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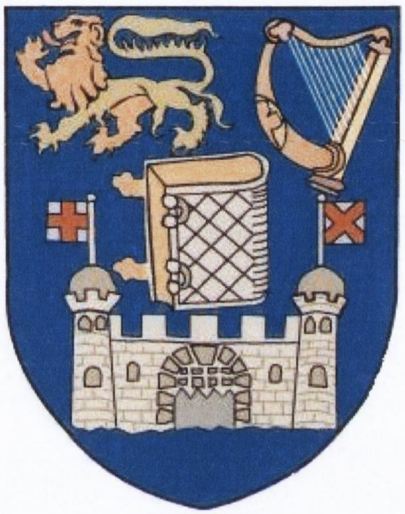
The Role of the Near-Surface Pathways in the Delivery of Flow and Nutrients to Streams in Irish Catchments



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2014

A thesis submitted for the degree of Doctor of Philosophy

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Declaration

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Summary

Management of pollution from diffuse agricultural and small point sources remains a significant challenge worldwide. Understanding and quantifying the contributions of flow and nutrients, through each hydro(geo)logical pathway, to the receptor of interest, is an important part of identifying the highest-risk, critical source areas (CSAs). The aim of this research was to develop an improved conceptual understanding of the near-surface pathways in the delivery of flow and nutrients to streams. The near-surface pathways included interflow, artificial drainage and flow in the transition zone, i.e. the weathered zone between the top of the bedrock and the overlying subsoils.

Field investigations were carried out in four study catchments, Gortinlieve, Co. Donegal, Glen Burn, Co. Down, Mattock. Co. Louth/Meath and Nuenna, Co. Kilkenny, ranging in size from 5 to 36 km^2. Conceptual models were developed to provide a four-dimensional hydro(geo)logical framework for understanding catchment dynamics. A programme of background and rain event water quality sampling was carried out in each catchment, in the river and the pathways, to gain insights into flow and nutrient transport. Chemical hydrograph separation methods were used to quantify the proportion of flow through each pathway. A deeper understanding of processes was achieved by integrating the results with those from physical hydrograph separation methods and hydrological modelling (NAM) that had been carried out by others.

A field-scale soil moisture dynamics study undertaken in the Mattock catchment corroborated the quantitative near-surface pathway estimates from the chemical hydrograph separation methods and further developed the conceptual model. Interflow comprised saturated and unsaturated lateral flow above lower permeability layers and was greatly enhanced by the artificial drainage network. The transition zone behaved like interflow in groundwater recharge areas, but was similar to shallow groundwater in groundwater discharge areas. Intermixing of near-surface pathways was common.

In catchments underlain by poorly productive aquifers, interflow was the main pathway contributing to streams in baseflow conditions. Overland flow was important during the early stages of rainfall events, but interflow became increasingly more dominant as the soils became more saturated. Increased soil saturation resulted in increased nitrate loads in the land drains and the river. The subsoils and the transition zone were found to be important stores of nitrate,

especially close to small point sources. The hydrogeological flow regime was an important controlling factor on the delivery of flow and nutrients through the land drains: higher permeability aerated zones, such as the transition zone in groundwater recharge areas, were high in nitrate. Phosphorus was high where it was delivered to the drains via macropores and shallow soil/subsoil. Higher concentrations were found adjacent to small point sources. A first flush effect was observed in nutrient concentrations in the early stages of events following dry periods.

This research has developed the understanding of the role of the near-surface pathways in catchments underlain by poorly productive aquifers. The application of several methods has integrated process understanding at field scale with catchment-scale assessments, an approach often recommended, but rarely seen in practice. The research has emphasized the need to develop three (or four) dimensional hydrogeological conceptual models as the foundation for future catchment science research. Preliminary work has been undertaken to develop a national map to depict the presence of land drains and the hydrogeological land drainage regime.

Research outcomes have contributed to a larger project, the *Pathways Project*, which has developed a suite of national catchment management support tools that identify the CSAs and will be used by regulatory and resource management agencies as part of implementation of the Water Framework Directive.

Acknowledgements

PhD thesis acknowledgements sections usually have a standard format: start with your supervisor and end with your family. Bruce, I hope you'll understand that in this instance I'm afraid I'll have to start with my family. Embarking on a PhD thesis as a working wife and mother of two young children was at best ambitious, but in truth, was nothing short of madness. In recognition of their endless patience, love and support, I'd like to dedicate this thesis to my long suffering husband Eoin, and my sons Aaron and Darragh, who could be forgiven for forgetting who I am. I am also indebted to my extended family for helping out with the kids; to my mother Lorna and Niall for putting up with me on week-long sojourns to 'get into the zone'; and to our friends the Maddens and the Musgraves for having the three lads to stay during school holidays to give me some space to think and work.

And so to my supervisor, Bruce Misstear. Notwithstanding the above (!), thank you for sowing the PhD seed in my mind, and for your gracious support, guidance and witty banter throughout. I have thoroughly enjoyed getting to grips with the subject matter, and I have relished the opportunity to get back into the field and to contribute to such a worthwhile project.

Thanks to students, staff and colleagues from Trinity College who were involved to varying degrees in this project. Special mention must go to Kevin Ryan for all the help with wiring my loggers which went above and beyond the call of duty; to Mark Kavanagh for generously sharing his expertise on the difficulties of analysing for low levels of phosphorus; to Paul Johnston for help and advice on the finer aspects of soil monitoring; and to Ronan O'Brien for help with fieldwork and Matlab routines. Thanks too to Pat Veale and to fellow environmental engineering postgrads for help and support in the field and in the lab.

This project was part of a wider multidisciplinary project that was delivered by a consortium of universities which meant that I also had the pleasure of working with staff and students from Queens University and University College Dublin. I would like to particularly thank Marie Archbold for keeping us all on track and for friendship and support throughout. Ray Flynn, Eva Mockler, Alison Orr, Ian Packham and the remainder of our project team; and Rachel Cassidy, Jean-Christophe Comte, Janka Nitsche, Katarina Pilatova and the rest of the Griffiths team; provided helpful input and discussions. There was also a small army of MSc and BEng students in Queens and TCD who collected an assortment of data that were very helpful in the development of the conceptual models. Thanks too to Robbie Meehan for generous advice as always on the subsoils.

A huge thank you goes to the Power family, who kindly allowed me to install my soil monitoring equipment on their land, and to all the other landholders in the four study catchments who helped out with access for taking samples and measurements. I am very grateful also to the Holmes family who allowed me to park in their driveway throughout my time in the Mattock, and who kept a watchful eye on me during late evenings in the field.

Finally, thanks to the EPA who funded the project and to the *Pathways Project* steering committee, Ian Cluckie, Donal Daly, Vincent Fitzsimons, Steve Fletcher, Phil Jordan and Taly Hunter Williams who provided helpful comments and review. Special thanks go to Donal Daly, without whose foresight the *Pathways Project* would never have come about. You have provided me with support, insights, guidance, friendship and opportunities throughout my professional career and for that I am truly grateful.

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Abbreviations

ACP	Agricultural Catchments Programme
ADC	acoustic Doppler current
AFBI	Agri-Food and Biosciences Institute
BFI	baseflow index
CAN	calcium ammonium nitrate
CO	catchment outlet
CSA	critical source area
DIN	dissolved inorganic nitrogen
DNRA	dissimilatory reduction of nitrate to ammonium
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
DP	deep percolation
DRP	dissolved reactive phosphorus
DUP	dissolved unreactive phosphorus
EFU	elementary functional units
EMMA	end member mixing analysis
EPA	Environmental Protection Agency
ET	evapotranspiration
FDC	flow duration curve
FLM	functional land management
GSI	Geological Survey of Ireland
GW	groundwater
HSMD	hybrid soil moisture deficit
ICP-AES	inductively couple plasma-atomic emission spectrometry
IF	interflow
LD	land drain
MRP	molybdate reactive phosphorus
NAM	Nedbore-Afstromings-Model
OD	ordnance datum
OF	overland flow
OSI	Ordnance Survey of Ireland

PCA	principal components analysis
PE	potential evapotranspiration
PSYCHIC	**P**hosphorus and **S**ediment **Y**ield **CH**aracterisation **I**n **C**atchments
Pl	poor aquifer which is generally unproductive except for local zones
PP	particulate phosphorus
Pu	poor aquifer which is generally unproductive
PUB	prediction in ungauged basin
QMRA	quantitative microbial risk assessment
QUB	Queen's University of Belfast
RAW	readily available water
SAC_{254}	specific absorbance capacity at a wavelength of 254 nm.
SCO	subcatchment outlet
SF	subsurface flow
SMART	**S**oil **M**oisture **A**ccounting **R**outine for **T**ransport
SM*n*	soil moisture sensor *n*
SMD	soil moisture deficit
SPR	source-pathway-receptor
SRP	soluble reactive phosphorus
SUVA	specific ultraviolet absorbance
TCD	Trinity College Dublin
TDR	time-domain reflectometry
TOC	total organic carbon
TON	total oxidizable nitrogen
TSS	total suspended solids
TZ	transition zone
UCD	University College Dublin
USEPA	US Environmental Protection Agency
UV	ultraviolet
WFD	Water Framework Directive
WWTP	wastewater treatment plant

Glossary of terms

The following glossary of terms is provided as a summary of the definitions of the main pathway terms used in this thesis for easy reference. The terms are described in more detail, and are referenced as appropriate, at first use throughout the text.

Baseflow	The flow component of a stream hydrograph that remains between rainfall events and responds slowly. Often presumed to be groundwater.
Effective rainfall	Rainfall minus actual evapotranspiration
Groundwater	Water stored or flowing through an aquifer in the saturated zone
Interflow	Lateral subsurface flow in the soils, subsoils and transition zone above the saturated zone
Overland flow	Water that flows in the top few centimetres on the land surface
Quickflow	The flow component of a stream hydrograph that responds to rainfall quickly. Often presumed to be overland flow.
Return flow	Subsurface water in the soils or subsoils that comes to the surface and flows as overland flow
Transition zone	The broken-up, weathered zone at the boundary between the top of the bedrock and the subsoils

1 Introduction

1.1 Background and context

Eutrophication of streams draining agricultural areas is a worldwide problem (Buss et al., 2005, Jordan et al., 2005, Tesoriero et al., 2009, Wei et al., 2013). It is caused by excess nutrients, i.e. nitrogen and phosphorus, in the aquatic environment (EPA, 2010), which alters the competitive balance between different plant and algae species; changes food sources, breeding habitats and shelter; and impacts on the whole ecosystem (Smith et al., 1999, Mainstone and Parr, 2002).

Phosphorus is present in the landscape in both organic and inorganic forms, and may be dissolved or present as a particulate, either adsorbed to soil particles or bound in mineral precipitates with iron, calcium or aluminium. Dissolved reactive phosphorus (DRP), which is largely inorganic, is the form of phosphorus that is most biologically available; however phosphorus cycles in and out of different forms with different processes as it moves through the landscape (Hyland et al., 2005). While this means that concentrations of particular phosphorus fractions can, and do change along a given pathway, in practice the processes that increase the biologically available phosphorus (other than by the addition of fertilizer) are slower than those that decrease it (Hyland et al., 2005). Over a short time scale such as a rainfall event therefore, the DRP fraction can be assumed to represent a 'worst case' scenario in terms of impacts on an aquatic receptor. The environmental quality standard for phosphorus in rivers in Ireland is for reactive phosphorus. Total phosphorus, on the other hand, is more appropriate for assessing the impacts on lakes because of the longer residence times and storage in the sediment.

