_3. The EPA IGV for NO_2, expressed as NO_2-N is 0.03 mg/l (EPA, 2003). A range of NO_2-N concentrations from less than 0.001 to 4.68 mg/l were observed in groundwater monitored at Curtin's farm (Table C.9, Appendix C). However, median NO_2-N results for each piezometer conform to the IGV of 0.03 mg/l. Results suggest that there is not a persistent problem, such as a constant release of NH_3 from an underground waste source. However, the high NO_2 concentrations, revealed by the maximum concentrations, suggest an intermittent problem most probably a function of agricultural activity at the land surface in this intrinsically vulnerable environment.

4.1.3.4 Groundwater Phosphorus (P) Concentrations

In this study all groundwater samples were analysed (unfiltered and unfiltered (0.45 μm) for P. Groundwater P concentration summary statistics for the unfiltered samples are presented in (Table C.10, Appendix C). A range of P concentrations for the unfiltered samples from less than 0.005-0.987 mg/l were observed over the monitoring period. Filtered samples had dissolved P concentrations in the range of 0.001-0.948 mg/l over the two measurement years.

Neither the Irish EPA (EPA, 2003) nor European drinking water legislation (EC, 1998) set P limits for groundwater. However, the trophic status of groundwater-fed surface water features is controlled by the nutrient content of the inflowing groundwater and P is the chief nutrient of concern (Coxon and Drew, 1998). Total P concentrations in excess of 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 P levels exceed 0.03 mg/l (McGarrigle, 1998). Although P was conventionally thought *not* to be a problem in groundwater because of its immobility (Kiely, 1997), these results provide evidence demonstrating the occurrence of P in groundwater, in this karstified environment. Kilroy *et al.* (1998) also showed that P was found in some Irish groundwaters at concentrations that induce eutrophication in surface waters.

Temporal trends in the responses of dissolved P concentrations (filtered samples) to R_{eff} in the groundwater beneath each of the four management zones for both years are shown in Figure C.3. The results show that there is a clear P response to R_{eff} and that P peaks occur in all treatments but are highest under the dirty water and one cut silage management zones.

4.2 Tracing Experiment Results

Summary tracing results for both subsoil and groundwater are presented in Table C.11, Appendix C. 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 maximum observed groundwater concentration, under spring recharge, tracer irrigation of 1 mm and a single irrigation of dirty water (15 mm). Indeed, Br was transported in the groundwater to three other piezometers before concentrations peaked at 1 m-depth in the active ceramic cups used in the experiment. This suggests that Br moved preferentially to the groundwater body and was more quickly transported through karstified bedrock than through the subsoil matrix. Bromide breakthrough behaviour was different for each of the eight ceramic cup locations but the maximum observed concentrations all occurred around the same time in June (approximately 140 days after Br application).

Bromide applied to the ground surface at the end of January responded to recharge and first appeared at the 1 m monitoring depth in 16-148 days in response to recharges, for the corresponding periods, of 66-195 mm, respectively. Bromide appeared in the groundwater (piezometer BHC7) 18 days after application at ground level in response to a total of 50 mm recharge and it persisted for a further 26 days. The maximum observed Br concentration in the groundwater was 5 mg/l some 44 days after it was applied, during which time 115 mm of effective recharge (some rainfall and some dirty water) entered the subsoil.

5. Analyses of Response Relationships

5.1. Groundwater Response to Recharge

Generally, it is observed that there is a clear groundwater nitrate response to meteorological loading. The response of the groundwater, 20 to 30 m bgl, to loadings was observed to be rapid; R_{eff} events affected a water-table rise almost instantaneously. Analysis demonstrates that recharge to the groundwater begins in October of each year and continues until May or June, generally. Within one month of the heavy block of winter recharge, observed to be 200 mm in the wettest winter month in both years, groundwater levels rise by up to 8 m. After the massive winter peak in groundwater levels the influence of further recharge is difficult to discern unless more than 50 mm of R_{eff} falls within a two-week period, then a 0.5 to 1.5m rise in water levels is observed.

Mean groundwater NO_3 concentrations were 15.2 mg/l in the first year and (2001-2002) 11.9mg/l in the second year (2002-2003). The obvious decline in groundwater NO_3 concentrations in the second monitoring year is most probably a result of meteorological conditions. It is not prudent to be definitive with just two years of data. However, the total R_{eff} in the second year was 547 mm compared with 503 mm in the first year (Table 5.1). The contrast was even more striking when only the winter recharge period was considered with 191 mm and 303 mm for the first and second years, respectively. Therefore, in the second winter there was approximately 50% more R_{eff}, there was a diluting of the NO_3 as it was flushed from the soil. This finding is crucial to our understanding that the control on groundwater NO_3 concentrations is hydrologically related. The timing of the recharge was also important: in the first year, soil N cycle activity was relatively uninterrupted by R_{eff} until January 2002, but in the second year, the N residence time was much shorter.

5.2. Groundwater Nitrate Response

The temporal behaviour of groundwater flow is said to explain the fluctuations in NO_3 concentrations when peaks in NO_3 concentrations correspond to the peaks in groundwater levels (de Vos, 2000). The response of averaged groundwater NO_3 concentrations and farm averaged groundwater level to cumulative R_{eff} data on Curtin's farm is shown in Figure 5.1. The first flush of winter recharge initially dilutes the NO_3 concentration. However, the subsequent NO_3 peak was greater than the value 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 and 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 54 mm RF_{eff} in one week caused in a 1.5 m rise in groundwater levels. This corresponded to a small decline in the NO_3 concentrations but within six weeks they had increased to values similar to those before the rise in water levels. However, all piezometers targeted different farm management zones receiving different N loads (Tables B.2 and B.3, Appendix B). There was a marked difference in groundwater NO_3 concentration depending on piezometer location (Figure C.2, Appendix C).

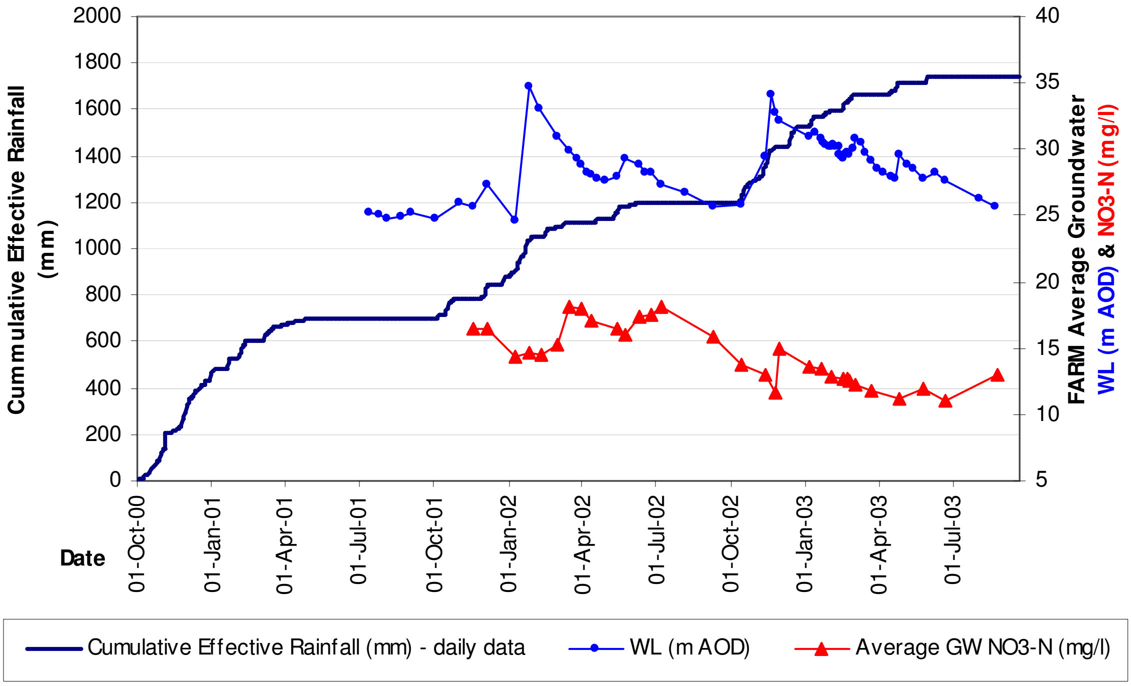

Figure 5.1 Average response of groundwater levels and groundwater nitrate concentrations to effective rainfall beneath Curtin's farm.

5.3. Groundwater Nitrate Response to Agricultural Management

Agricultural management 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 (refer to Figure A.1, Appendix A, for zone delineation at Curtin's farm).

The annual variation in groundwater NO_3 concentrations for any of the piezometers ranged from 3.5 mg/l to 19 mg/l. The temporal trends in groundwater NO_3 responses to R_{eff} for each of the four management scenarios in the first and second monitoring years are shown in Figure D.1, Appendix D. However, the groundwater at any location may be influenced not only by the agricultural management 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 trend response (Figure D.1(d), Appendix D) the two bores are approximately 200m apart (see Figure C.1, Appendix C).

A groundwater NO_3 response was discernible in response to the different agricultural management scenarios. The highest NO_3 concentrations were observed beneath the dirty water management area. Increased organic N loadings, from both dirty water irrigation and grazing (Tables B.2 and B.3, Appendix B), were identified as significant pressures in the dirty water irrigation area.

A popular question is: how can it be ascertained that nitrate observed in the groundwater was delivered by recharge from the ground surface above?

5.4. Demarcating Seasonal Effect of Recharge on Groundwater Nitrate

The fundamental issue is whether the delivery of recharge to the groundwater impacts negatively on groundwater quality at Curtin's farm. Changes in the concentrations of agricultural contaminants, such as NO_3, 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. Trends in groundwater NO_3 concentration have been obtained. However, 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 NO_3 in the groundwater originated in the subsoil requires some form of seasonal analysis.

An interesting approach is to divide each hydrological year into recharge and non-recharge seasons and to analyse the relationship between groundwater NO_3 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 NO_3 in the groundwater system and also the processes that have influenced the observed concentrations, including other ions (Note D.1, Appendix D).

In the first monitoring year all piezometers, except BHC.2 and BHC.3, have considerably higher groundwater NO_3 concentrations under recharge conditions (Figure D.2a, Appendix D). This contributes to the evidence that recharge carries a NO_3 load to the groundwater. Further deviation from the 1:1 line indicates a large annual range in groundwater NO_3 concentrations, which suggests either higher loading or higher vulnerability to contamination. In the second year (Figure D.2b, Appendix D) the same recharge and non-recharge groundwater NO_3 concentration responses are repeated.

5.5. Key Nitrogen Loading Driving Groundwater Response – Grazing Animals

One key question of this research was to identify if a particular N source could be related to elevated nitrate concentrations in groundwater. Detailed loadings data were generated from daily records kept at Curtin's farm (see section 3.7.2). 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 N loadings could be examined. An analysis of the individual piezometer groundwater NO_3 response to the N loadings associated with the management scenario was conducted. In terms of temporal analyses, it was difficult to discern which specific N loading is the most significant with respect to groundwater NO_3 status. Indeed, all N applications occur in close proximity and are related.

The most significantly discernable temporal response was that to meteorological loading. The most significant influence on leachate generation, and consequent groundwater NO_3 concentrations, is rainfall. However, given the unsuitability of defining a groundwater NO_3 protection strategy based on weather prediction, as a working methodology for dairy farm managers, a simpler load response relationship was investigated.

While detailed loadings analysis concentrated on determination of N loading rates, a simpler issue appeared in the form of the wide variation in the number of days that each plot was grazed in any year. These data were collected for calculation of N deposited by grazing animals. Analysis of this data suggested that grazing activity and the groundwater NO_3 trends were related, at least for some piezometers.