Nitrogen is also present in both organic and organic forms, and may be particulate or dissolved. Nitrate is the most stable and therefore most commonly found form of nitrogen, and it is the most readily available to plants. As nitrate and most soils in temperate regions are both negatively charged, nitrate is not retained in the soils and can be easily leached if excess is applied (Di and Cameron, 2002).

The origins of the excess nutrients in Ireland are (a) major point sources, such as wastewater from agglomerations, and (b) diffuse sources from agriculture and small point sources, such as farmyards and poorly sited or managed domestic waste water treatment systems (EPA, 2010). Significant investment has been made in recent years in controlling the large point sources, but the diffuse and small point sources remain a significant issue. Diffuse sources of pollution are

typically widespread, less well regulated and difficult to manage. They are a key threat to water quality and aquatic ecosystem health in many parts of the world and remain a significant challenge in meeting water management objectives (Novotny, 1999, EC, 2000, Heathwaite et al., 2005, Archbold et al., 2010, Patoine et al., 2012, Stockwell et al., 2012).

The Water Framework Directive (WFD) (EC, 2000) is a major piece of EU legislation designed to protect, preserve and improve the aquatic environment while encouraging the sustainable use of water. Under the WFD, member states are required to implement programmes of measures in river basin districts with a view to achieving and maintaining 'Good Status' environmental objectives in all water bodies by 2015 (or by 2021 or 2027 in certain circumstances). In comparison to our EU neighbours, water quality in Ireland is relatively good, yet more than half of all river water bodies are at less than Good Status (EPA, 2010), and there are increasing pressures in most catchments that have the potential to further degrade water quality. The main reason for the failure to meet the Good Status objectives in Ireland is eutrophication.

1.2 A risk-based approach: Source-Pathway-Receptor model

A risk-based approach to the management of diffuse sources of pollution is essential to focus the management effort so that targeted, efficient, and cost effective mitigation measures can be implemented in places where they will have the best outcomes. The Source-Pathway-Receptor (SPR) model provides a useful environmental risk management framework which is implemented widely (Ansell and Wharton, 1992, Haygarth et al., 2005, Schulte et al., 2006).

1.2.1 Sources

Diffuse sources of nutrients in the landscape arise from a range of land uses, although agriculture is the most important. Smith et al. (2005) reported that 58% of phosphorus losses to rivers in Northern Ireland come from agriculture. Agricultural activities, such as application of artificial fertilizers and animal manures, farmyard runoff, and poorly managed animal watering and feed sites are important sources of diffuse contaminants, although poorly sited domestic onsite waste water treatment systems, forestry and other land-use activities are also a factor (EPA, 2010, EPA, 2012). Nitrate losses are known to be highest from land under tillage (Thomsen and Christensen, 1998). Addiscott (1996) suggested however, that nitrogen fertilizer applied in spring is less important as a source than decaying organic matter in wet and warm autumn soils leading to winter leaching. Tunney et al. (2000) showed that farmyard runoff was the source of between 37 and 45% of export of phosphorus from the farm at baseflows, and between 22 and 35% during events. They noted that farmyards had a disproportionately higher impact during summer rainfall events as the soil moisture deficits in the fields reduced the quantities of runoff.

In addition to nutrients, many of these sources also generate water-borne pathogens, which are an important human health issue in Ireland (Hynds et al., 2012). For example, Edwards et al. (2012) found that despite many fields being grazed and/or receiving regular applications of slurry/manure in a headwaters stream catchment in northeast Scotland, 60% of the total flux of faecal indicator organisms originated from farmyards. Agricultural practices are also commonly a source of sediment (Harrod and Theurer, 2002) which is an issue in aquatic environments due to impacts on habitat, fish mortality, and light availability for primary production. Bilotta et al. (2008) reported that while there has been a strong focus on soil erosion from arable land and steep catchments, agricultural grassland catchments can also contribute significantly. Sediment can also be instrumental in the transport of other particulate contaminants, especially phosphorus (Thompson et al., 2014).

Nutrients are removed each year in crops and animal products and so need to be replenished via imported animal feed, fertilizers and manures. Ideally the system should be in balance with only sufficient nutrients being added to replace those that are lost, but balance is difficult to achieve. Soil phosphorus levels, for example, need also to be taken into account as phosphorus is stored in the soils. Rainfall and antecedent soil moisture conditions prior to and after the application of fertilizers play a very significant role in whether and how nutrients are transferred from the land surface to a water resource (Misselbrook et al., 1995, Nash et al., 2000). It is widely known that excess application of nutrients can result in losses to groundwater or surface water, which may lead to eutrophication and consequent damage to the health of aquatic ecosystems (Haygarth et al., 2005, Domagalski and Johnson, 2012, Doody et al., 2012).

1.2.2 Receptors

The receptors are the aquatic resources that require protection from contaminants, such as drinking water wells, surface water streams and groundwater-dependent wetlands. Different receptors have different contaminant standards or limits, depending on their interactions. Drinking water supplies for instance, have a standard for nitrate recommended by the World Health Organization due to its implications for human health, although there has been recent debate as to whether they are appropriate (van Grinsven et al., 2006); there are no equivalent health concerns about phosphorus so limits have not been set. In the aquatic environment, plants depend on both nitrogen and phosphorus for growth, and can be limited by one, or other, or both. Traditionally, phosphorus has been known as the key limiting nutrient in rivers (Mainstone and Parr, 2002) and in lakes (Schindler, 1977), but more recently it has been shown that nitrogen is equally as important (Elser et al., 2007). Excess nitrate is an especially important factor in

eutrophication in the estuarine environment (Rabalais, 2002) so it is important that nitrate loads in upstream rivers are adequately managed.

In Ireland, the environmental quality standard for phosphorus for river water bodies is a mean concentration of <0.035 mg/l molybdate reactive phosphorus (MRP) as phosphorus (EC, 2009), which is the Good/Moderate status boundary as required under the WFD. The threshold value for estuarine and near shore coastal waters is 0.04 to 0.06 mg/l as phosphorus depends on the level of salinity (Clabby et al., 2008). Where a groundwater body provides more than 50% of the hydraulic load to a surface water body not at Good status, then the threshold value for groundwater quality is also a mean annual concentration of 0.035 mg/l as phosphorus to protect against groundwater as a pathway delivering high phosphorus (EC, 2010). The typical concentrations of phosphorus in wastes are several orders of magnitude higher than this limit, e.g. 0.6 mg/l in cattle slurry (Martinez-Suller et al., 2010); 2 mg/l in septic tank discharge (EPA, 2009); and 52 mg/l in dairy farmyard runoff (Ryan, 1991), so the risks of failing to meet the WFD objectives because of elevated phosphorus in the Irish rainfall climate are high.

There is currently no equivalent formal environmental quality standard for nitrogen in rivers, although an interim surrogate standard of 1.8 mg/l as nitrogen for the Good/Moderate threshold boundary has been adopted (EPA, 2013). Threshold values of 0.25 to 2.6 mg/l as nitrogen (depending on salinity) are in place for estuaries (Clabby et al., 2008), whereas for groundwater, the limit is 8.5 mg/l as nitrogen based on the Drinking Water Standards (S.I. No 278 of 2007).

1.2.3 Pathways

The pathways are the hydro(geo)logical linkages or transport routes for contaminant delivery from the sources to the receptors, and they can also facilitate attenuation of contaminants in certain circumstances. Pathways can be above or below ground, or a mixture of both, and are specific to the nature of the contaminant being transported. Nitrate, being a highly mobile negatively charged ion, tends to infiltrate readily if not taken up by plants, and is delivered to streams via subsurface pathways (Kröger et al., 2007, Tesoriero et al., 2009). Phosphorus, on the other hand, is largely immobile and is readily adsorbed in soils that are not already phosphorus-saturated, particularly in the presence of clays, calcium, iron and aluminium ions (Jordan et al., 2005). Larger quantities of phosphorus are therefore typically delivered in particulate form via overland flow, but nevertheless, significant quantities of dissolved phosphorus (and particulate phosphorus in preferential pathways) can also be delivered via the subsurface pathways (O'Reilly, 2006).

Contaminant sources without a pathway link to a receptor do not pose a risk to that receptor. Assessing the nature of the pathway linkages between the sources and the receptors, with a view to providing the evidence base for sensible environmental management decision making, is the subject of an increasingly large body of research.

1.2.4 Critical source areas

Critical source areas (CSAs) can be defined as the places within a catchment where the sources of a contaminant are linked hydrologically to the aquatic receptors of interest. CSAs are contaminant specific because different substances are transported and attenuated differently within the soils, subsoils and bedrock, and respond differently in rainfall events (Melland et al., 2012b, Thompson et al., 2012). The concept of CSAs has been around for a long time and is considered to be a useful means of prioritizing resources when implementing programmes of measures to achieve the best environmental outcomes (Maas et al., 1985, Haygarth et al., 2005, Heathwaite et al., 2005, Strauss et al., 2007, Daly, 2013). The approach reflects the understanding that relatively small areas of a catchment typically contribute disproportionately high amounts of contaminants (Ghebremichael et al., 2013). CSAs combine knowledge of the sources and the pathways, and as they represent the highest-risk areas, targeting them for programmes of measures ensures the most cost effective use of resources (Srinivasan and McDowell, 2009). CSAs can vary dynamically with rainfall conditions, which in Ireland means varying seasonally as well as spatially due to the climatic differences between the northwest and the southeast (Schulte et al., 2006).

Due to its role as a limiting nutrient, the transport of phosphorus in catchments has received much attention in the literature and CSA approaches are often used to determine the highest-risk areas. Surface or near-surface delivery pathways are dominant in the transport of phosphorus, so typically CSA models have applied a surface runoff connectivity approach using predominantly the topography as the principal controlling factor (Heathwaite et al., 2005, Strauss et al., 2007, Hahn, 2012).

Less emphasis has been put on defining CSAs for the transport of nitrogen to streams (Melland et al., 2012a). This may be because nitrate, which is the dominant form of nitrogen in the agricultural landscape at the catchment scale, tends to be delivered via subsurface pathways and groundwater has therefore tended to be the aquatic receptor of interest (Wang and Yang, 2008). However, groundwater is linked hydrologically to surface water and therefore contaminants entering groundwater are also likely to pose a risk to surface water at some time in the future, depending on the hydraulic properties of the aquifer, the attenuation and dilution processes, and the nature of the groundwater-surface water interactions in the hyporheic zone (Ranalli and Macalady, 2010). In contrast to phosphorus studies, a full three-dimensional hydrogeological

conceptual understanding of the groundwater flow dynamics in a catchment is therefore essential for determining the fate and transport of nitrate.

The most effective management measures are implemented by targeting the CSAs (Doody et al., 2012). For example, in free-draining catchments where nitrate delivered to streams via subsurface pathways is an issue, the installation of buffer strips to intercept fertilizer runoff via overland flow would be ineffective (Mellander et al., 2012, Ibrahim et al., 2013). Buffer strips would be of benefit however, where soils are poorly drained and surface runoff of sediment and particulate phosphorus are prevalent. Quantifying the nature of the hydro(geo)logical pathway linkages and the attenuation processes that occur along them, are therefore important elements in the implementation of successful mitigation measures (Wall et al., 2011).

There are significant opportunities in Ireland for growth in agriculture with the lifting of the dairy quota and the Food Harvest 2020 policy agenda (DAFF, 2011), yet significant improvements in water quality still need to be made, even under the existing levels of development. Identifying the CSAs (and understanding the hydro(geo)logical pathway linkages) is a key priority so that cost effective measures can be targeted.