On an annual basis, a positive correlation was found between the number of days that the herd grazed a particular plot, in one grazing season, and the average groundwater NO_3 concentration recorded in that plot's associated piezometer in the following recharge period (see Appendix D, Figure D.3). It is clear that increased grazing intensity resulted in higher concentrations of NO_3 in groundwater. This finding is discussed more fully in section 7.8.

The relationship between grazing days and observed groundwater NO_3 concentrations should be regarded 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 grazing day relationship shows that increasing grazing animal intensity increases the potential for NO_3 delivery to the groundwater. The organic N loading rate is therefore a crucial factor in managing nitrogen loss to groundwater.

6. Modelling Nitrate Leaching from Dairy Farming Agriculture to Groundwater

Much detail regarding specific model applications is available in the literature and numerous models were considered in the course of a review completed within this research contract. The modelling review considers concepts of importance to effective modelling of NO_3 leaching through each subsurface zone, discusses the results of field-applications of many models and modelling approaches. The full review is presented in the full-length research report and also in Bartley (2003). In this report a list of each model reviewed, categorised by the subsurface scale of investigation, is presented in Appendix E. The following is a summary of the approach selected.

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 existing models describe the leaching process at plot or field scale. The National Research Council (NRC, 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 Ireland's 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 NO_3 concentrations). The simpler functional approaches 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. 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. Selection of an appropriate national modelling strategy for simulation of NO_3 leaching from dairy farming to groundwater requires full consideration of Ireland's available data.

The NCYCLE model (Scholefield *et al.*, 1991) has been selected to simulate NO_3 leaching from a typical Irish intensive dairy farm. This root-zone model is considered to be of most relevance to the factors influencing NO_3 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 a UK team (Ryan et al, 2006). The NCYCLE model will be employed in this work to simulate NO_3 available to leaching from each different agricultural management in operation on a typical Irish dairy farm. The simulated leaching rate from NCYCLE, will then act as the source term for simulation of NO_3 leaching to groundwater.

Nitrate leaching through the unsaturated zone will not be simulated using a specific unsaturated zone model. Instead, the hydrogeological Risk Assessment Model - RAM (ESI, 2000) was selected for unsaturated and saturated zone modelling 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 Nitrates 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.

7. Discussion

7.1. Intrinsic Site Characteristics

At Curtin's farm the subsoil is thin (0-4 m thickness, but at least 2 m 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 NO_3 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 elevation beneath Curtin's farm throughout the two-year monitoring period was 30 m AOD (25 m bgl).

7.2 Groundwater Vulnerability

The groundwater vulnerability rating is 'extreme' according to the GSI vulnerability assessment methodology (Fitzsimons *et al.*, 2003). Groundwater nitrate concentrations observed beneath Curtin's farm reflected this. Results from a similar experiment at Johnstown Castle (Bartley, 2003) 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 NO_3 concentrations.

7.3. Groundwater Recharge Determinations

Daily R_{eff} 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). Water levels in all the piezometers were observed to decline steadily throughout the summer period (July to September) and so it is concluded that the R_{eff} calculation method is validated for determination of total meteorological loading to the groundwater system. One shortcoming of the R_{eff} 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.

7.4. 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 masks 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 25-28 m bgl, within a short period on Curtin's farm. Within one month of the heavy block of winter recharge, observed to be 200 mm in the wettest winter month in both years, groundwater levels rise by up to 8 m, on average. After the massive winter peak in groundwater levels the influence of further recharge on groundwater levels was difficult to discern unless more than 50 mm RF_{eff} falls within a two-week period. Under this circumstance, a 0.5-1.5 m rise in water levels was observed.

7.5. Determination of Agronomic Nitrogen Loadings

The amounts of N applied to the land, in both inorganic and organic forms, were calculated. Detailed N loadings analysis demonstrated that fertiliser N application rates vary only by 50 to 60 kg/ha between the different agronomic management zones. Inorganic N application rates across managements ranged from 290 to 340 kg/ha in the first year (2001-2002). Inorganic N application rates were slightly lower on average, in the second year, ranging from 248 to 310 kg/ha. The farm area weighted inorganic N fertiliser application rate were

306 and 290 kg/ha in the first (2001-2002) and second (2002 – 2003) years, respectively. Therefore, the observed spatial variations in groundwater NO_3 concentrations are most probably attributable to N sources other than that from inorganic fertiliser.

Total organic N loading rates varied significantly in each management zone. In both years, the average total organic N loading rate was highest in the area dedicated to dirty water treatment relative to the other three management zones: the dirty water treatment area received more than double the organic N loading rate of the grazing only area. The average organic N load contributed by grazing animals was calculated to be 179 kg/ha and 198 kg/ha in the grazing only and dirty water treatment zones, respectively, in the first year (2001 – 2002). However, the additional organic N load from the dirty water irrigation resulted in almost doubling the total organic N load to 378 kg/ha. In the second monitoring year (2002 - 2003), the organic N loading was 471 kg/ha for the dirty water treatment zone. Groundwater NO_3 concentrations were observed to be highest under the dirty water treatment area. This zone facilitated more intensive animal grazing, with respect to all other zones. The significance of these loadings with respect to the Nitrates Directive (EC, 1991a) is noteworthy in that the Directive decrees a maximum organic N loading rate of 170 kg/ha.

Farm-area weighted average organic N application rates suggest values of 216 kg/ha and 248 kg/ha in the first and second years, respectively. 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).

In this work, the organic N loading rate was deemed to be the critical loading source (see section 3.7.3).

7.6. Groundwater Nitrate Response

Nitrate concentrations in the groundwater monitored beneath Curtin's farm are elevated with respect to local groundwater values. The observed groundwater NO_3-N concentrations almost always exceeded the EPA IGV of 5.6 mg/l. The Nitrates Directive (EEC, 1991) parametric threshold of 11.3 mg/l NO_3-N was also continuously beached in many of the piezometers on the farm. Of potentially more importance with respect to future environmental quality criteria, are the measured groundwater NO_3 concentrations in the context of the 2.6 mg/l NO_3-N eutrophication criteria for estuaries defined by the EPA (2001). Groundwater NO_3-N concentrations observed at some locations beneath Curtin's Farm were sometimes ten times greater than 2.6mg/l. The observed maximum NH_4-N concentrations in the groundwater at most boreholes are excessive and 77% of the monitoring locations reveal peak concentrations that breach the EPA IGV (EPA, 2003). These results highlight a significantly vulnerable groundwater.

Analysis of NO_3 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 R_{eff} transported the NO_3 to the groundwater body. Generally, it is observed that there is a clear groundwater NO_3 response to meteorological loading. Groundwater NO_3 concentrations were observed to rise in response to significant rainfall events in spring and summer but fell proportionately with autumn and winter recharges. 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 is not sustained and groundwater quality was observed to be detrimentally impacted by NO_3 recharge via matrix flow.

There was a marked difference in groundwater NO_3 concentration depending on piezometer location. The groundwater NO_3 response corresponded to differing agricultural practice in different locations on the farm. The highest concentrations were observed beneath the dirty water treatment area where grazing intensity and organic N loadings were higher than at any other location on the farm. There was a decline in groundwater NO_3 concentrations in the second year that is probably a result of meteorological conditions. In the second year, almost fifty percent more R_{eff} fell in the winter, acting to dilute NO_3 as it was flushed from the soil. The timing of the recharge was also important. In the first year, N deposited in the soil throughout the grazing season resided until January 2002. In the second year, the residence time of deposited N was much shorter.

Literature providing groundwater NO_3 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 NO_3 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 NO_3 through a karst spring basin in an agricultural catchment. They observed average NO_3-N concentrations at the point of spring discharge to be 4.09 mg/l and 5.07 mg/l during storm and non-storm flow, respectively. These concentrations are low with respect to the observed range of groundwater NO_3-N concentrations beneath Curtin's farm (ranging up to 31 mg/l). 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 NO_3-N concentration of their aquifer was 1 mg/l. Available background groundwater NO_3-N concentrations in north Cork average less 5mg/l (Cork County Council, 1998, 2003; O'Connell, 2003) and therefore, the high groundwater concentrations observed at Curtin's farm require that agricultural activity in vulnerable environments be more controlled.

7.7. Loadings Driving Groundwater Response

The most significantly discernable temporal response was that to meteorological loading. It became clear that the most recognizable influence, temporally, was the pattern of R_{eff} and N loading occurring relatively close together. However, given the unsuitability of defining a groundwater NO_3-N protection strategy based on weather prediction, as a working methodology for dairy farm managers, a simpler load response relationship was investigated. The fundamental issue is whether the delivery of recharge to the groundwater impacts negatively on groundwater quality at Curtin's farm.

On an annual time-scale, there was a positive correlation between the grazing intensity at the farm plot scale and the average NO_3 concentration observed in groundwater samples extracted from piezometers in the same plots in the following recharge period. Using the GSI vulnerability assessment methodology, it is the nature of the cover that determines intrinsic vulnerability. However, the observed relationship between grazing intensity and NO_3 response in groundwater at 25-30 m bgl shows that increased grazing intensity increases the potential for NO_3 delivery to the groundwater.

7.8. Substantiating the Effect of Grazing Intensity on Groundwater Quality

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 N in the urine, especially in the context of dual porosity subsurface flow.

The literature supports correlation between grazing day numbers and NO_3 leaching. Cuttle and 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 NO_3 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. Stout *et al.* (1997) estimate from field studies on grassland systems stocked at 2.2 cows/ha and grazed for 180 days that about 70% of the NO_3-N leached would come from urine deposited on the pasture. Those authors also conclude that management intensive grazing must be considered a livestock production system component that can have negative water quality impacts if not properly managed. Wachendorf *et al.* (2004) studied grazed grassland systems on a freely draining sandy soil and found that leaching losses in rotational grazing systems were elevated due to the high N return by grazing animals. 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 N, P and K.

McGechan and Topp (2004) found higher NO_3 losses from grazed fields compared to fields receiving slurry and cut for silage. They also found that NO_3 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 NO_3-N concentrations in the range of 10.7 to 16.6 mg/l at 25m bgl, which are similar to those recorded in the present study. Rodvang *et al.* (2004) report average groundwater NO_3-N concentrations in the range of 12.5 to 17.4 mg/l at 8 m depth in their aquifer and conclude that piezometers located in areas of high agricultural intensity contain significantly higher NO_3 than in areas of lower agricultural intensity.

Lysimeter studies predominate recent publications on NO_3 leaching from grassland (e.g. Di *et al.*, 1998; Silva *et al.*1999; Loiseau *et al.*, 2001; Decau *et al.*, 2004). Each of these report their principal findings to be the deleterious effect of grazing animals on NO_3 loss from grassland. Loiseau *et al.* (2001) conclude that grazing management is likely to be the main factor driving N leaching under grazed swards. Silva *et al.* (1999) measured peak NO_3-N concentrations of 120 mg/l at 0.9 m depth beneath a urine patch. Decau *et al.* (2004) found that low winter drainage and grazing management resulted in a higher impact on waters' NO_3 status than N fertiliser management; the impact of grazing was found to be more important than fertilisation at rates up to 300 kg/ha N (Curtin's farm average annual N fertiliser application was 290 kg/ha).

7.9. Bromide Tracing Experiment

The tracer tests showed that the time of travel for solutes from ground surface, through the subsoil, to the groundwater body was in the order of months. Peak groundwater concentrations occurred after approximately 44 days under spring recharge and a single dirty water irrigation rate of 15 mm. Bromide was transported in the groundwater, approximately 200 m horizontally, and observed to peak in these other piezometers two months before the Br arrived at 1 m-depth in most of the ceramic cups in the subsoil of the field in which the tracer was applied.

The Br tracing experiment, conducted in the spring season, suggests that the horizontal groundwater velocity was ~ 8 m/day in the central farm area. Other Irish karst groundwater research (e.g. Coxon and Drew, 1986; Drew *et al.*, 1995; Coxon and 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 28 m 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 N from grazing animal's depositions have an impact on groundwater NO_3-N concentrations in the immediate vicinity of piezometers.

7.10. Dual Mechanisms of Solute Transport

Tracing experiment results suggest that Br 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 and 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. 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 and Knighton, 1997) and in a sandy unsaturated zone (Kung, 1990a and b).

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 and 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 NO_3 groundwater concentrations observed within a karstified system. However, results of the research presented here suggest that preferential flow incidences were the cause of observed dilution in groundwater NO_3 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. In our situation, preferential flow contributes recharge to groundwater that has by-passed the soil matrix and so does not carry NO_3 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 NO_3 recharge via matrix flow.

7.11. Groundwater Phosphorus Concentrations

A P signature was observed in response to recharge events at numerous locations in both years studied. A factor to consider is P concentrations in the soils of Curtin's farm (Figure A.2, Appendix A). Although P is strongly adsorbed onto positively charged soil particles, it has been shown to leach from freely draining soils that are P saturated. However, P may have moved preferentially to the groundwater body. Groundwater P concentrations were observed to respond in a completely opposite fashion to observed NO_3 trends under potential preferential flow conditions in that water table peaks were sometimes associated with P peaks at some locations at Curtin's farm.

Dills and Heathwaite (1996) suggested preferential flow as a mechanism for P to bypass the soil's natural sorbing capacity. Phosphorus movement due to oversaturation of the soil matrix with P has been observed in free draining soils of coarse texture (Haynes and Williams, 1992; Ozanne *et al.*, 1961; Richards *et al.*, 1998). Chen *et al.* (1996) demonstrated P leaching from sandy soils with high permeability under similar conditions to those which exist on Curtin's farm. In those cases, P was assumed to move with infiltrating water that percolates through the soil matrix. However, this research proposes that the groundwater P observations at Curtin's farm are indeed a result of preferential flow because of the apparent close relationship between R_{eff} and subsequent rapid groundwater level increases, in association with the observed P and NH_4 concentration peaks in the groundwater.

7.12. Further Evidence of the Potential for Preferential Flow

Groundwater NH_4 peak concentrations were sometimes observed in association with NO_3 concentration troughs at Curtin's farm. McGechan and Topp (2004) observed NH_4 transport, from previously marked urine patches, by preferential flow, which was activated by urine deposited on wet ground. This provides further support to our suggestion that NH_4 (and P) moves preferentially to groundwater at Curtin's farm. 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 (preferential) flow in contaminant transport scenarios.

Preferential flow paths can explain the anomalous results in some studies where greater concentrations of solutes are observed at depth than in more shallow layers (Fetter, 1999). Kung (1990a and 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 have 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.

7.13. Agricultural Signature in the Groundwater

The agricultural signature in the groundwater beneath Curtin's Farm is strong at some locations. In terms of general hydrochemistry, most piezometers yielded EC values between 800 and 900 µS/cm, which are within the EPA IGV (EPA, 2003) standards. However, one piezometer, BHC.4, consistently breached the EPA IGV for groundwater EC, 1000 µS/cm, during the monitoring period. Median P concentrations at BHC.4 were also elevated with respect to those observed at other locations. Generally the groundwater beneath the farm conformed to the Drinking Water Standards (DELG, 2000) for K (12 mg/l) and the IGV K value of 5 mg/l. However, BHC.3 and BHC.4 consistently breached the higher 12mg/l K concentration. There may be some leakage to BHC.3 and BHC.4 from the adjacent farmyard but the underground slurry tanks cannot be deemed the entire source of the problem because K concentrations are highest in the summer. Results presented highlight the effect of groundwater solute concentrations being influenced from multiple sources and directions 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, all affect groundwater quality at Curtin's farm.

In the course of soil fertility investigations, for agronomic purposes, K levels in the topsoil of Curtin's farm were observed to be approximately 80 mg/l in the grazing and silage areas, but in the dirty water treatment area topsoil K levels measured 200-300 mg/l (Figure A.3, Appendix A). This is another measure of the nutrient loading of the dirty water management area. Dirty water irrigation occurs every day on this farm, and on other Irish dairy farms. Dirty water is implicated as a contaminant source that requires more thoughtful management because in autumn 2002 there was a definite K contamination incidence in many piezometers. The K content of irrigated dirty water is high: Ryan (1990) reported K concentrations greater than 200mg/l in dirty water from an Irish dairy farm. Sandy soils, such as those at Curtin's, have little capacity to retain K by cation exchange (Whitehead, 1995) and the elevated topsoil K concentrations in the dirty water irrigation area would suggest that any capacity to retain K has already been reached. Bohlke (2002) suggests that observations of K, P and SO_4 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 K concentrations were consistently below the IGV of 5 mg/l at BHC.1. The K contamination event was first detected in BHC.7, after dirty water was irrigated in August 2002 in the plot in which BHC.7 was located, and then in all other piezometers around BHC.7. This K migration was detected at a time when there had been no calculated R_{eff} recharge to the system in the previous three months. However, over 60 mm of rainfall had occurred and perhaps some recharge occurred that was missed by the monitoring programme. The second K contamination incident at BHC.7 occurred in March 2003, again one month after dirty water irrigation in the plot. The water table elevation maps and tracing experiment suggest that groundwater radiates from this area and so this borehole is one that allows clearest interpretation of hydrochemical analyses in terms of overlying land use and management practices.

A further observation concerns the problematic way in which the dirty water area is managed. Nitrogen fertiliser is applied incrementally throughout the season on Curtin's, and most other dairy farms. In the dirty water plots of Curtin's farm, fertiliser is usually applied a couple of days before the irrigator enters the field. The N loading pattern is to allow animals to graze a field intensively, then apply N fertiliser at a rate of ~50 kg/ha and then irrigate with dirty water, all within the same week. This loading pattern must create an enhanced leaching environment.

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. This suggests 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 (as supported by subsoil hydraulic conductivity investigations carried out in the course of our research). 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 P levels in the topsoil of the dirty water and slurry areas of Curtin's farm substantiate these recommendations. However, it was not possible to confidently assess the impact of slurry alone on groundwater quality at Curtin's farm because multiple sources and up gradient directions influenced groundwater NO_3 concentrations.

7.14. Modelling Nitrate Leaching from Dairy Farming to Groundwater

The risk assessment concept for groundwater was further progressed by successful testing of the hydrogeological risk assessment model RAM (ESI, 2000) for the karstified hydrogeological system at Curtin's farm. RAM facilitated user-friendly representation of the hydrogeological pathways governing NO_3 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 agronomic NCYCLE model (Scholefield *et al.*, 1991) was validated as an adequate methodology for source term definition of peak NO_3 leachate concentration from the root zone, on an annual basis. However, 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 N concentrations. The ultimate integrator of N concentrations is the groundwater and the key receptor may be remote from the individual farm (e.g. estuaries).

7.15. Reducing Nitrate Leaching

A turn of the century review of leaching reported that the key to reducing NO_3 leaching is by preventing the accumulation of mineral N in the soil profile before the leaching season starts (Di and Cameron, 2002). This can be achieved by an integrated approach with regard to N applications, crop harvest and post-harvest livestock management in grazed pastures (Di and Cameron, 2002). The most current computer simulations of the effect of grazing animals on N 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 and 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 of groundwater contamination 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 N sources and aquifer vulnerability to NO_3 in shallow groundwaters of the US. He employed a multivariate logistic regression model and found that vulnerability of groundwater to contamination by NO_3 depends not on a single factor but on the combined, simultaneous influence of factors representing N loading sources and aquifer susceptibility characteristics, which adds statistical validation to the vulnerability concept. Much of the USGS work stresses the long time lag between N application at the surface and its delivery to the groundwater body. Contrastingly, our research has demonstrated the rapid response of groundwater in a vulnerable area of north Cork to hydrological and agronomic loadings. 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 result in an observable improvement in groundwater quality in the short term, which is essentially good news for dairy farming in vulnerable conditions.

8. Conclusions

8.1. Overview

A principal objective of this research was to assess the groundwater NO_3 concentrations beneath grassland and its response to dairy farming agricultural practice in an intrinsically vulnerable area. The study farm was in north Cork, Ireland, on freely draining subsoil over a karst groundwater body. Curtin's farm currently operates at a stocking rate of 2.4 LU/ha. In the Nitrates Directive (EC, 1991a) an organic nitrogen limit of 170 kg N/ha implies a limit of 2 LU/ha.

Four distinct management zones operated on a typical dairy farm namely, grazing only pasture, a dirty water treatment area that was managed in rotation with grazing, a one-cut silage growing area and a two-cut silage growing area, each of which were grazed after silage production. The results of this research provide further evidence of the link between agricultural practice in dairy farming and NO_3 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.

8.2. 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.

Groundwater NO_3 concentrations beneath Curtin's farm were nearly always elevated. In the 2001-2002 hydrological year, groundwater concentrations at ~28 m bgl varied from 3 to 31 mg/l NO_3-N, depending on the location of the piezometers in relation to the agronomic management areas. In the following hydrological year, the observed spatial variation in groundwater NO_3-N concentration was from 4 to 23mg/l.

The groundwater NO_3 response was discernible under small areas of differing agricultural managements. In other words, high NO_3 concentrations were generally observed under high N rather than low N inputs and out of season N inputs.

Analysis of NO_3 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 NO_3 concentrations were observed to rise in response to significant rainfall events in spring and summer but decreased, initially, with autumn and winter recharges due to recharge dilution effects. However, despite this decrease the NO_3 concentrations were observed to increase again in spring.

Nitrate concentrations in the groundwater monitored beneath Curtin's farm were elevated with respect to local background groundwater NO_3 status. Background groundwater concentrations in north Cork average less than 5 mg/l NO_3-N. The high groundwater NO_3 concentrations observed beneath Curtin's farm require that agricultural activity be more controlled in such vulnerable areas.

The observed peak concentrations of NH_4 in the groundwater at most boreholes were elevated and 77% of the monitoring locations revealed peak concentrations that breach the EPA IGV.

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, K, NH_4 and NO_2 peaks were observed in groundwater at over 25 m bgl, which suggests a highly vulnerable hydrogeological setting.

Incidences of groundwater contamination were also 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 should result in better groundwater quality.

8.3. Response to Agronomic Management

The timing and rate of N applications are one of the determining factors in nitrate leaching. The potential exists for large leaching losses following N fertiliser applications in late winter/spring. In some instances, groundwater NH_4, NO_2 and NO_3 concentration trends suggest that grazing activity and fertilisation in spring, followed by R_{eff} 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 N load available for potential loss.

The impact of late winter applications of N fertiliser was also observed to be detrimental to groundwater quality when R_{eff} occurred after inorganic fertiliser was applied.

The most useful integral measure of the N 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 NO_3 in the groundwater. The organic N loading rate is therefore a crucial factor in managing N loss to groundwater. This finding supports the aim of the Nitrates Directive (EC, 1991a) to restrict grazing intensity in vulnerable areas.

8.4. Driving Mechanisms

With respect to identification of the loadings that most significantly influence groundwater NO_3 concentrations – R_{eff}, or hydraulic loading, and the intensity of animal grazing were identified as the main drivers on the system.

The hydraulic loading, be it recharge from dirty water irrigation, recharge as rainfall or cattle urinations, is a key factor that determines NO_3 delivery to ground water. Nitrogen applications in excess of plant growth requirements increased the risk of leaching but recharge has been shown to be the ultimate driver of leachate generation.

8.5. Role of Hydrometeorological Loadings

Despite similar peak groundwater NO_3 concentrations in both years, in the second year there was a marked reduction in mean concentration. Winter R_{eff} in the second year was double that recorded in the first year, which means that the same available NO_3 loss load was diluted, potentially two-fold. The responsiveness of the system was thereby demonstrated: the NO_3 response in the groundwater was 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 for application to event-scale studies.

8.6. Tracing Experiment Results and Preferential Flow

Surface applied Br was observed to migrate though 2.5 m of subsoil to the groundwater body, at 28 m bgl, in less than three weeks. Indeed Br was observed in the groundwater body before it was observed in most subsoil ceramic cups installed at 1m below ground level. Bromide migrated 200 m horizontally in the groundwater body before peak concentration was observed in the ceramic cups. This strongly confirmed subsurface preferential flow and rapid hydrogeological response times.