1.3 Pathways Project

This PhD research was carried out within a large multidisciplinary project, known as *The Contaminant Movement along Pathways Project*, or the *Pathways Project* in short. The project was funded by the Environmental Protection Agency (EPA) and was carried out by a consortium of university partners including Trinity College Dublin (TCD), the Queen's University of Belfast (QUB) and University College Dublin (UCD). The overall aim of the project was to integrate knowledge of hydrological processes, and the fate and transport of diffuse contaminants delivered to aquatic receptors via the different hydro(geo)logical pathways. These findings were used to develop and populate a suite of catchment management support tools to assist in the implementation of the WFD (Archbold et al., 2010).

Four contaminants of interest were investigated and modelled throughout the project: nitrogen, phosphorus, pathogens and suspended sediment. Preliminary investigations also considered incorporating pesticides into the contaminant suite, but due to the lack of Irish pesticide data it was determined at an early stage in the project that this would not be feasible.

The objectives of the *Pathways Project* were:

1. Identification of significant hydrological pathways within river basin districts;
2. Quantification of flows along the identified hydrological pathways;

3. Identification of the significance of these pathways for diffuse pollutant transport and attenuation, with particular emphasis on the attenuation of nutrients (nitrogen and phosphorus species), and particulate matter (pathogenic micro-organisms and sediments);
4. Identification of CSAs contributing diffuse pollutants to groundwater, surface water and relevant ecological receptors; and
5. Development of a catchment management support tool using data collected during the study in line with the requirements of the end-user.

The suite of tools will be used by the EPA to characterize catchments for the purposes of WFD implementation and to carry out catchment scenario analyses relating to, for example, land use or climate change (Deakin et al., 2013). The tools have national coverage, can be used in both gauged and ungauged catchments, and are available at the subcatchment scale.

As part of the *Pathways Project*, field studies to inform the development of the catchment management support tool were carried out in four study catchments, which are summarized in Table 1.1. The catchments were selected by the project team and steering committee with the aid of a multi-criteria selection methodology but ultimately, the two most critical factors were (a) the presence of existing high quality borehole monitoring infrastructure and historical data, and (b) representativeness of a range of hydrogeological and climatic settings typical in Ireland. Several researchers worked on different issues in a range of catchments. In addition, three of the catchments (Mattock, Glen Burn and Gortinlieve) were also the research catchments for a sister project, the *Griffiths Project*, investigating the hydrogeological characteristics of Ireland's poorly productive rocks. This collaboration had advantages in terms of sharing infrastructure, data collection and resources.

Table 1.1. Study catchments.

Catchment	County	Size (km^2)	Aquifer	Subsoils	Soils
Mattock	Louth/Meath	17	Pl/Pu	Low permeability clayey tills, some gravels	Poorly drained
Nuenna	Kilkenny	36	Rk_d	Moderate permeability limestone till, gravel	Well drained
Gortinlieve	Donegal	5	Pl	Low permeability clayey tills, alluvium	Poorly drained
Glen Burn	Down	5	Pl/Pu	Low permeability drumlin tills over shallow rock	Poorly drained

[1]Aquifer categories are from the Geological Survey of Ireland classification system. Pl and Pu are poorly productive aquifers, although there is some additional permeability in local fault zones in Pl rocks. Rk_d aquifers are regionally important karstified aquifers with dominantly diffuse flow (DoELG et al., 1999).

1.4 Hydro(geo)logical flow pathways

The pathways investigated in the *Pathways Project* are based on a conceptual model developed by Daly and Hunter Williams as part of a further characterization study during the development of the Irish river basin district plans (Figure 1.1). The model has four pathways: overland flow, interflow, shallow groundwater flow and deep groundwater flow.

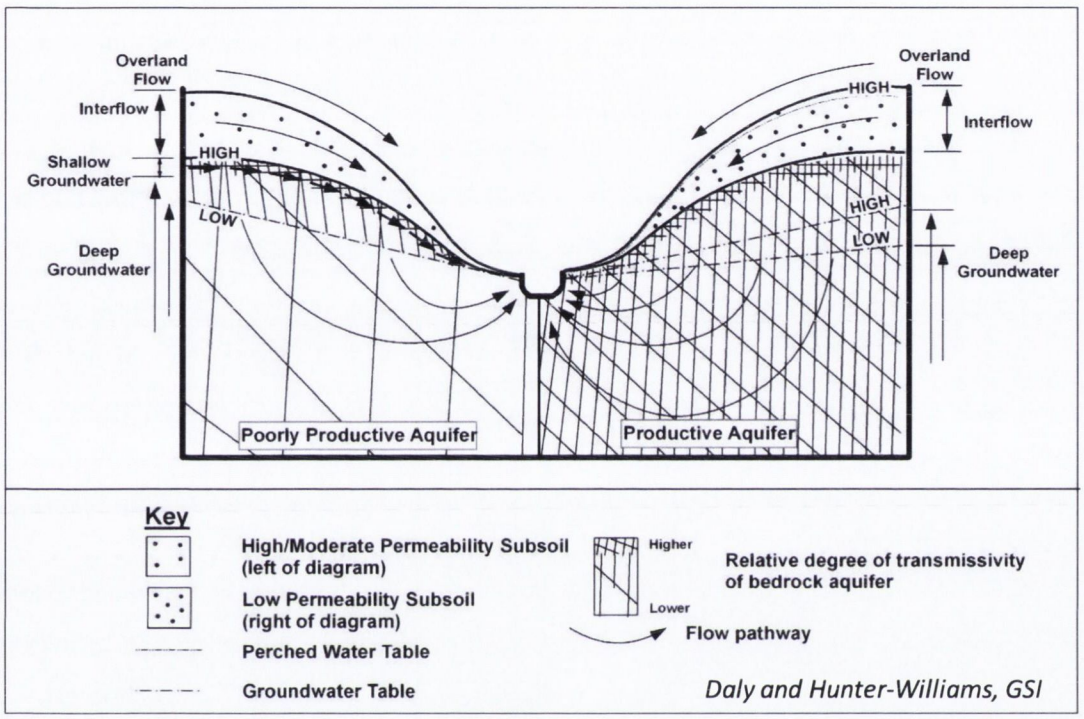

Figure 1.1. Conceptual model of the dominant hydro(geo)logical flow pathways contributing to a stream (from Daly and Hunter Williams, as reported in RPS (2008))

Overland flow is sheet flow occurring on the land surface (Shaw, 1994). In Ireland, it commonly occurs only after the soil becomes saturated, i.e. saturation excess overland flow (Nash et al., 2002) although infiltration excess overland flow is also known to occur (Doody et al., 2010). Overland flow is sometimes termed surface runoff or direct runoff and it produces a rapid response in a stream hydrograph.

Interflow is defined in different ways in the literature but it is generally taken to be any lateral subsurface flow that occurs between the ground surface and the water table (Dingman, 2002, Nash et al., 2002, Chin, 2006). It can occur in both the topsoil and subsoil, and may include unsaturated matrix flow, bypass or macropore flow, and saturated flow where there are locally perched water tables. Interflow may also include artificial field drainage (Archbold et al., 2010).

Shallow Groundwater flow occurs within the upper 5 to 15 m of bedrock where the rocks are highly fractured, and it is considered to be the main groundwater pathway in poorly productive

aquifers. The transition zone, which is the broken-up, highly weathered zone at the interface between the bedrock and the overlying subsoils, is a subset of the shallow groundwater pathway (Moe et al., 2010). Deep Groundwater flow occurs in the main body of the bedrock aquifer and is of greater importance in highly productive aquifers (Archbold et al., 2010).

As part of a comprehensive review at the commencement of the *Pathways Project,* the original conceptual model was revised slightly in two ways. First, as noted in Nash et al. (2002), because overland flow, whether saturation excess or infiltration excess overland flow, and interflow occurring immediately below the soil surface are 'difficult to functionally separate', overland flow was taken to include sheet flow and flow in the upper 20 mm of soil. Second, in the original conceptual model, flow in artificial field drains was included with overland flow due to its rapid response times and sediment carrying capacity, similar to overland flow. However, the project review identified that significant attenuation of pollutants such as phosphorus and pathogens may also occur in field drains, and that they might be better placed with interflow in the modelling. This was left as an issue that was to be resolved as the project progressed. In addition, as the transition zone can be unsaturated close to the catchment divide, and saturated in stream valleys, its role in the transport of nutrients was unclear, so further investigation was required.

A major challenge for the *Pathways Project* was to both qualitatively and quantitatively characterize the contribution of each of the hydro(geo)logical pathways to Irish streams and rivers, and their roles in the transport and attenuation of the contaminants of interest.

1.5 Aims and objectives of this research

The bedrock in Ireland is highly heterogeneous and there has been a complex and extensive glacial history, which together have given rise to a wide variety of soils and subsoils with differing degrees of permeability in both the vertical and horizontal directions, which means that the soils and subsoils must play a significant role in water and contaminant transport processes. However, their role is not well understood (Archbold et al., 2010).

This doctoral research fits primarily within the first three of the *Pathways Project* objectives. Its overall aim was to develop an improved characterization of the role of the near-surface pathways in the delivery of flow and nutrients to streams. For the purposes of this research, the near-surface pathways are those in the soils and subsoils, including interflow, flow through artificial field drainage systems, and those in the transition zone where the depth to the bedrock is relatively shallow. The project was a field-based study that was carried out to different levels of detail in the four study catchments common to all the *Pathways Project* researchers (Table 1.1).

The interflow, artificial drainage and transition zone pathways have received comparatively little attention in the literature in general, in comparison to the overland flow and groundwater pathways. This may be partially a result of the high degree of variability and complexity in measuring them, but they have also traditionally fallen into a sort of 'no man's land' between the disciplines of engineering hydrology, which traditionally focussed more on flooding and overland flow, agricultural and soil science, where the upper soil zone and surface hydrology is of most concern, and hydrogeology, in which the interest is more on deeper (often bedrock) groundwater flow. The interflow pathway also includes a wide range of different flow generation processes that operate at different scales, including unsaturated and saturated flow, matrix and preferential flow, and flow in deep soils and subsoils, and in landscapes that may be drained or not drained and influenced by a range of different land uses. It has been more typical in the literature for researchers to study just one or two of these processes in detail or conduct studies at just one scale (Haygarth et al., 2005), or to consider pollutants in isolation of one another (Granger et al., 2010), rather than take an integrated approach.

This research was aimed at bridging this gap to present an improved conceptual model that characterizes the role of the near-surface pathways in stream flow generation and nutrient transport in Ireland, in the context of the full three-dimensional geological and hydro(geo)logical profile. The purpose of the characterization was to contribute to the identification of CSAs for WFD management purposes. While this research has been carried out in four catchments on the island of Ireland, the improved understanding of how the near-surface pathways contribute to catchment hydrology and nutrient transport will also be applicable in other countries with comparably complex geology, rich glacial history and temperate climates, such as the United Kingdom and other parts of western Europe.

The objectives of this research were to:

1. Carry out a critical review of the four-pathway conceptual model used in previous catchment studies in Ireland;
2. Determine the proportion of flow that is delivered to streams via the different pathways using chemical hydrograph separation and other methods;
3. Examine the dynamics of soil moisture in the soils and subsoils in one catchment to support the conceptualization of the interflow pathway;
4. Investigate the role of artificial field drainage in the delivery of flow and nutrients to streams;
5. Develop an improved conceptual model for the contribution of the near-surface pathways to stream flow and nutrient transfer in Irish catchments.

1.6 Thesis structure

This thesis uses the four-pathway catchment conceptual model as a basis to conduct an initial review of the current understanding of the role of each of the pathways in stream flow generation and nutrient transfer (Chapter 2). Methods and approaches for quantifying the contributions of the pathways to streams are reviewed in Chapter 3. From both of these review chapters, the research gaps are identified and an appropriate research methodology is outlined in Chapter 4. Chapter 5 is the first of the results chapters where the research methodology is applied to develop conceptual models for the four study catchments, with particular emphasis on the near-surface pathways. Chapter 6 presents the pathways separation assessments and discusses implications for nutrient transport. Chapter 7 reports on the soil dynamics study which was used to investigate the interflow pathway in more detail and to test the findings of Chapter 6. Chapter 8 explores the role of artificial drainage and considers how best to generate a land drain map for Ireland. Chapter 9 presents a discussion of the research findings and an improved pathways conceptual model. Conclusions and recommendations for further research are also provided.

2 Review of hydro(geo)logical pathways and their contributions to streams

2.1 Introduction

This chapter reviews the role of each of the four pathways described in the working conceptual model in Section 1.4. A description of each pathway is provided, followed by a summary of the relevant flow generation mechanisms and nutrient transport. The main focus of the review is on the near-surface pathways, but as they are only one part of a continuum of flow components that make up the stream hydrograph, it is important that they are addressed in the context of all the other pathways.

This review considers the role of artificial drainage and the transition zone separately. While they were incorporated as subsets of the interflow and shallow groundwater pathway, respectively, in the working conceptual model, special consideration is warranted to begin to better understand their role.

2.2 Overland flow

2.2.1 Definition

Overland typically occurs as either infiltration excess overland flow or saturation excess overland flow. Infiltration excess overland flows occurs when the infiltration capacity of the soil is exceeded by the rainfall, as in the classic Hortonian infiltration excess overland flow (Horton, 1933), and it is typically thought to occur predominantly in arid areas, or in places where the permeability of the soils is low or the rainfall intensity is high (Dingman, 2002). Saturation excess overland flow occurs when the underlying soils become saturated and can no longer accept any further infiltration. It is common in low intensity rainfall, humid climates where antecedent soil moisture conditions are frequently wet (Nash et al., 2002).

2.2.2 Delivery of flow

Irrespective of which overland flow generation mechanism is applicable, it is now known that limited parts of a catchment generate a disproportionately large proportion of overland flow. These areas, known as partial or variable source areas, only represent a small fraction of the overall catchment area, and they expand and contract seasonally, and during storm events, depending on antecedent conditions, rainfall, soil and geological characteristics and topography

(Hewlett and Hibbert, 1967, Dunne and Black, 1970). Rainfall events of a similar size may generate very different overland flow responses depending on the antecedent conditions (Sen et al., 2010, Thompson et al., 2012).

In low intensity rainfall regions, such as in Ireland, the infiltration capacity of permeable soils is generally not exceeded, and overland flow is only generated in soils that become saturated after a time. This gives rise to saturation excess overland flow and it is considered to be the primary overland flow generation mechanism in Ireland and the United Kingdom (Diamond and Shanley, 1998, Haygarth et al., 2000, Diamond and Sills, 2001, Archbold et al., 2010). However, exceptions can occur in steep terrain where runoff is more highly dependent on the slope than saturation.

It has been determined from a range of plot-scale studies that overland flow comprises from 3 to 73% of rainfall in Ireland (Table 2.1). Diamond and Sills (2001) suggested however, that approximately two-thirds of Irish mineral soils were likely to be at the lower end of the range. Diamond and Shanley (1998) found that, except on poorly drained soils, the infiltration capacity in summer in Ireland exceeded or equalled the five-year return rainfall rate, indicating only a very small risk of summer overland flow occurring. In winter however, the infiltration capacity at three of their sites, including freely drained sites, was less than 2.5 mm/h, indicating a significant risk of overland flow occurring. In another study in the Dripsey catchment, Co. Cork (Tunney et al., 2000), measurements of field soil hydraulic conductivity of 2.5×10^{-5} m/s (or 90 mm/h) were obtained, which indicated that unless the soils were saturated from below, there was sufficient permeability in the soils to accept rainfall and Hortonian overland flow was unlikely. O'Reilly (2006) found that overland flow was largely controlled by rainfall rate and that much of it was generated from areas that were saturated, i.e. saturation excess overland flow.

Table 2.1. Examples of overland flow as a proportion of rainfall in plot-scale studies.

Site conditions	Overland flow contribution	Location	Reference
Gley, high water table, drained	62% annual rainfall	Johnstown Castle, Wexford	(Kurz et al., 2005a)
Sandy loam, gley at 30 cm. Drainage unknown	36% annual rainfall	Johnstown Castle, Wexford	(Kurz et al., 2005a)
Gley soil derived from shale till over greywacke	19% annual rainfall in a wet year (2002/2003) 3% annual rainfall in a dry year (2003/2004)	CENIT, Hillsborough	(Watson et al., 2007)
Clays, drained	Event 1 (25 mm): 16-39% event rain Event 2 (12 mm): 29-73% event rain Event 3 (29 mm): 27-47% event rain 2.1-6.9 times the flow in the drains	Johnstown Castle, Wexford	(Ibrahim et al., 2013)
Clays	62% rainfall over 125 days 84% rainfall over 47 days	IGER site, Devon	(Misselbrook et al., 1995)

Despite the extensive evidence for the dominance of saturation excess overland flow in Ireland, research on a grassland drumlin site at Hillsborough, Co. Down, found that although saturated excess overland flow did occur, 59% of overland flow events occurred as infiltration excess overland flow when the soil moisture was below field capacity. Regression analysis was used to establish that under these circumstances, the most important measured variable governing the probability of runoff occurring was rainfall intensity (Doody et al., 2010). Another more detailed study at the same site confirmed that the rainfall intensity was a significant factor for the 14 largest events in 2011 (Thompson et al., 2012). However, all but one of the 14 events had maximum rainfall intensities of >2 mm/h and since the average rainfall intensity in Ireland is typically less than 2 mm/h (www.met.ie), it is possible that the infiltration excess model may only be appropriate for more intense than average rainfall events.

While rainfall intensity is clearly a key driver in the generation of overland flow, the infiltration characteristics of the soils and underlying geology are also important (Sen et al., 2010). In a study at Johnstown Castle, a higher water table, shallow depth to bedrock and more clayey soils were found to increase the proportion of overland flow in adjacent identical plots that were isolated hydrologically (Ibrahim et al., 2013). Wilcock and Essery (1984) found that the mean infiltration capacity of brown earths over boulder clays in the low-lying, small agricultural Ballysally catchment in Northern Ireland, ranged from 0.6 mm/h in January to 9 mm/h in June, and was frequently lower than the rainfall intensity. The annual soil moisture ranged from 46 to 59% across all 11 sites, and there was an inverse relationship between soil moisture content and the infiltration capacity. Very little intra-site variability was observed in comparison to other studies, which was attributed to the low permeability of the soils and subsoils. The primary controlling factors in the development of overland flow at Ballysally were found to be the percentage of organic matter and the slope. The authors concluded that Hortonian overland flow was a possible flow mechanism. They also noted, however, that the rainfall acceptance in this and other Northern Ireland catchments was lower than conventionally accepted, and suggested that this may have been the reason that the Flood Studies Report (NERC, 1975) substantially underestimated the mean annual flood values in Northern Ireland. Compacted or trampled areas (Kurz et al., 2006), vehicular tracks (Harrod and Theurer, 2002, Heathwaite et al., 2005) and soil water repellency (Doody et al., 2010) also reduce the infiltration capacity and storage and therefore increase the generation of overland flow.

Perhaps the most important factor in the generation of saturation excess overland flow is the degree of connectivity of the saturated areas with each other and the stream (Yang and Chu, 2013). For example, in the detailed study at the Co. Down site, the contributing areas for the

measured overland flow events varied from 20% to 80% of the hillslope plots of 0.2 ha in size. Threshold behaviours were observed when the areas generating overland flow became connected, which led to exponential increases in the overland flow volumes (Thompson et al., 2012). Although there was a strong relationship between the size of the contributing area and the volume of overland flow, the relationship improved when the contributing area was >40 m^2. Proportionally more overland flow was generated on small contributing areas on the lower slopes of the plots and it was hypothesized that this was due to the added contribution of return flow, i.e. subsurface flow discharging at the surface as overland flow. This highlights the importance of the connectivity of saturated areas in the generation of subsurface flows as well as overland flow. Further discussion is provided in the following sections.

The majority of research into the proportion of overland flow (and interflow) in the water balance in Ireland has been carried out at plot scale (Kurz et al., 2005a, Doody et al., 2010, Ibrahim et al., 2013). While plots have the advantage of hydrological isolation, it is known that the size of the plot can impact on the amount of overland flow generated. For example, Ibrahim et al. (2013) reported that smaller plots generate proportionally more overland flow and suggested that increasing plot size might be a means of reducing nutrient losses to waterbodies. Sharpley and Kleinman (2003) reported similar findings, noting that scale has an important bearing on the hydrology of a site and therefore the nutrient dynamics. McDowell and Sharpley (2002) found that particulate phosphorus increased in overland flow with increasing distance down slope due to the dominance of saturated conditions on the lower slopes and therefore the phosphorus runoff. So, despite their advantages for conducting detailed research studies, it is clear that there are issues of representivity with scaling up plot-scale studies to catchment scale that are dependent on the catchment setting and the hydro(geo)logy of the small plot sites. This was addressed in this project by combining plot-scale studies with a catchment-scale approach (refer to Section 4.1).

2.2.3 Nutrient transport

Overland flow is considered to be the main pathway contributing phosphorus losses to streams (Haygarth et al., 2000, Tunney et al., 2000, Kurz et al., 2005a) and it is recognized that the majority of the phosphorus export load often occurs during a limited number of high flow events (Burke et al., 1974b, Jordan et al., 2005). In grassland catchments, which represent the vast majority of agricultural land in Ireland, phosphorus is applied at the surface as inorganic fertilizer or organic agricultural wastes, which may be spread as organic fertilizers or deposited by grazing animals. Under ideal circumstances, the DRP fraction, which is the fraction with greatest potential impact for aquatic ecosystems, is taken up by the plants and soil biota, leaving a predominance of

dissolved unreactive phosphorus (DUP) and particulate phosphorus (PP) in surface runoff. For example, Kurz et al. (2006) found that where grazing animals are present, the dominant fraction in overland flow tends to be PP and DUP, which are mostly organic. This is because of the increase in the organic fraction applied at the surface, as well as the reduction in infiltration capacity due to compaction by grazing animals, which increases the proportion of overland flow overall. PP is also the dominant fraction in arable settings and in high-intensity rainfall events where the raindrops physically dislodge particles that have phosphorus attached. However, the fraction of PP is not typically high in ungrazed grassland sites because the particles get trapped within the vegetation and the infiltration capacity is higher, but it can be dominant along animal or farm machinery tracks (Heathwaite and Dils, 2000).

DRP has been found to be high in overland flow if a rainfall event occurs before it has had a chance to be taken up (Ibrahim et al., 2013), or where the soil phosphorus is already high (Humphreys et al., 1999, Tunney et al., 2000, Kurz et al., 2005a), or where the soils are saturated with respect to phosphorus. There are a limited number of phosphorus binding sites and once they have become saturated, the risk of phosphorus leaching increases (Hooda et al., 2000, Daly et al., 2001, Andersson et al., 2013). Two previous studies in Irish conditions found that DRP was no longer present in overland flow 40 and 44 days after fertilizing. Interestingly, Kurz et al. (2005a) found that DRP in overland flow decreased after the application of urea, which they attributed to extra DRP being taken up in the rapid growth that occurred because of the addition of nitrogen. On a long-term basis in grazed and fertilized catchments, however, DRP was found to be the dominant form of phosphorus in overland flow (Haygarth et al., 1998, Kurz et al., 2005a), which poses a threat to aquatic ecosystems.