Maximum vertical travel velocity to the groundwater body was ~1.66 m/day. Groundwater horizontal velocity was calculated to be ~8 m/day. This is of significance to groundwater movement to the local river.

Groundwater P and NH_4 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 NO_3 concentrations is quite opposite to the P response because NO_3 is not readily available at the soil surface; it is within the soil matrix arising from the N cycle. However, subsequent to preferential flow, matrix flow acts to transport NO_3 to the groundwater body.

The observed initial decrease in groundwater NO_3 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 NO_3 concentration. Subsequent slow percolation through the soil matrix, in spring, results in NO_3 enriched recharge to the groundwater body that does not significantly effect the water table elevation but does cause an increase in groundwater NO_3 concentrations.

8.7. 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 complying with the Nitrates Directive (EC, 1991a). The NCYCLE nitrogen loading model (Scholefield *et al.*, 1991) in combination with the networking routing RAM (ESI, 2000) model simulates annual peak groundwater NO_3 concentrations reasonably well in the studied area but further model development and validation will be necessary for wider geographical application.

The observed groundwater NO_3 response at Curtin's farm has a clear temporal dimension. Future modelling of NO_3 leaching and the 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 NO_3 load available for leaching.

9. Summary and Implications for Agricultural Practices

- The results of this research provide further evidence of the link between agricultural practice in dairy farming and NO_3 groundwater concentrations in Ireland.
- This research was conducted on a fully operational dairy farm operating in an area previously designated by the GSI as vulnerable to groundwater contamination.
- The Nitrates Directive (EEC, 1991) organic nitrogen limit of 170 kg N/ha implies a 2 LU/ha limit. The farm under investigation operated at a stocking rate of 2.4 LU/ha, which suggests an organic loading rate of approximately 200kg N/ha. Mineral N fertiliser application rates were 300 kg/ha, approximately.
- Groundwater NO_3 concentrations observed beneath Curtin's farm ranged from 4 – 31 mg/l. Lower concentrations were observed in the summer and in zones of relatively lower grazing intensity on the farm. Problematic NO_3 concentrations were observed throughout the year in areas that were more intensively grazed and also dirty water irrigation zones. The significance of the contribution of grazing animal's intensity, in vulnerable environments, is the major contribution of this research to scientific knowledge.

- The organic N loading rate is therefore a crucial factor in managing N loss to groundwater. This finding, in association with the observed elevated groundwater NO_3 concentrations, supports the aim of the Nitrates Directive (EEC, 1991) to restrict grazing intensity in vulnerable areas.
- Results from a similar experiment at Johnstown Castle (Bartley, 2003) add further validation to the vulnerability concept in the context of NO_3 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 NO_3 concentrations.
- These results indicate that regionalisation of organic N loading limitations, in light of intrinsic hydrogeological and meteorological conditions, might form more prudent policy under the Nitrates Directive (EEC, 1991) and the Water Framework Directive (EC, 2000).
- Other monitoring results show that the agricultural signature in the groundwater beneath Curtin's Farm is strong at some locations. In addition to high NO_3 concentrations, P, K, NH_4 and NO_2 spikes were observed in groundwater at over 25 m below ground level, which confirm a highly vulnerable hydrogeological setting.
- Also, the research provides evidence of subsurface preferential flow. Solute transport was observed to move through the subsoil to groundwater by two flow mechanisms: preferential flow and flow through the soil matrix. This finding has implications for P and pathogen migration from farming practice at the ground surface and Irish water resource quality, in the context of environmental and public health responsibilities.
- The potential exists for large leaching losses following N fertiliser applications in spring. The response was weather dependent. Given that the weather is uncontrollable, the only management option is to reduce the N load available for potential loss. The impact of late winter applications of N fertiliser was also observed to be detrimental to groundwater quality when R_{eff} occurred after inorganic fertiliser was applied.
- Incidences of groundwater contamination were also identified in response to dirty water irrigation periods. Intensive animal grazing, stores of nutrients in the soil and dirty water irrigation, coupled with a free draining soil and vulnerable hydrogeological conditions, are strong factors affecting groundwater quality at Curtin's farm.
- Slurry applications at Teagasc recommended rates and according to Good Farming Practice, applied during the growing season, do not result in significant NO_3 leaching to groundwater, which is to say that the groundwater NO_3 responses in the silage growing zones could not be related to slurry applications.
- This work has demonstrated the rapid response of groundwater hydrochemistry to hydrological and agronomic loadings in hydrogeologically vulnerable conditions at Curtin's farm. This has beneficial implications for dairy farming in that the significance of a rapidly responding hydrogeological system is that all improvements in management, specifically reducing grazing intensity and grazing rotation over wider areas of the farm, should result in an observable improvement in groundwater quality.
- The most prudent future research strategy would be to reduce farming intensity at Curtin's farm to below the Nitrates Directive (EEC, 1991) 170kg N/ha limit and monitor

the response in the groundwater over a similar, or longer, time period of the research presented in this report.

- Teagasc soil P and K 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.

- 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). 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. The literature suggests that the main aim should be to restrict the amount of N in the rootzone at the end of the growing season (Garwood and Ryden, 1986; Steenvoorden, 1989; Addiscott et al., 1991; and Whitehead, 1995). Modification of the dietary intake of animals and, on areas where there is a known risk of NO_3 leaching, taking cattle off the land earlier in Autumn are other literature suggestions for reducing leaching risk (Addiscott et al., 1991).

- Daly, (2004) suggests that the findings of this research apply to areas in Ireland with similar physical setting (i.e. shallow free draining soil and subsoil over a karstified limestone aquifer – estimated to be at least 8% of the country) and similar recharge conditions. In vulnerable areas where the average recharge rates are lower (such as in the east midlands) the agrochemical signal in the groundwater could be higher. The findings are not applicable to areas with poorly draining soils and subsoils, and in most areas underlain by poorly productive aquifers, as denitrification is likely to occur in these areas.

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Appendix A: Maps Relating to the Study Farm

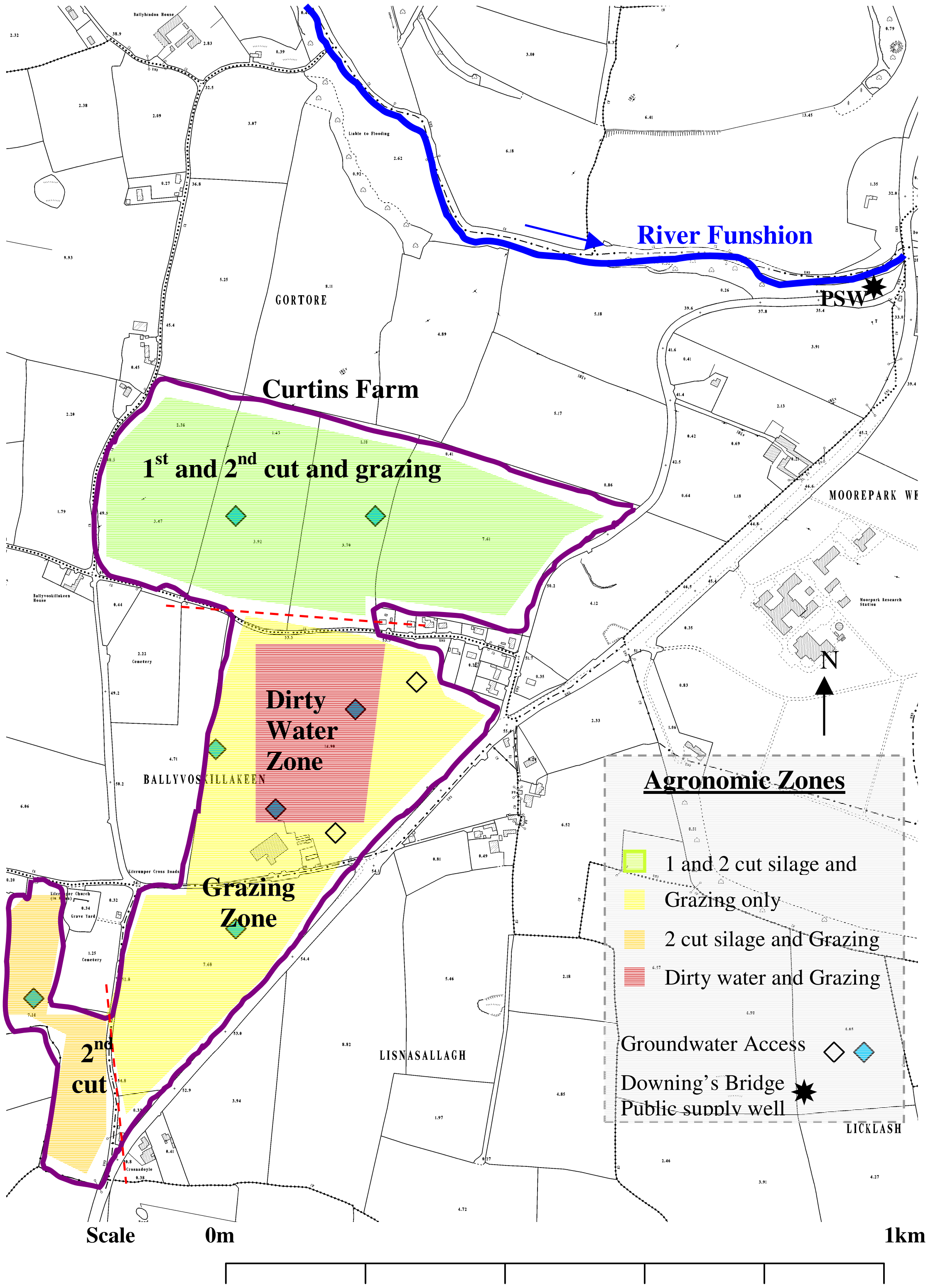


Figure A.1 Agronomic management zones on Curtin's farm.