O'Reilly (2006) observed that the dominant fraction of phosphorus in samples taken during a rainfall event changed from particulate phosphorus in the early stages of surface runoff to dissolved phosphorus as the event progressed and the CSA expanded. The dissolved phosphorus was subsequently diluted as surface overland flow increased until steady state conditions at which the minimum phosphorus concentrations were observed. However, Kurz et al. (2005a) found that there was no clear relationship between phosphorus and overland flow, which demonstrated that there are also other factors involved. Schulte et al. (2006) also noted that while the annual phosphorus loss from agriculture may be dominated by a few large rainfall events, the role of the smaller events should not be underestimated because their high frequency means they can still transport a significant load. Tunney et al. (2000) reported, for example, that while 75% of the annual DRP loads in the Dripsey catchment were generated during peak flows, 19% was generated during elevated baseflows and 6% during baseflow. Analysis by Logue (1971)

shows that the highest intensity rainfall events in Ireland tend to occur during the summer between June and October, thus, although the majority of phosphorus is lost during the wet winter months (Melland et al., 2012b), there can also be significant losses of phosphorus in the summer months (Kurz et al., 2005b).

The proportion of nitrate in Irish catchments that is delivered via overland flow to streams is typically very small (Burke et al., 1974b, Kurz et al., 2005a, Kurz et al., 2006). Burke et al. (1974b) found that nitrate in overland flow amounted to up to only 3% of the load applied where there was no drainage and <1% of the load applied where the land had been drained because the proportion of overland flow was less. All studies found that the highest loads of nitrate and total oxidizable nitrogen (TON, i.e. nitrate + nitrite) in overland flow occur when a rain event occurs soon after fertilizer has been applied. However, when best practice has been observed, the applied inorganic nitrogen is usually taken up quickly by the plants, or leaches down through the soil profile before it has the opportunity to run off. There was no nitrogen observed in overland flow 40-44 days after fertilizer application (Burke et al., 1974b, Kurz et al., 2005a).

Of the nitrogen that is transported in overland flow in Irish catchments, the majority is in organic form (Watson et al., 2000b, Kurz et al., 2006, Ibrahim et al., 2013), and may be dissolved or particulate nitrogen. Kurz et al. (2006) found in a series of nine rainfall simulator experiments on grazed land at Johnstown Castle that the mean total organic nitrogen in overland flow ranged from 1.32 to 19.23 mg/l as nitrogen, with the highest values occurring immediately after the cattle had access to the land. Results from a UK study (Heathwaite and Johnes, 1996) also showed that the organic fraction was dominant in runoff from both prepared ground and lightly grazed grass (8 beef cattle/ha), while NH_4 was the dominant nitrogen species in runoff from heavily grazed ground (16 beef cattle/ha). However, all species of nitrogen measured in surface runoff from cereals and temporary grass were below the limits of detection. While the average Irish stocking density is far less than even lightly stocked land in the United Kingdom at 1.9 LU/ha (Horan et al., 2012), similar high organic loads are likely to be found in Ireland at point locations where the animals congregate (e.g. feeders, water access points, farm tracks, etc.).

It is clear from the literature, therefore, that in Irish grassland catchments, DRP losses from overland flow are a significant threat to aquatic ecosystems, and that the extent and connectivity of the saturated areas, and the hydrology play a significant role. Understanding the nature of the saturated areas and how they function in the landscape requires a deeper, three-dimensional understanding of the hydro(geo)logical pathway framework than has previously been considered. Nitrate losses via the overland flow pathway are less important because the majority of any excess leaches downwards and is transported via deeper pathways.

2.3 Interflow

2.3.1 Pathway definition

There are many different definitions for interflow in the literature. It is sometimes described as unsaturated Darcian flow in the soil matrix, or pipe flow in macropores or preferential flow features, such as cracks in the soils, fauna burrows and plant roots, that largely bypasses the unsaturated soil matrix. It may occur as unsaturated flow, or as flow in saturated zones of very limited extent caused by soil horizons of a lower hydraulic conductivity that impede vertical infiltration (Dingman, 2002, Archbold et al., 2010). Wilson (1990) acknowledged that interflow may include 'water travelling horizontally through the upper horizons of the soil, perhaps in artificial tile drain systems'.

Some of the early researchers, such as Hewlett and Hibbert (1967) and Sklash and Farvolden (1979), identified that subsurface flows, i.e. interflow and groundwater respectively, were important in the stream hydrograph, but traditionally these were considered to be too slow to contribute to storm flows. Dunne and Black (1970) found, for example, that subsurface stormflow was too small, too late and too insensitive to fluctuations in rainfall intensity to add significantly to the stormflow in the channel. Beven (1989) restricts the definition of interflow to 'the near-surface flow of water within the soil profile resulting in seepage to a stream channel *within the time frame of a storm hydrograph*'. Seiler et al. (2002) noted that although matrix flow is too slow (0.7–1.2 m/year) to contribute to the hydrograph, preferential flow through macropores (>0.5 m/d) can be as rapid as overland flow.

For the purposes of the *Pathways Project*, interflow is simply considered as any lateral subsurface flow between the ground surface and the water table (Archbold et al., 2010) but it is clear from the range of definitions that there are several different processes involved. It can be broadly determined from the literature that interflow occurs both as matrix flow and through macropores, but that it is the flow through the macropores that is likely to contribute most to storm flows and potentially therefore also contribute the most in terms of nutrient transport. It is also acknowledged that there is a continuum of processes, pathways and response times in the soils, from infiltration excess overland flow, saturation excess overland flow, return flow where subsurface flow comes back to the surface and becomes overland flow, through to discharge through the soil matrix, preferential flowpaths, the drainage network and the transition zone (Beven, 1989). Thus, it would seem important that studies considering the transfer of nutrients from the land surface to the stream should be (a) integrated so that significant contributions from one or more processes or pathways are not inadvertently omitted; and (b) catchment based so that heterogeneities in the soils at particular sites do not give a limited or biased outcome.

2.3.2 Delivery of flow

2.3.2.1 Unsaturated flow

Flow through soils is typically represented using the Darcy-Richards equation in many hydrological studies (Beven and Germann, 2013). Darcy's Law (Darcy, 1856) states that the flow is directly proportional to the hydraulic conductivity of the soil and the change in head over the flowpath as follows:

$$q = -K\frac{\partial h}{\partial z} \qquad \text{Eqn 2.1}$$

where q is the discharge per unit area; K is the hydraulic conductivity of the soil; and δh/δz is the vertical hydraulic gradient. The principle of conservation of mass states that any change in discharge with depth has to be balanced with a change in the soil moisture:

$$\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial z} = 0 \qquad \text{Eqn 2.2}$$

where θ is the soil moisture content. Combining Eqns 2.1 and 2.2 gives the Richards equation (1931):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K\theta\left(\frac{\partial \psi}{\partial z} + 1\right)\right] \qquad \text{Eqn 2.3}$$

where ψ is the pressure head and z is the elevation above an arbitrary datum. It is an assumption of the Darcy-Richards equation, however, that soils are porous and homogeneous, which limits the scale of applicability in the field. The advection-dispersion concept of solute transport inherent in the equation also does not adequately represent solute transport through preferential flowpaths. In recognition of this, modifications of the equation have evolved to incorporate dual porosity or dual permeability scenarios, e.g. HYDRUS. However, Beven and Germann (2013) suggest that they are inadequate for hillslope and catchment-scale studies because of the heterogeneities of subsurface materials, the role of preferential flowpaths, and the other assumptions of the methods that flow is saturated and laminar.

2.3.2.2 Field capacity

In unsaturated soils, interflow is typically assumed to be linked to the field capacity, i.e. the maximum amount of water that can be stored in a soil (Veihmeyer and Hendrickson, 1949), or the amount of water held in the soil after excess water has drained away and the amount of downward movement of water has materially decreased. Unless there are large macropores

present, interflow is only likely to occur when the soil moisture content is above field capacity and there is excess water to drain.

At matric potentials close to zero, the soil is close to saturation and there is excess soil water that drains. Drainage continues until the soil reaches field capacity. The field capacity is often taken to be the soil moisture content that occurs at a soil water potential of –0.33 bar and it is lower for sandy soils than for clayey soils (Dingman, 2002). In the absence of further rainfall, the soil moisture content continues to decrease and a soil moisture deficit develops when the moisture content reduces below field capacity. Under these conditions, soil water is bound more tightly in the soil matrix and the suction (or soil water potential) increases such that it becomes more difficult for plants to extract the water. Eventually, at the wilting point, the tension becomes too high for the plants to effectively extract the moisture and the plants come under stress.

Field capacity depends on many factors, the most important of which are soil texture, uniformity and depth. It can be predicted in the field by measuring the non-linear relationship between the soil moisture content and the soil water potential and developing a soil water retention curve, which is specific to different soil types (Dingman, 2002). A number of different theoretical soil water retention curves have been generated by various authors such as van Genuchten (1980) and Brooks and Corey (1964).

A study in the Dripsey catchment, Co. Cork (Tunney et al., 2000), found that in vertical soil profiles, the water content increased above field capacity (36%) at depths of 10–30 cm in June, which was considered to be an interflow layer (Figure 2.1). In contrast, field capacity at the Co. Down site discussed in Section 2.2, was found to be much higher at 56% (Doody et al., 2010) and Watson et al. (2000a) found that interflow via the drains at the site usually only commenced in October, and that there was generally no subsurface flow in summer unless the season was particularly wet.

2.3.2.3 Macropores

If macropores are present, and they are large enough and well connected, flow through them can take place independently of the field capacity (Beven and Germann, 2013). For example, in dry antecedent conditions in fine sandy loam soils in a field plot experiment in Oklahoma, Lehman and Ahuja (1985) found that 94% of potassium bromide tracer applied on the land surface made its way into groundwater before the onset of overland flow and interflow, despite only 31% of the flow discharging through the groundwater pathway overall.

In field tracer experiments in China, Sheng et al. (2014) found that in an unsaturated loam soil,

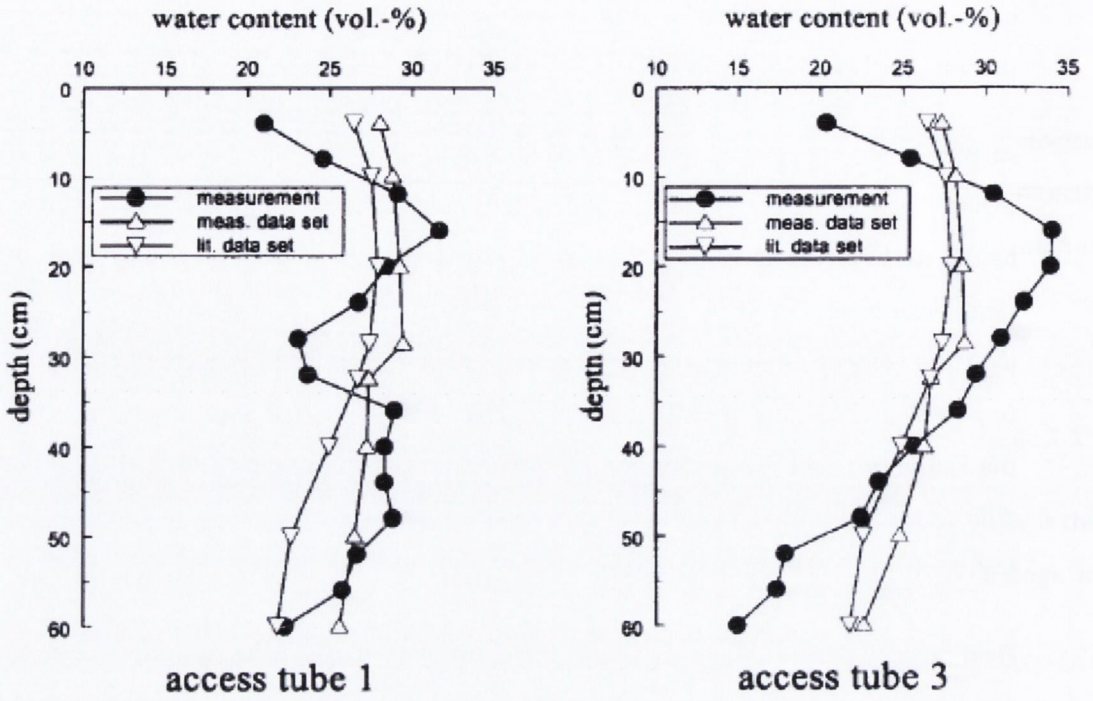

Figure 2.1. Profiles of soil moisture with depth; 28th June 1997, Dripsey catchment (from Tunney et al. (2000). Note the rise in soil moisture content at 10–30 cm depth which was attributed to interflow.

macropores were present in the upper 20 cm in one plot but not in the other, whereas in the United Kingdom, Germann and Beven (1981) found them at the soil/subsoil interface in a core from 20 to 35 cm depth. In a forested hillslope study site in Japan, Sidle et al. (2001) found that although individual macropore segments are typically <0.5 m in length, they have a tendency to self-organize into larger preferential flow systems as sites become wetter.

Some authors have noted that flow through macropores can be as fast as overland flow and several orders of magnitude quicker than matrix flow (Seiler et al. (2002). A piston flow or translatory flow mechanism takes place that follows the Poiseuille principle, i.e. where water applied to one end of a saturated pipe causes an instantaneous displacement of water at the other end, irrespective of the length of the pipe. This has been said by some to contribute to the rapid response of the hydrograph to rain falling on the land surface often at some distance from the main channel (Buttle, 1994).

Kirby et al. (1991) found in a research catchment in Plynlimon in Wales, that soil moisture was more dependent on local factors including variability in soil properties and microtopography than on larger scale factors such as the position of the sampling point, the slope or the slope aspect, and that it varied rapidly over time. This suggests that the development of interflow may be driven by local-scale structural heterogeneities, emphasizing the importance of a three-dimensional approach.

The balance of matrix versus preferential flow through the soils is important because it has implications for the speed of delivery of flow and attenuation of contaminants. An Irish study in a site underlain by free-draining soils and subsoils, overlying a karst limestone aquifer, found that there was a rapid breakthrough in soil solution (8 days) and in groundwater (34 days) of the bromide tracer applied at the surface indicating that there was preferential flow. However, the time to maximum concentration was more indicative of matrix dominant flow in the soils and subsoils (Richards et al., 2005).

2.3.2.4 Capillary fringe

Another flow mechanism that is reported to contribute to the rapid hydrograph response depends on the capillary fringe, which is the zone above the water table that remains saturated under negative pressure or tension (Abdul and Gillham, 1989). Gillham (1984) showed that where the water table is shallow and the capillary fringe extends to the surface, the addition of a very small amount of rainfall can result in an immediate rise in the water table that is much larger than would be expected based on the specific yield and the amount of rainfall. Typically these sorts of conditions occur on the lower hillslopes close to the stream channels, and where the hydraulic conductivity of the soils is high enough, the rapid increase in hydraulic gradient can quickly deliver significant quantities of pre-event water to the stream (Abdul and Gillham, 1989, Jayatilaka and Gillham, 1996, Gillham and Jayatilaka, 1998). This is known as the groundwater ridging effect (Sklash and Farvolden, 1979).

However, in a comment on Jayatilaka and Gillham's paper (1996), McDonnell and Buttle (1998) refuted the role of the capillary fringe, instead asserting the dominance of macropore flow. In their response, Gillham and Jayatilaka (1998) noted that while their model was generated based on their experiences in gently undulating, non-forested catchments, McDonnell and Buttle's arguments in favour of macropore flow were based largely on their respective experiences in steeply sloping forested catchments where the capillary fringe would be unlikely to be present. This interesting scientific debate, which was fortunately played out in public, emphasizes the huge variability in streamflow generation mechanisms in different hydro(geo)logical and land-use settings. Perhaps more importantly, however, it also highlights the difficulties in extrapolating findings from one catchment to another.

2.3.2.5 Pressure waves

Pressure waves through the subsurface due to the Lisse effect can also rapidly bring water into streams. The Lisse effect occurs when infiltration from intense rain over a shallow water table creates an effective seal at the soil surface, trapping air in the unsaturated zone that is further compressed as the wetting front advances. This can cause rapid and large changes in the water

table (Waswa et al., 2013). However, Weeks (2002) suggested that the Lisse effect is a rarely observed phenomenon and suggests it is not as important as originally thought because of the counter upward pressure exerted at the base of the wetting front.

2.3.2.6 Contrasts in permeability

The contrasts in the permeabilities in the soils and the depth to the impeding layer are two key factors that influence the lateral development of interflow. Some authors have argued that it is the contrast in permeability that is the primary driver and that a change of at least one order of magnitude is required (Robinson, 1990). In practice, however, the depth to the lower permeability layer is usually the depth of the topsoil in grassland and the depth of the plough layer in arable land; this ranges from 25 cm in clay soils to 40 cm in sandy soils. At a research site in Ballinamore, Co. Leitrim, for example, the saturated hydraulic conductivity of the topsoil was 13 mm/h, whereas that of the underlying subsoil at 0.25 m depth was four orders of magnitude less and was considered to only contribute to baseflow and not storm flow (Burke et al., 1974a). Clay soils frequented by heavy machinery and soils that have been artificially drained may have the lower permeability layer at the surface.

Ahuja and Ross (1983) found in a theoretical study that in a two-layered soil with contrasting hydraulic conductivities, interflow occurred in two regions: (a) downslope flow within the main body of the soil and (b) additional infiltration and flow near the seepage face due to the steeper hydraulic gradients. The length of slope that contributed to the flow near the seepage face was linearly related to the ratio of the hydraulic conductivities of the two layers. Where the subsoil had lower conductivity than the topsoil, the flowlines were as might be anticipated, with horizontal flow in the soil layers upslope and a relatively small area impacted by the discharge occurring at the seepage face. Where the subsoil had higher conductivity than the topsoil (such as might occur in the field where there is artificial drainage), the rate of infiltration and the volume of soil traversed by the interflow near the seepage face increased several fold. This in turn also increased the area and rates of infiltration through the topsoil at the upper end of the slope.

In the Irish landscape, the soil profile typically comprises an upper layer, the A horizon, which is the organic-rich layer and an underlying heavily leached horizon. The B horizon is the layer below this, in which the leached minerals and clays accumulate, and this overlies the C horizon which comprises the parent material (Finch et al., 1983). Typical Irish soils thus have two distinct permeability changes at the A/B and B/C horizons which have been found in other studies to encourage the development of interflow (Cox et al., 2005, Jin et al., 2011).[1]

[1] Refer to Figure 4.5 for a photo of the soil profile at the field site with the three horizons highlighted.

It is clear from the literature that there is evidence for a range of flow and transport processes in the soils that can generate interflow, but there is ongoing debate on whether any of them can generate enough water, and rapidly enough, to achieve the observed responses in the hydrograph (McGlynn et al., 2002). Many authors are now suggesting that a deeper perspective, down to the bedrock layer, may instead hold the key (Tromp-van Meerveld and McDonnell, 2006, Bachmair and Weiler, 2012, Gabrielli et al., 2012). This is further explored in the discussion on the transition zone pathway.

2.3.3 Nutrient transport

As discussed in Section 1.2.3, nitrogen and phosphorus behave differently in the subsurface, which influences their ability to be transported via interflow, and their susceptibility to attenuation. Nitrate, being more conservative tends to be transported via the deeper pathways, whereas phosphorus is readily adsorbed to particles in the upper soil layers and is more susceptible to delivery via overland flow. For example, at a grassland hillslope site in Australia, Melland et al. (2008) found phosphorus yields were an order of magnitude smaller along interflow pathways (0.027 kg/ha/y) than in overland flow; in contrast, there were up to five times more nitrogen loads in interflow (3.2–10.6 kg/ha/y nitrogen) than in overland flow. Heckrath et al. (1995) observed that up to 60 mg/kg Olsen phosphorus was retained in the more permeable plough layer, and was subsequently released in drainage water.

The upper organic soil layer is also where the majority of denitrification takes places. Denitrification is the process by which anaerobic denitrifying bacteria use the oxygen from nitrate and the remaining nitrogen is released. It is common in saturated soils, where there is an adequate source of carbon, a good supply of nitrate, temperature >4°C and the denitrifying bacteria (Ryan et al., 1998). In an Irish lab-based experiment on Irish soil cores, Ryan et al. (1998) found that 80% of the denitrification that took place, did so in the top 10 cm of the soil. It has been reported that 5 to 95% of the leached nitrogen can be denitrified depending on soil conditions (Buss et al., 2005, Humphreys et al., 2008), or from 3 to 45% of the nitrogen that is applied (Jordan, 1989, Ryan et al., 1998, Jahangir et al., 2012). Nevertheless, the presence of preferential flowpaths allows the leached nitrogen to bypass the denitrifying layer (Booltink, 1995).

Despite its tendency to remain in the upper soil layer, significant quantities of phosphorus have been reported in subsurface flow from grassland soils (Heckrath et al., 1995, Sims et al., 1998). Tunney et al. (2000) found in the Dripsey catchment that although the concentration of phosphorus decreased with depth in the soil, the interflow zone between 10 and 40 cm was responsible for the transport of dissolved phosphorus to streams. It is considered likely that flow

through preferential flowpaths and macropores are important subsurface transport mechanisms for phosphorus (Heathwaite and Dils, 2000, O'Reilly, 2006, Ibrahim et al., 2013). In an Irish study, O'Reilly (2006) found that in a site with moderately permeable soils, the composition of phosphorus in the shallow subsurface flow was similar to that in overland flow, demonstrating that macropores played a significant transport role. Where matrix flow is dominant, the majority of phosphorus is in dissolved form (Ibrahim et al., 2013).

Subsurface pathways such as interflow, groundwater and drainage pathways have traditionally been given less attention in the literature in the context of transport of phosphorus because of the assumption of almost complete phosphorus adsorption by the soil matrix, resulting in very low leaching. There is increasing evidence, however, that phosphorus can be a factor in subsurface pathways and that it can be either in particulate or dissolved form, depending on the presence of preferential flow pathways. Phosphorus concentrations in groundwater in the karst limestones in the west of Ireland for example, are high enough to place the connected surface water receptors at risk (EPA, 2010).

2.4 Artificial drainage flow

2.4.1 Pathway definition

Land drains have been a part of Irish agriculture since the 1700s, particularly in the early to mid 1900s with the introduction of various national grant-aided schemes to encourage development (Bruton and Convery, 1982). The purpose of drains is to help relieve a drainage problem that, in turn, improves soil conditions and hence achieves greater productivity from the affected land. Robinson (1990) estimated that artificial field drainage increased crop yield in the United Kingdom by 10 to 25%.

Drains may be installed randomly to drain a spring line or a wet area, or may be more systematically installed at regular intervals across a field, eventually discharging into a collector drain and/or the main drainage channel (Tuohy et al., 2012). The Hooghoudt equation, which relates rainfall, soil permeability, drain depth and water table depth, can be used to determine the most efficient drain spacing, but in practice, drain construction has tended to follow local traditions and experiences rather than any scientific method. Soil horizons with hydraulic conductivity of <0.1 m/d are considered to be effectively impermeable for the purposes of their contributions to drain flow (Luthin, 1957).