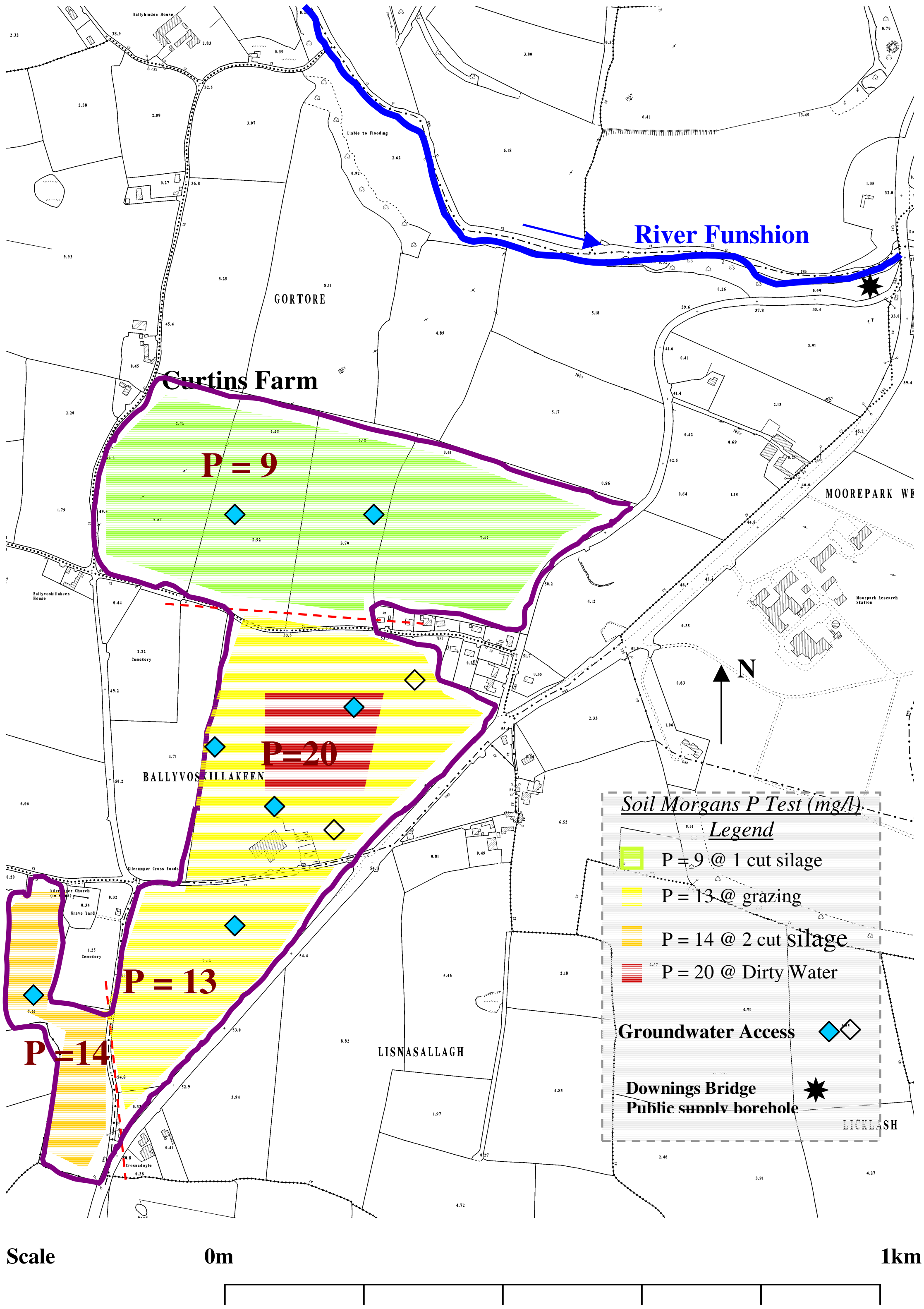


Figure A.2 Topsoil phosphorus (Morgans P) levels at Curtin's farm (January 2002).

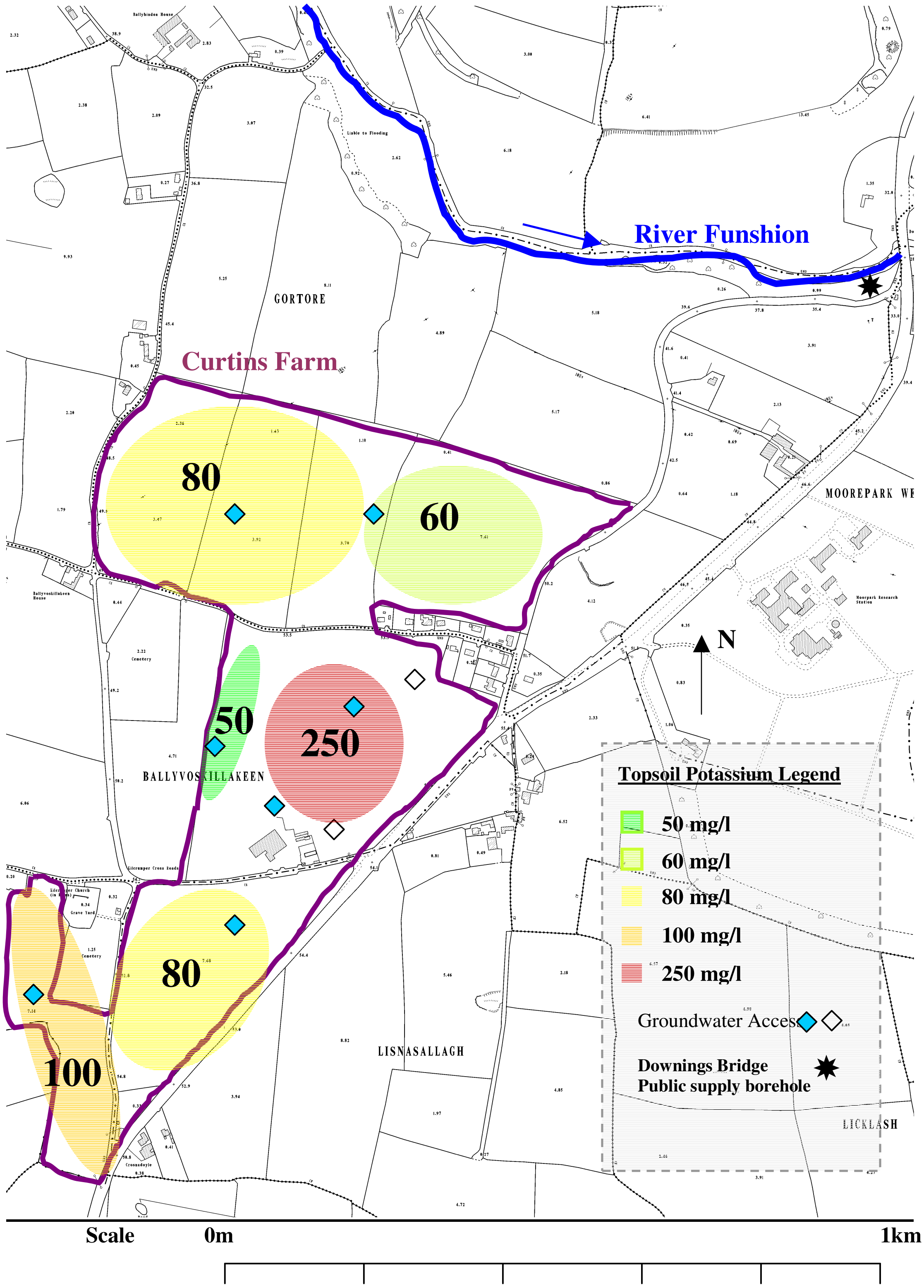


Figure A.3 Topsoil potassium (K) levels at Curtin'sf farm (January 2002).

Appendix B: Methodologies

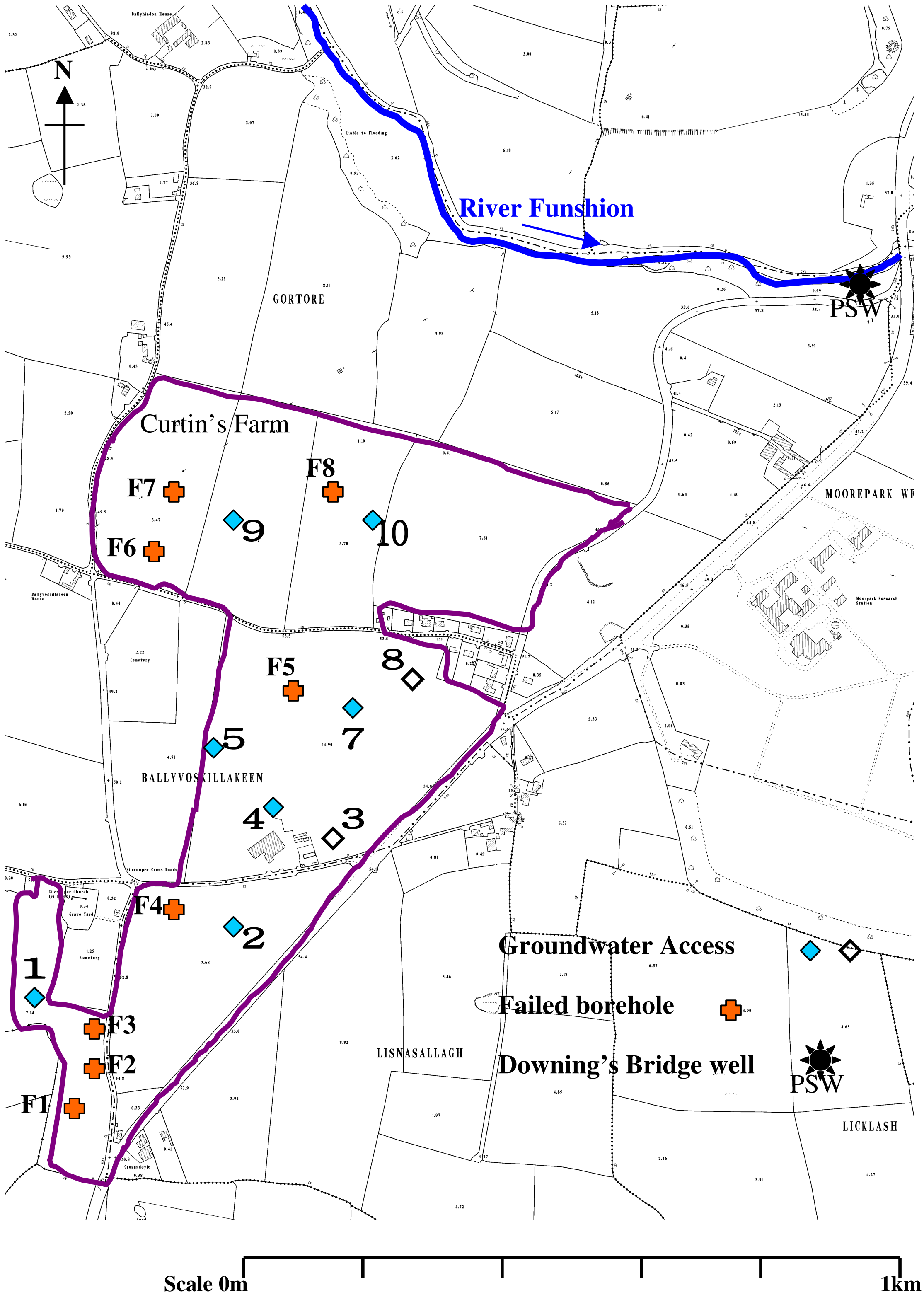


Figure B.1 All drilling locations, showing both failed (e.g. **F1**) and successful boreholes (e.g. **1** on this figure refers to the usual project borehole notation BHC.1, *etc.*).