Pipe drains were traditionally constructed of clay tiles (30 cm long by 7.5 cm internal diameter), and were hence known as tile drains, but they have generally been replaced by plastic drainage

pipes since the 1970s as they are much easier to handle. Pipe drain life expectancy is typically 30–50 years although many continue to function beyond that time where there is a good hydraulic gradient and a low fine silt content in the soil. Wet surface soils tend to be drained at spacings of 5–15 m and a depth of no more than 0.75 m; groundwater drains can be spaced at up to 40 m and may be installed at depths up to 1.5 m. 'Moling' or 'subsoiling', which is a mechanical means of improving soil drainage by creating cracks (i.e. preferential flowpaths) in the soils and subsoils, respectively, is often carried out in Ireland in conjunction with the installation of tile drains to improve efficiency. Unless backfilled with gravel (gravel moles), moles require regular maintenance and renewal. Maintenance is also beneficial for tile or pipe drains.

2.4.2 Delivery of flow

The hydrological function of a catchment may be significantly influenced by the presence of artificial drainage. A study on the impact of artificial land drainage on river flows in the United Kingdom found that the drainage of heavy clay soils reduced high and medium flow peaks, because the extent of surface saturation was reduced, thus leaving more storage in the soil and therefore less surface runoff (Robinson, 1990). On more permeable soils not usually prone to surface saturation, however, drainage increases the speed of subsurface discharge and increases peak flows. The study also found that drainage increased baseflows. At the catchment scale, arterial channel improvements, i.e. works in the main stream channel, which often, but not always, accompany field drainage, increased flow peaks downstream because of the reduction in overbank flooding and storage. The net change of field drainage and arterial channel improvements was to increase both peak flows and baseflows, and shorten the catchment response time (Robinson, 1990).

In a plot-scale study at Johnstown Castle, Ibrahim et al. (2013) found that in four adjacent plots with identical subsurface drainage design and similar soils, the sites with the shallower water tables and thinner soils and subsoils had increased drain flow in wet antecedent conditions as the drains were draining groundwater. They found that differences in drain flow between adjacent plots during the same event were greater than the differences between events on the same plot. This suggests that the drainage problem may have an impact on the quantity of flow discharging from the drains.

In an Irish study on the very low permeability shaley tills in Ballinamore, Co. Leitrim, a study of the hydrology of two adjacent field plots, before and after one of them was mole drained, found that the maximum flows from the drained plot were lower than in the undrained plot, but that baseflows were higher such that the total measured flows were similar (Burke et al., 1974b). There were seasonal differences, however; in the summer months the drained plot peaks were

higher than those from the undrained plots while in the winter, the reverse was the case. This seasonal difference was attributed to the delivery of bypass flow through soil shrinkage cracks in the summer months, which may also have implications for the delivery of nutrients. The drainage also largely eliminated the saturation in the topsoil layer to the extent that the annual average overland flow measured was an order of magnitude less than in the adjacent plot. However, it must be acknowledged that their site was a Teagasc research site that had been recently drained by a well-respected drainage engineer (Mulqueen) and it is probable that the drainage was far more efficient than it might have been elsewhere in Ireland.

At an experimental site in Devon with clayey soils, Bilotta et al. (2008) found that there was 50% more discharge from a non-drained site compared to an adjacent drained site, but within the drained site, 50-66% of the discharge was via the drains. The drains were a combination of mole drains with collectors at a depth of 0.85 cm. In another example, the maximum flow from the single drain outflow from a 33 ha field in the United Kingdom, over a 6-month period, was 0.57 l/s/ha, which was in response to a heavy rainfall event of 13 mm/h. The lag time between the heaviest rain and the greatest flow was between 45 min and 1 h (Beardmore (1851) cited in Robinson (1990)). This emphasizes that flow rates from land drains can be quite significant.

Musy et al. (1989) suggest that it is useful to consider flow through artificial drainage channels in terms of two sets of separate hydrological responses: first, the transport of rainfall from the land surface through the soil to the drain, which may be via matrix flow or preferential flowpaths; and second, from the drain into the permanent stream channel network, which is more akin to flow through a pipe network. In one study, the differentiation was likened to conduit flow versus diffuse flow in karst environments (Schilling and Helmers, 2008).

Better maintained drains will greatly enhance the transfer function in comparison to the natural drainage network; lag times may be evident where there are collapses, blockages and extensive weed growth in the open ditches. Mulqueen (1971) found that mole drains that were poorly constructed, i.e. drawn downhill instead of uphill, silted up within 12 months, while those that were drawn uphill were flowing but were blocked in places. Galvin (1983) also noted that artificial drains need regular maintenance as the life of a mole drain was expected to be 1 to 3 years and reported that, among a range of drainage designs, gravel moles were found to be the least subject to collapse and decline in drainage efficiency. In contrast, however, Mulqueen (1998) found that mole drains installed in a forestry site in Sligo were found to be still functioning well 26 years later. Over the course of a 9-year study at the CENIT site in Co. Down, it was found that the efficiency of flow interception by the specially constructed drainage system decreased by an average of 39% (Watson et al., 2000a).

Thus, the construction and maintenance of artificial drainage has a significant bearing on its hydrological functioning in the field and the question remains as to whether studies that have investigated the role of drainage on well-developed and maintained plot-scale research farms are truly representative of working farms. This issue is being taken into consideration in a current major research programme being carried out by Teagasc into field drainage in Ireland (Fenton, *pers. comm.*).

2.4.3 Nutrient transport

Artificial field drainage is reported by some authors to reduce the moisture content in the soils and hence reduce the proportion of overland flow (Burke et al., 1974a), which in turn reduces the losses of nitrogen, phosphorus and sediment from the field (Huang et al., 2002). Others report that artificial drainage is an important delivery mechanism for both nitrate and phosphorus. For example, in the lowland agricultural areas of the Netherlands, it was found by Rozemeijer et al. (2010) that tile drains contributed 80% of the total annual discharge and 89–93% of the total annual NO_3 and heavy metal loads. McIsaac and Hu (2004) found that the higher the intensity of tile drainage in the agricultural watersheds of Illinois, the higher the nitrogen flux in the river. A study of 45 subcatchments of the Odra River in Germany, Poland and the Czech Republic found that up to 33.1% of the total nitrogen input into the river resulted from tile drainage (Behrendt et al. (2004), in German; cited in Hirt et al. (2005)). In a study of three watersheds in Illinois, Royer et al. (2006) found that artificial field drainage was the primary delivery pathway of nitrate to rivers and that field drains and overland flow delivered DRP, whereas PP was almost exclusively from overland flow. They noted that nearly all the nutrient export load occurred when the flows were greater than the median discharge, and that extreme discharges (≥90th percentile) were responsible for >50% of the nitrogen load and >80% of the phosphorus. Stamm et al. (1998) and Heathwaite and Dils (2000) showed that the delivery of phosphorus was accelerated to streams where fields were artificially drained, to the extent that Heathwaite et al. (2005) incorporated land drains into their connectivity model for delineating CSAs for phosphate.

In an intensive study at two poorly drained catchments in Co. Louth and Co. Wexford, it was found that shallow, perched, saturated subsoils layers, which were underlain by clayey layers and drained by the ditch and tile drain networks, were the key pathways for the transport of nitrate (Mellander et al., 2012). More diffuse return flow from seeps and springs at breaks in slope were also important. In the Louth catchment, it was found using geophysics that the low permeability layer lay between 0.5 and 3 m below ground surface confirming that the near-surface pathways play a significant role in the transport of nitrogen. Nitrate concentrations and loads both increased with a quickflow response with discharge in winter, which is in contrast to the more

typical dilution effect that takes place when nitrate is delivered via the groundwater pathway (Soulsby et al., 2003a, Byrne, 2011). This was likely to be because the area of saturated soils above the clayey layer increased with increasingly wet antecedent conditions. The ditches were a key transport pathway for phosphorus, although it was noted that small point sources were an important factor (Melland et al., 2012b).

There is now a reasonable body of evidence in the literature that field drains can carry significant concentrations of nutrients that can cause eutrophication in streams. For example, the annual flow-weighted mean total phosphorus concentrations in drainflow at the Agri-Food and Biosciences Institute (AFBI) research site in Co. Down was found by Watson and Matthews (2008) to range from 187 to 273 mg/l as phosphorus, which they reported is well above the concentrations believed to trigger eutrophication. Much lower values, but still just above the Good-Moderate WFD status boundary, were found by O'Reilly (2006). Haygarth et al. (1998) found that the dominant form of phosphorus in drain flow was DRP and emphasized the important role that land drains can play in causing ecological impact in streams. Ni Chathain et al. (2012) noted that land drains are especially important in the relatively undeveloped High Status catchments which are often highly sensitive and suggested that although a map and database of land drainage was not available for Ireland, it would be a useful management tool.

2.5 Transition zone flow

2.5.1 Pathway definition

The transition zone is the very broken, rubbly and weathered rock horizon that occurs at the boundary between the bedrock and the overlying subsoils. It may be infilled with subsoil matrix and may resemble gravel or gravelly till in the purer limestones (Fitzsimons et al., 2005), or it may be absent altogether (Moe et al., 2010). It is recognized in the international literature as a combination of saprolite and saprock in tropical and arid regions, and as the upper weathered bedrock in temperate and cold regions (Comte et al., 2012). Comte et al. (2012) defined it in Irish conditions as the decomposed bedrock and broken bedrock horizons that may, or may not, overly the fissured bedrock. The use of the term 'transition zone' in the context of a hydro(geo)logical pathway appears to have been originally introduced by the Geological Survey of Ireland (Fitzsimons et al., 2005).

2.5.2 Delivery of flow

Early work in a catchment in California by Wilson and Dietrich (1987) (cited in Gabrielli et al. (2012)) found that fracture pathways within the shallow weathered bedrock overlain by colluvium contributed to stormflow when the storage filled and the underlying more competent bedrock

forced water upwards and laterally to contribute to the stream. Researchers at the paired experimental upland catchments in Plynlimon in Wales also observed that shallow groundwater flow in the shattered broken-up grit (sandstone) below the peat was a significant contributor to flow in the stream (Kirby et al., 1991), proving that shallow groundwater from poorly productive rocks could provide a significant proportion of streamflow (Haria and Shand, 2006). Haria and Shand (2006) observed that pressure waves in response to recharge upslope caused a rapid displacement of shallow groundwaters up into the soils, whereupon it was transported laterally downslope through a fast flow horizon at the soil-bedrock interface leaving the upper soil horizons largely unsaturated. It was only where there was a discontinuity in the lateral fast flow horizon that water was forced up to the surface as return flow. In effect, both of these studies were observing flow in the transition zone pathway although it was not recognized as a distinct pathway.

As discussed in Section 2.3.2, it has recently been acknowledged in the hydrological literature that the bedrock and the deeper soil/subsoil pathways are likely to play a more significant role in storm flow generation than previously thought. Attention is being focussed on the topography of the soil-bedrock interface (i.e. the transition zone pathway), which is now known to be an important catchment-wide control on subsurface flow contributions to streams (Freer et al., 2002, Shahedi, 2008). For example, at the highly instrumented and well-researched Panola Watershed near Altlanta, Georgia, it has been recognized that there is a threshold, 'fill and spill' effect in the development of subsurface flows. Once more than 55 mm of rain falls, depressions in the bedrock surface fill up and spill over into any microtopographic relief in the bedrock surface, resulting in interconnectivity with each other and the trench. Flow occurs in the downslope direction once localized saturated areas connect. When connectivity is achieved, the instantaneous subsurface stormflow rate to a trench was found to increase more than fivefold and the total subsurface stormflow was more than 75 times larger than before (Tromp-van Meerveld and McDonnell, 2006). Similar findings were reported by Liang and Uchida (2013) from numerical modelling studies based on the Aratani catchment in Japan. They suggested that the fill and spill mechanism is dependent on the soil depth and the topography of the top of the bedrock surface, and that it would be preferable to define variable source areas using soil depth and a topographic wetness index at the soil-bedrock interface, rather than by the more traditional 'distance to the valley bottom' approach. Soil properties and topography were found to be more important catchment characteristics than vegetation in a field study carried out by Bachmair and Weiler (2012).