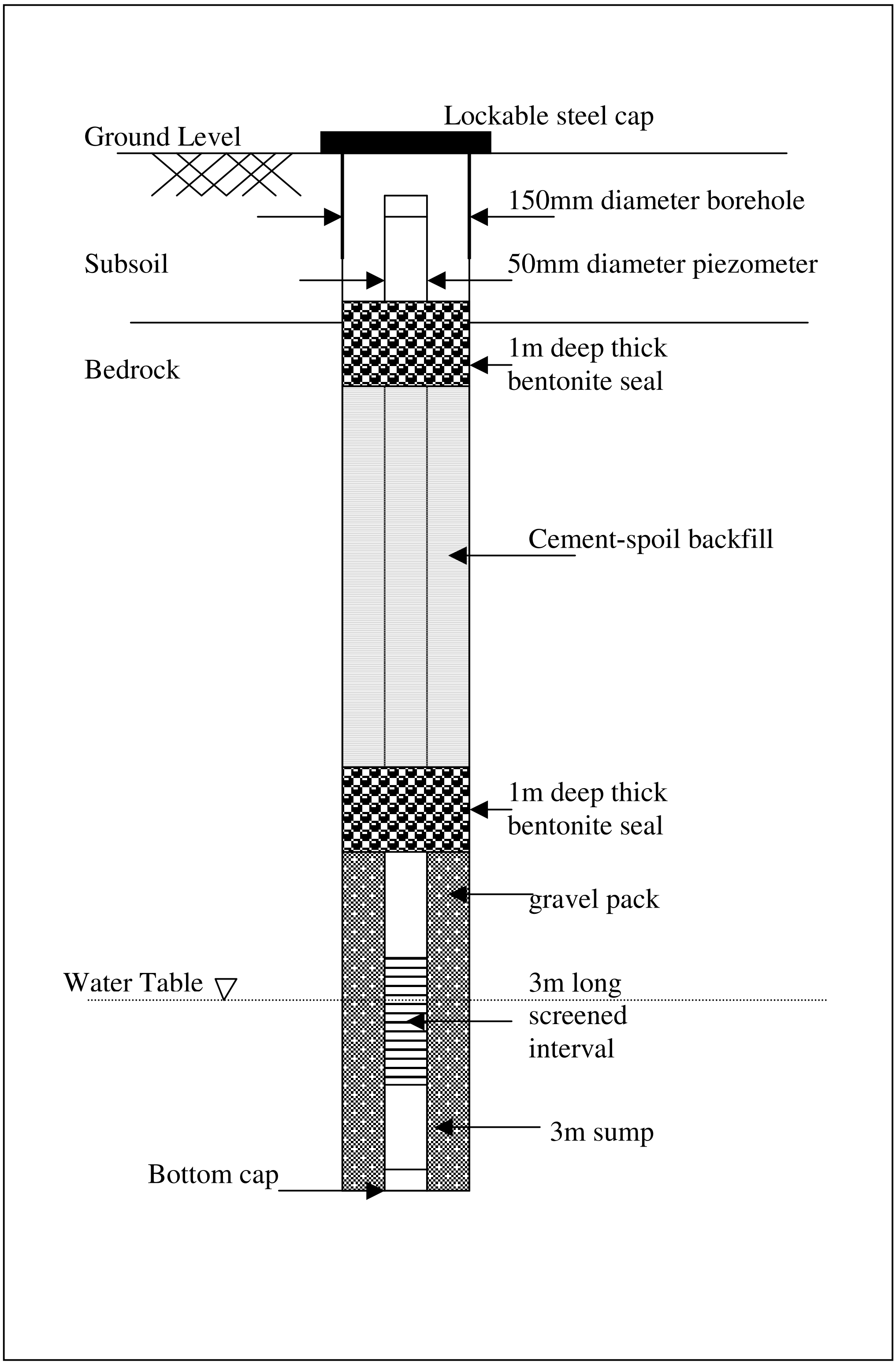


Figure B.2 Schematic detail of piezometer installations (not to scale).

Figure B.3 Sampling set-up at a Curtin's farm borehole (generator not shown).

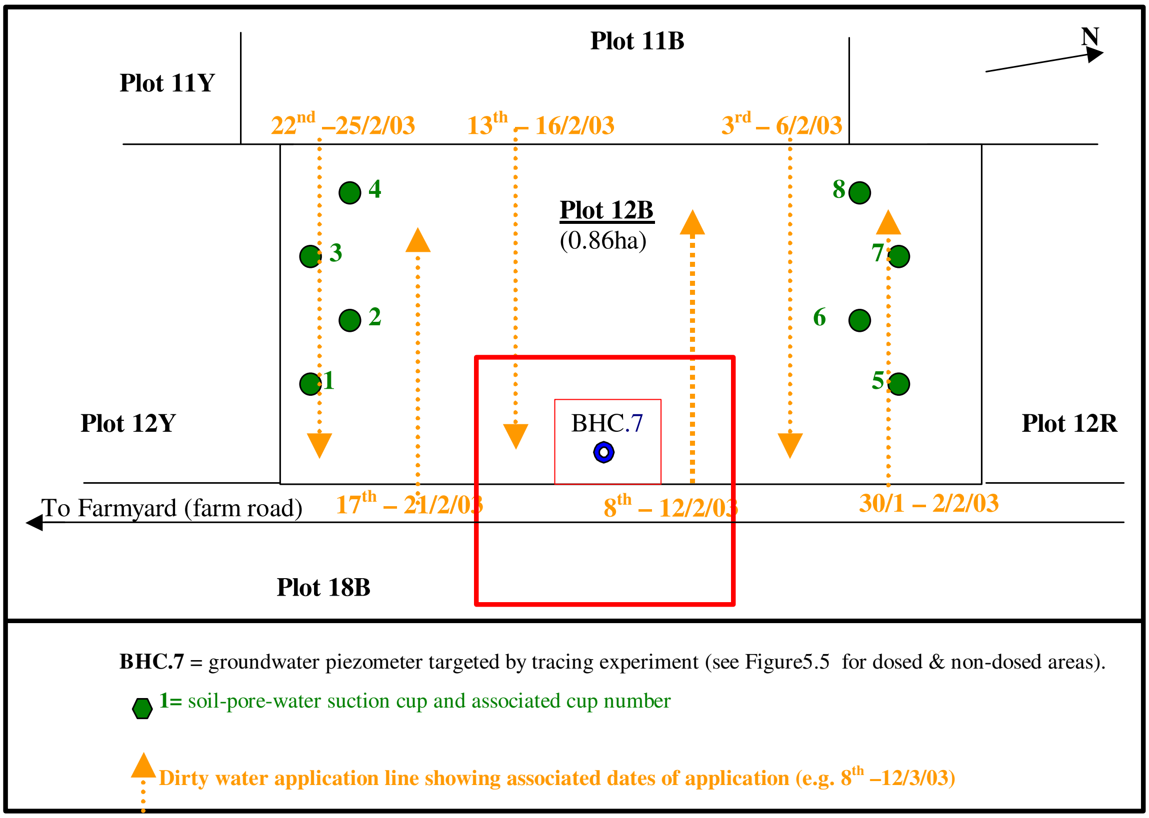


Figure B.4 Schematic representation of targeted instrumentation in the tracing-experiment's plot and recorded movement of the dirty water irrigator (not to scale).

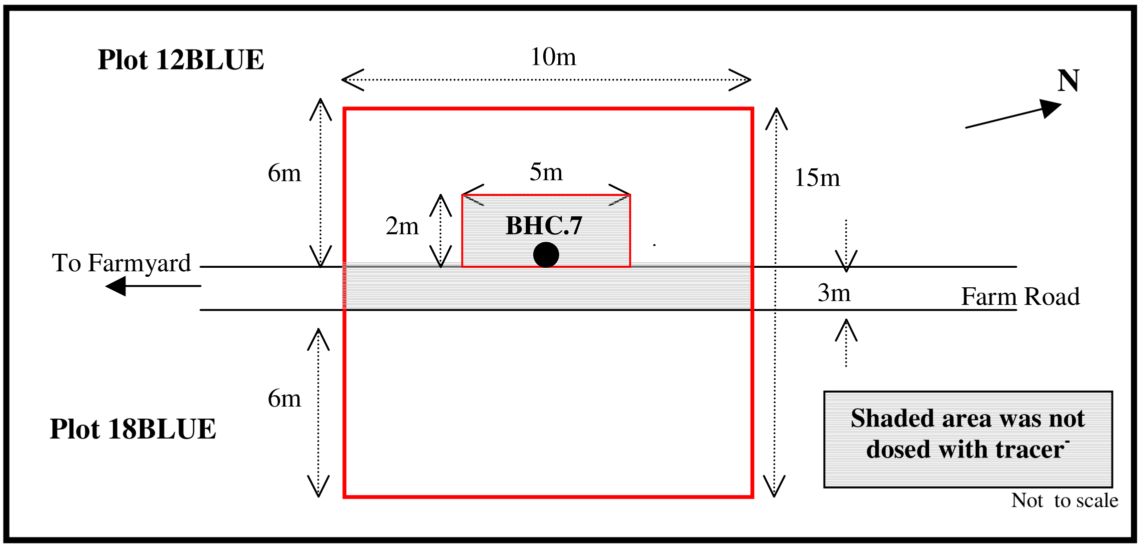


Figure B.5 Schematic for the tracer-dosed area around groundwater piezometer BHC.7. The shaded area shows the 40m^2 surface area that was not dosed with the tracer, KBr. (not to scale).

Table B.1 Farm gate nitrogen balance for Curtin's farm (source data: Curtin's farm manager)

	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%**

Table B.2 Calculated average annual total nitrogen (N) loading rates (kg/ha) 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)	Recycled Organic N (kg/ha)			
			Total Organic N (kg/ha)	Contributors to Total Organic N load		
				Grazing Animals	Dirty Water	Slurry
Grazing Only	22	**295**	**179**	179	None	None
Dirty Water and Grazing	7	**290**	**378**	198	180	None
One-Cut Silage and Grazing	7.5	**285**	**230**	138	None	92
Two-Cut Silage and Grazing	12.7	**340**	**194**	98	None	96
Area Weighted Application Rate (kg/ha)		306	216	152	26	38

Table B.3 Calculated average annual total nitrogen (N) loading rates (kg/ha) 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)	Recycled Organic N (kg/ha)			
			Total Organic N (kg/ha)	Contributors to Total Organic N load		
				Grazing Animals	Dirty Water	Slurry
Grazing Only	22	**290**	**165**	165	None	None
Dirty Water and Grazing	7	**248**	**471**	211	260	None
One-Cut Silage and Grazing	7.5	**298**	**256**	121	None	135
Two-Cut Silage and Grazing	12.7	**310**	**263**	76	None	187
Area Weighted Application Rate (kg/ha/yr)		290	248	142	38	69

Appendix C: Groundwater Monitoring Results

3 The location of each piezometer is presented in association with interpolated water table contours in Figure C.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 B.1 shows this bore as F5). **Data pertaining to BHC.10 is included here but was not considered in the analyses because of some form of structural failure that occurred mid-way throughout the experiment.** Groundwater nitrate-nitrogen concentrations, for the day on which the water levels were recorded, are also shown on Figure C.1.

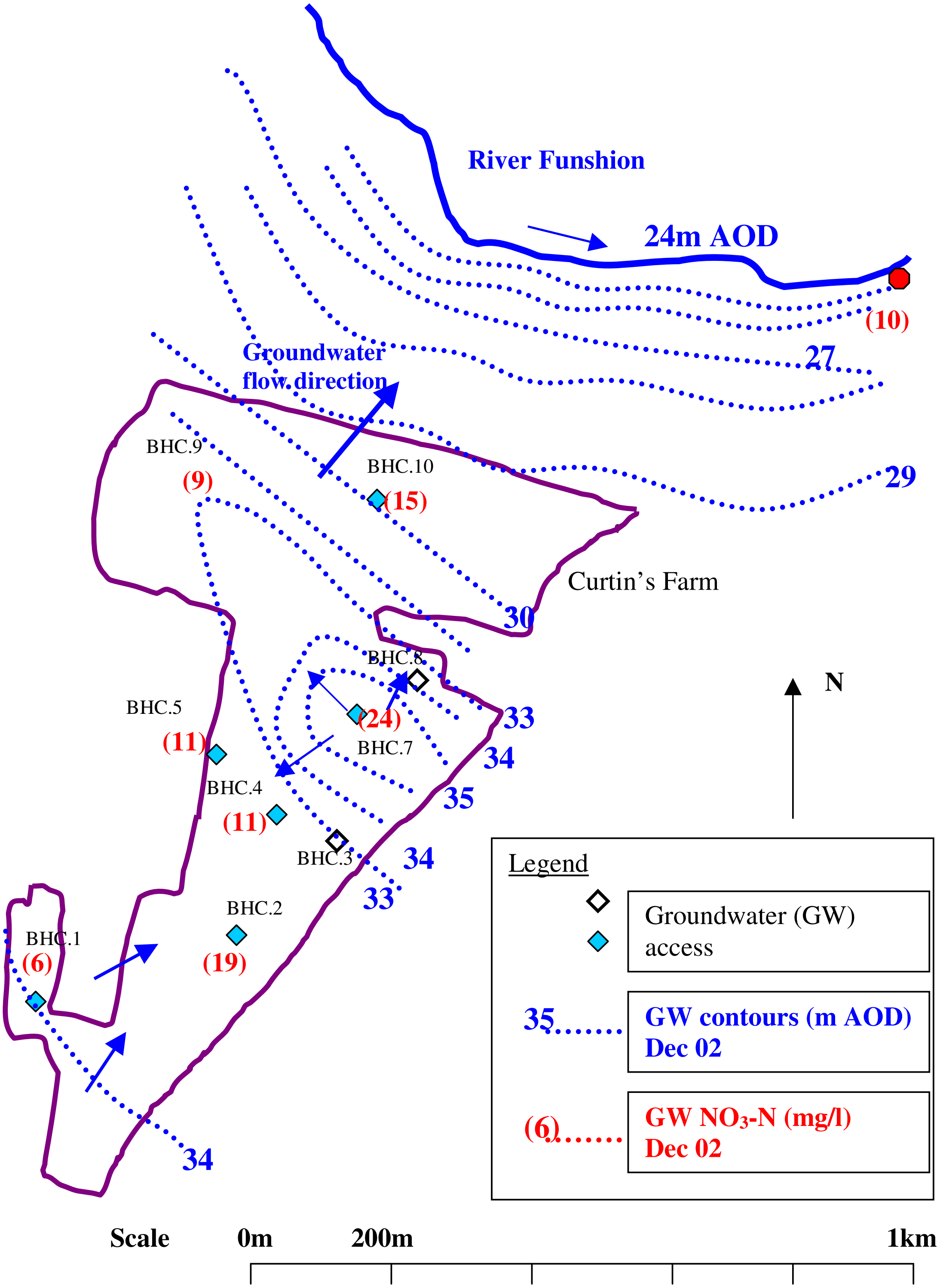
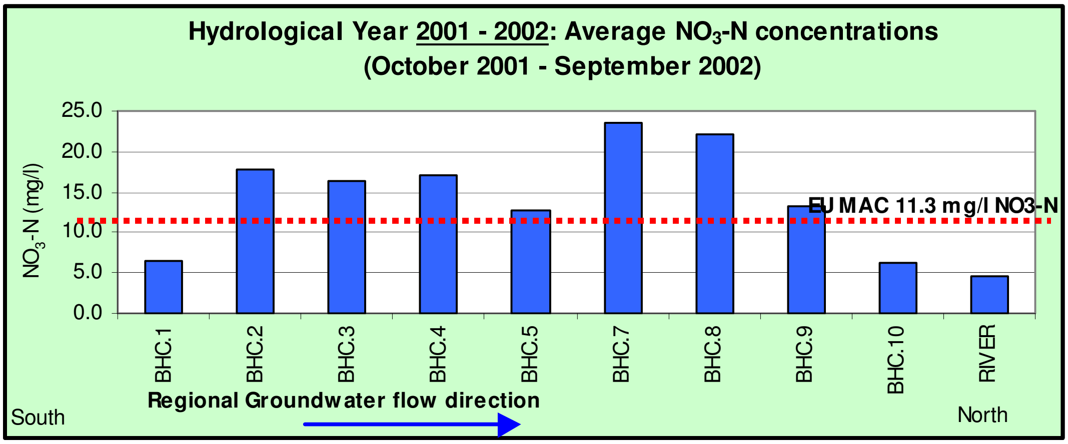


Figure C.1 Groundwater contours, flow directions and nitrate (mg/l NO_3-N) concentrations at piezometer locations on Curtin's farm, December 2002.

(a)



(b)

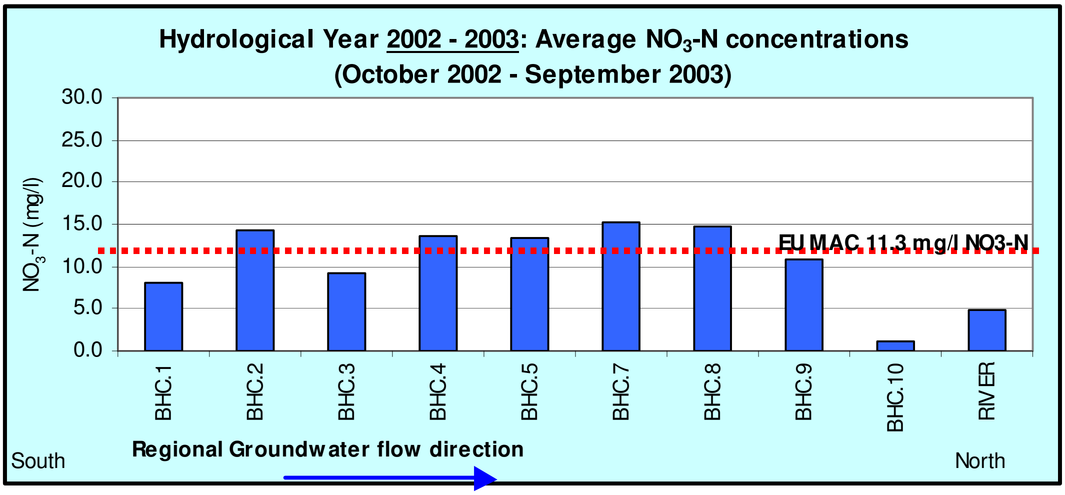


Figure C.2 Average groundwater NO_3-N concentrations for the 10 piezometers and the river Funshion for (a) the hydrological year 2001-2003 and (b) the hydrological year 2002-2003. The horizontal dashed red line in each chart denotes the parametric limit (EC, 1998), which was historically referred to using MAC terminology. The regional groundwater flow, towards the River Funshion, is shown on both graphs.

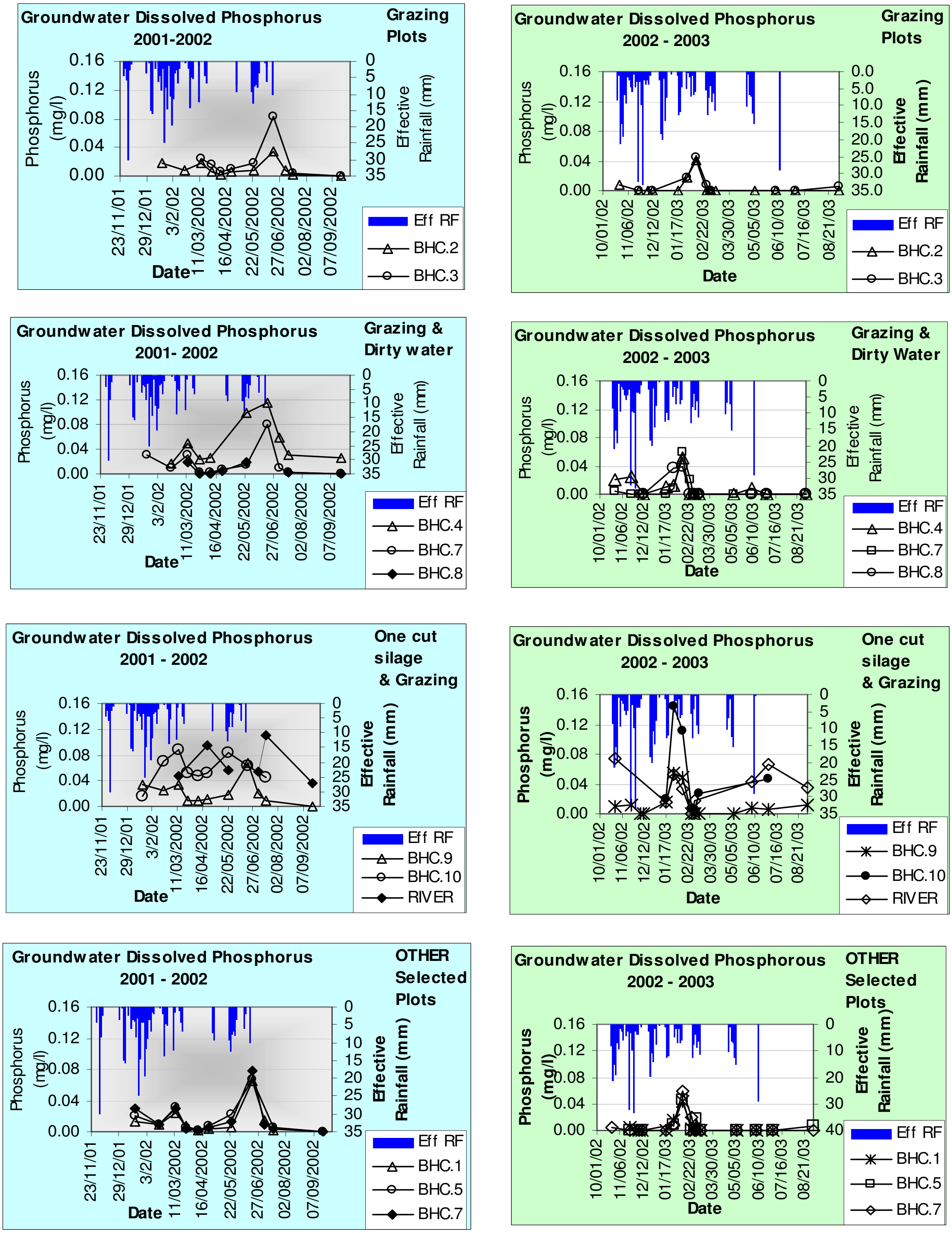


Figure C.3 Groundwater dissolved phosphorus concentrations and effective rainfall at Curtin's farm for the two monitoring periods (2001-2002 and 2002-2003) for each of the four agronomic management areas.

Table C.1 Summary of electrical conductivity measurements (μS/cm) from the 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

Table C.2 Summary potassium concentrations (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

Table C.3 Summary sodium (mg/l) 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**

Table C.4 Summary chloride (mg/l) 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

Table C.5 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

Table C.6 Summary sulphate data (mg/l) 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

Table C.7 Summary of nitrate (mg/l) concentrations at Curtin's farm piezometers and the River Funshion (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

Table C.8 Summary of groundwater ammonium concentrations (mg/l) at Curtin's farm piezometers and the River Funshion (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

Table C.9 Summary of groundwater nitrite concentrations (mg/l) at Curtin's farm piezometers 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

Table C.10 Summary of groundwater phosphorus concentrations (mg/l P) for all piezometers at Curtin's farm and the River Funshion (2001-2003). These results are for raw, unfiltered, groundwater.

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

Table C.11 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)

*Note: ceramic cup number five accidentally received a double dosing of dirty water.

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 max observed bromide	Recharge prior to max observed bromide$^+$	Max observed bromide 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**		**Max observed 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

Appendix D: Groundwater Nitrate Responses

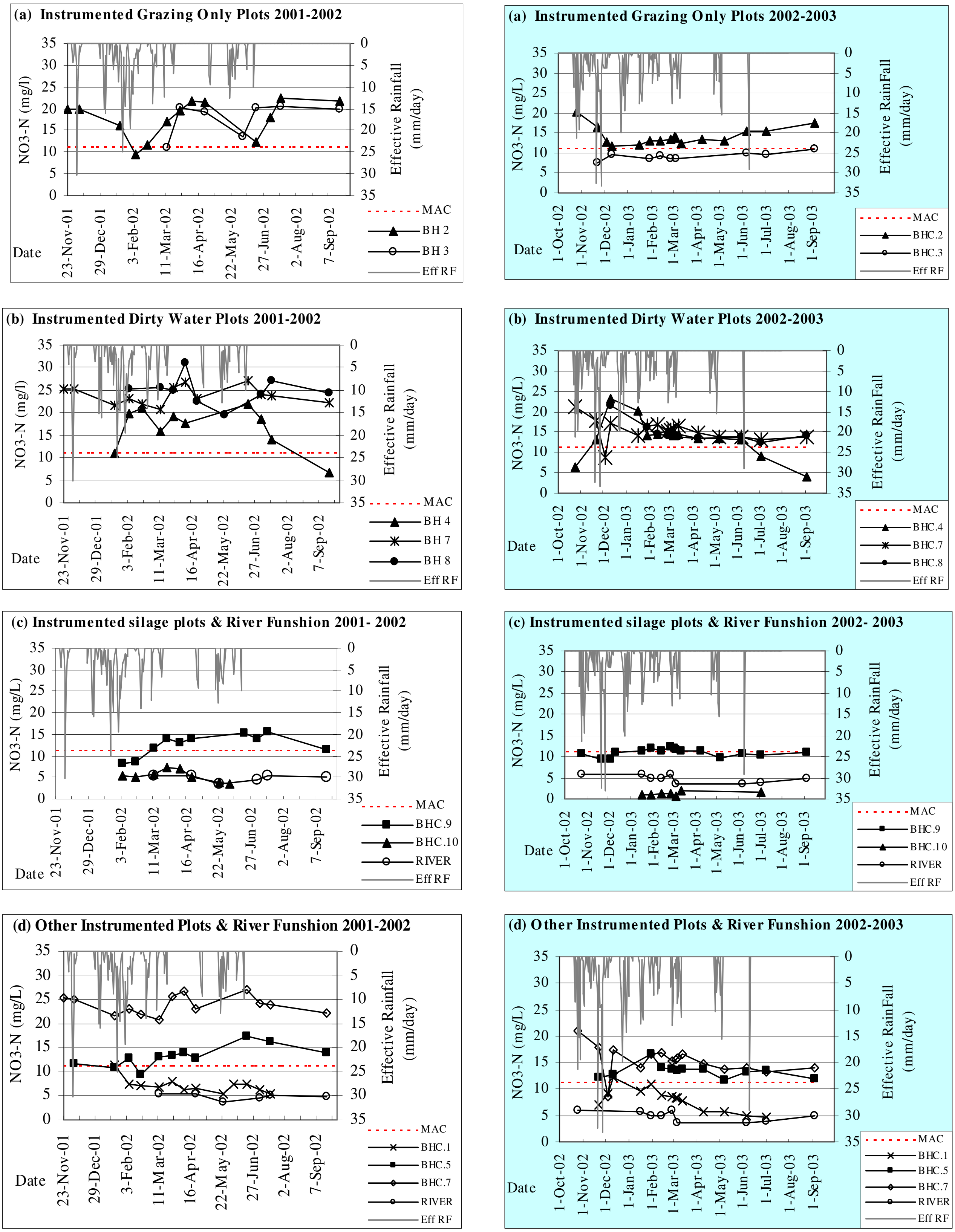


Figure D.1 Temporal groundwater nitrate (mg/l NO_3-N) trends grouped by agricultural treatment for the two monitoring periods (2001-2002 and 2002-2003) for each of the four agronomic management areas

Recharge and Non-Recharge Nitrate Concentrations

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.

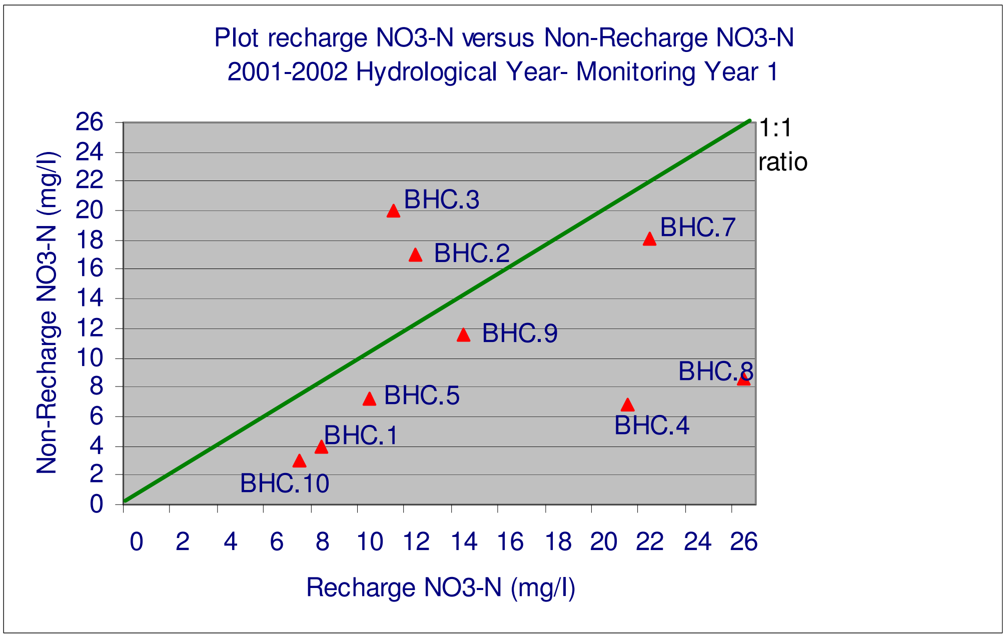
- Evidence for addition of surface-derived nitrate is provided by a positive correlation between nitrate and phosphate concentrations during the recharge season. A positive correlation between recharge nitrate and recharge phosphorus demonstrates that the source of these two ions is from fertiliser applied 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 R_{eff} 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'.

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 the farm yard, silage pit, underground slurry tanks and septic tank (the septic tank served six non-resident farm employees). 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 was examined and found to be potentially one impact, but not the only one, on groundwater quality at these locations. 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.

(a)



(b)

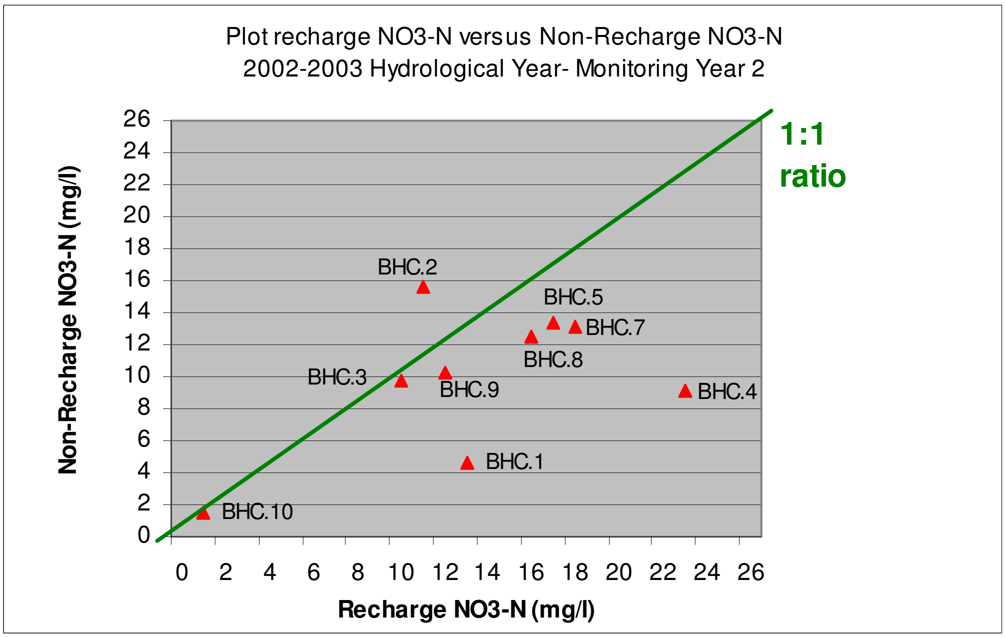
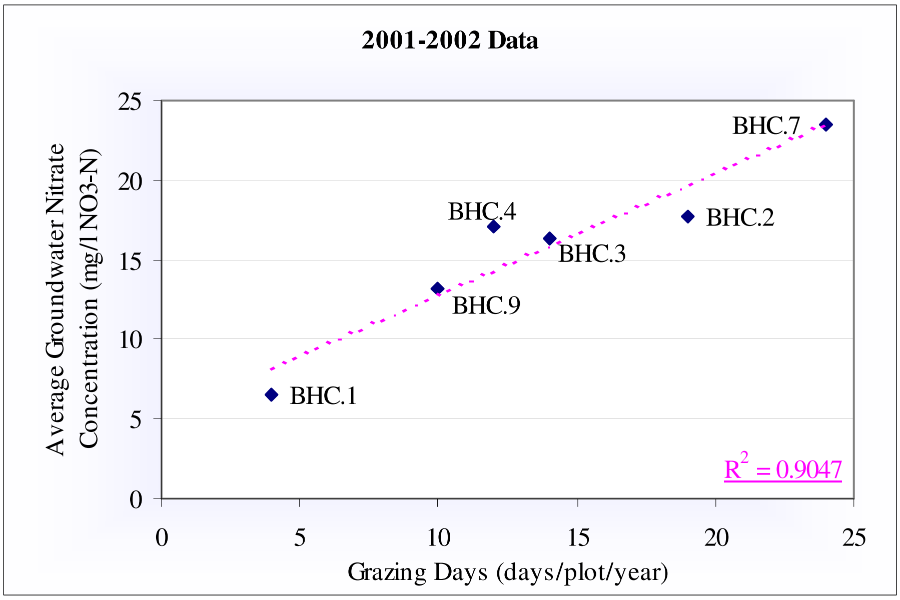


Figure D.2 Plots of recharge versus non-recharge groundwater nitrate (mg/l NO_3-N) concentrations for (a) 2001-2002 and (b) 2002-2003.

Grazing Day Relationship

In this analysis 'Grazing Days' signifies the number of full days that a plot was grazed by the herd. BHC.5 was not included because its plot was not grazed and the uncertainty regarding the integrity of BHC.10 also ruled out its use in this analysis. The raw data are presented in Bartley (2003).

(a)



(b)

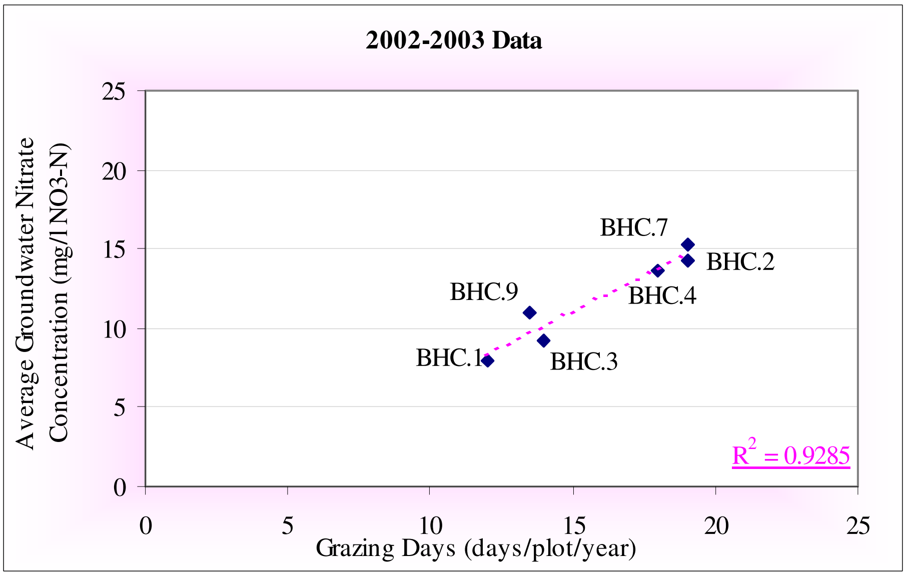


Figure D.3 The relationship between a plots' grazing days (herd) and average groundwater nitrate concentration observed in that plot's piezometer in the following year for (a) 2001 herd grazing days data and 2001-2002 average groundwater nitrate concentration data and (b) 2002 herd grazing days data and 2002-2003 average groundwater nitrate concentration data (trend lines have been added and the R^2 of the trend line is also shown).

Appendix E: Models Reviewed

Modelling Review (Bartley, 2003)

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).

The unsaturated zone nitrate leaching models discussed and tabulated in the review are as follows:

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

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 and Storm (1993);
- Lasserre *et al.* (1999);
- GLEAMS (Leonard *et al.*, 1987, Knisel, 1993);
- DRASTIC (Aller *et al.*, 1987);
- MODFLOW (Harbaugh and McDonald, 1996) and MT3D (Zheng, 1990);
- RAM (ESI, 2000).

Other models, not strictly groundwater models, 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 and Anthony, 2000);
- INCA (Whitehead *et al.*, 1998);
- NCATCH (Scholefield and Rodda, 1992);
- Van Herpe *et al.* (1998; 1999; 2002);
- Arheimer and Brandt (1998).