Recent work in two benchmark research catchments, the HJ experimental catchment in Oregon, and the Maimai catchment in New Zealand, have demonstrated that the role of the soil-bedrock

interface is different in different geological conditions. In the Maimai catchment, the water table generally remained below the soil-bedrock interface and did not contribute significantly to event-based hillslope runoff. It did, however, respond significantly to storm events indicating a direct connection between the groundwater and hillslope processes. Groundwater was found to seep out generally into the hillslope in the riparian zone. In the Oregon catchment, a fractured and transmissive fracture zone in the upper 1 m of weathered bedrock (i.e. the transition zone) was found to conduct rapid lateral subsurface storm flow and lateral discharge. Interestingly however, the origin of the water in the weathered bedrock zone was a mix of vertically infiltrating soil water and rainwater, and not a rise in bedrock groundwater. Thus, the bedrock groundwater at the soil-bedrock interface was not found to contribute directly to storm flow (Gabrielli et al., 2012).

The transition zone is well recognized in Ireland anecdotally as a water-bearing zone when drilling (Ball, D., *pers. comm.*) and as a permeable zone for the development of artificial drainage (Gleeson, T., *pers. comm.*). It is highly probable that the large numbers of shallow hand-dug wells in Ireland (www.gsi.ie/mapping) exploit groundwater from this permeable zone (as well as from shallow sand and gravel aquifers). However, there is a paucity of scientific evidence on the role of the transition zone in Ireland and it was consequently targeted for specific monitoring as part of the EPA's poorly productive rocks monitoring programme (Moe et al., 2010).

The fill and spill hypothesis may well be applicable in Ireland but it must be noted that the Panola, Oregon and Maimai catchments (and the Arantani catchment) are steep-sided forested catchments, with often shallow soils and no glacial deposits. This will result in very different hydrological properties than the gently sloping, agricultural, glaciated catchments in Ireland. Nevertheless the broad concept may have application to the transition zone in Ireland.

These findings suggest that the transition zone is likely to behave differently in different hydrogeological settings, and may operate somewhat independently of the underlying bedrock, depending on the permeability of the underlying competent bedrock. Therefore, it may not necessarily be appropriate in all circumstances to consider it as a subset of the shallow groundwater pathway. This issue was considered during this research in the context of how best to incorporate the transition zone in the hydrological model in the catchment management tool (Chapter 9).

2.5.3 Nutrient transport

As studies on flow in the transition zone are limited, so too are studies on the transport of nutrients specifically through this pathway, as distinct from 'shallow groundwater', 'deep soils', or simply 'subsurface flow'. Haria and Shand (2006) noted at Plynlimon that the highly fractured

lateral transport zone at the soil-bedrock interface, which was at a depth of 1.5 m near the stream, was a means of bringing bedrock-derived groundwater and soil water from the deeper soil horizons rapidly to the stream. The subsoils were predominantly peat however, which would have presented a different hydrological regime than glacial tills. In their catchment, this pathway was a source of aluminium, but by extension, the same processes would surely also apply in catchments where the transition zone, deep soils and/or shallow groundwater may be a source of nitrogen or phosphorus.

In the Panola catchment, van Verseveld et al. (2009) found that what they called the 'transient groundwater' pathway was a transport pathway for dissolved inorganic nitrogen (DIN). They also found that the upper organic-rich soil layer and the transient groundwater were both high in specific UV absorbance (SUVA), dissolved organic carbon (DOC) and total nitrogen concentrations; whereas SUVA, DOC and dissolved organic nitrogen (DON) decreased with depth in lysimeters. Deep groundwater discharging from a spring was found to be low in SUVA, DOC and nitrogen. The authors concluded that this reflected rapid vertical infiltration of the organic matter to the soil-bedrock interface via preferential flowpaths, followed by lateral transport along the soil-bedrock interface. Similar flow transport mechanisms were observed in a catchment in Canada in a similar landscape setting (Hill et al., 1999) but, in contrast, the dominant nitrogen fraction was DON. This was due to the depletion of the inorganic nitrogen by biogeochemical processes in the organic horizon.

Although these catchments are all very different hydrologically to those found in Ireland, there nevertheless, remains a possibility that the transition zone in Ireland could be a significant pathway for the delivery of nutrients from both the shallow groundwater and the deeper soils, depending on its position in the landscape.

2.6 Shallow and deep groundwater flow

2.6.1 Pathway definition

There are discrepancies in the hydrological literature in places about what exactly is meant by the term groundwater, and whether it includes subsurface water in unsaturated and/or saturated soils, or refers only to water in saturated aquifers. If a loose generalization is possible, literature originating from the hydrogeological sciences is typically more focussed on groundwater in aquifers, i.e. water-bearing reservoirs capable of yielding enough water to satisfy a particular demand (Driscoll, 1986). Definitions from the hydrological sciences may include subsurface flows through saturated or unsaturated soils (Mellander et al., 2012). Very different flow and nutrient

transfer functions may operate in each because of the role of the soil matrix, so it is important to provide a clear definition up front.

In the *Pathways Project*, groundwater is taken to mean flow through the bedrock aquifers, as well as flow through mapped sand and gravel aquifers in the limited areas where they are present. The majority of Ireland's groundwater is present in bedrock aquifers. The Irish working conceptual model divides groundwater flow into shallow groundwater and deep groundwater pathways (Figure 2.2). Shallow groundwater occurs in the upper part of the bedrock where the rock is highly weathered and there is a dense network of open joints, bedding planes and fractures. The lower limit of the shallow groundwater zone is taken to be the lowest summer water level in unpumped conditions (Fitzsimons et al., 2005). The transition zone, as described earlier, is the upper few metres of bedrock at the interface with the overlying soils (Figure 2.2). Flow in the deeper groundwater pathway is through larger discrete faults or fault zones. In these zones, groundwater flow depends on the permeability of the fracture zones and their degree of interconnection. The

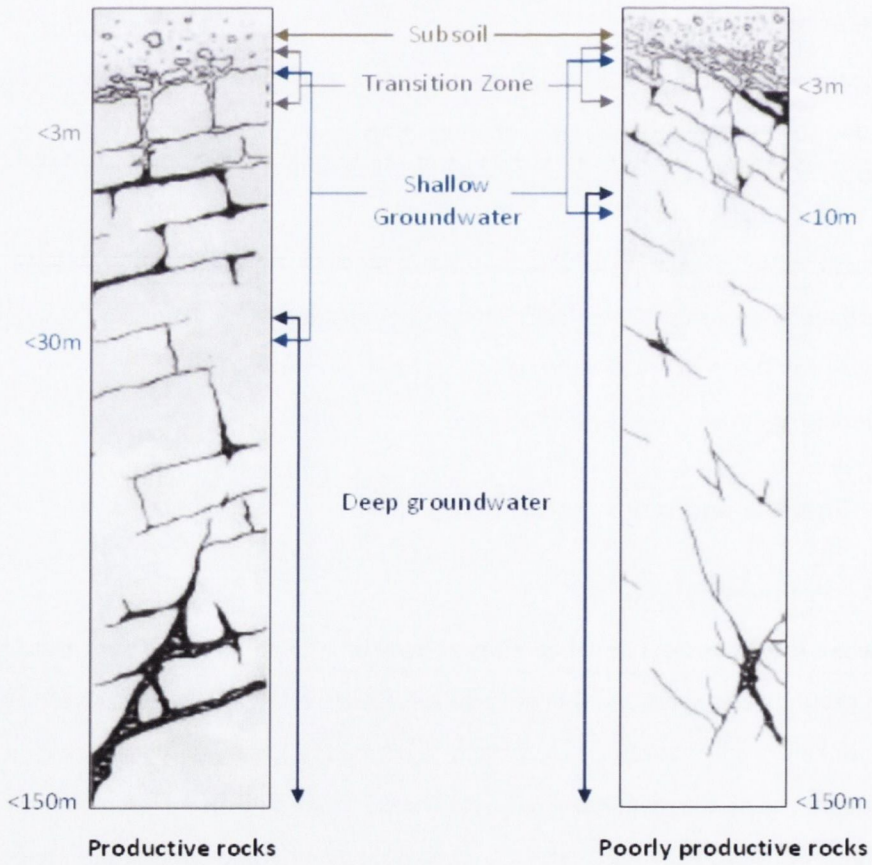

Figure 2.2. Conceptualization of the transition zone, shallow groundwater and deep groundwater pathways. Modified from Fitzsimons et al. (2005).

interactions between deep groundwater and streamflow depend on the degree of interconnection between the fault zone with the stream channel. Borehole records from Ireland suggest that production wells into deep groundwater have rarely exceeded 120 m in depth, but some deeper fractures up to 150 m below ground surface have been found, for example in the Carboniferous limestones in Lisheen mine (Fitzsimons et al., 2005).

2.6.2 Delivery of flow

Since the introduction of chemical hydrograph separation methods (Pinder and Jones, 1969, Sklash and Farvolden, 1979), it has been recognized that pre-event groundwater contributions to stream flow can be significant, and that the contribution can be both during baseflow periods and storm flows. A review on hydrograph separation studies by Buttle (1994) found that 75% of stream flows in all studies were from groundwater.

Research at Plynlimon has found that a compartmentalized groundwater system contributes to the stream (Haria and Shand, 2004), and that there are both diffuse seepages of groundwater along the length of the stream channel, as well as larger contributions at discrete locations (Haria et al., 2013). The Aberdeen catchment science research group in Scotland has found that while the upland montane catchments drive the responsiveness of larger scale catchments, the lowland catchments are dominated by the slower groundwater baseflow characteristics (Tetzlaff et al., 2011).

It has largely been assumed in catchment hydrology studies, however, that the majority of the subsurface flow comes from the soils and that the bedrock is impermeable (Haria et al., 2013). This is not surprising given that many of the well-known hydrological experimental research catchments (e.g. Panola (USA), Plynlimon (Wales), Girnock Burn (Scotland), Maimai (New Zealand)) are located in upland areas, with thin and/or peaty soils overlying poorly productive rocks. However, researchers have recently started to place greater emphasis on understanding the role of bedrock groundwater contributions to stream flows, including groundwater from low permeability bedrock (Tetzlaff and Soulsby, 2008, Tetzlaff et al., 2011, Gabrielli et al., 2012, Haria et al., 2013).

Ireland's bedrock aquifers are dominated by secondary permeability, i.e. groundwater flows through fractures and fissures in the rock, and there is no flow through the rock matrix such as can occur in the Sherwood Sandstone and the Chalk in the United Kingdom (Robins and Misstear, 2000). The development of the fractures is dependent on the lithology of the rocks and the structural deformation history. In general, the higher the degree of fracturing and the lower the content of fine-grained shaley rocks, the higher the permeability and the better the aquifer. This

is because the fine-grained rocks tend to weather to clayey particles and thus infill the fractures and restrict flow (Deakin, 1994, Fitzsimons et al., 2005). The Geological Survey of Ireland has categorized groundwater into Regionally Important, Locally Important and Poor aquifers, or productive and poorly productive (DoELG et al., 1999).

In the poorly productive rocks, which include the shales, mudstones and greywackes present in three of the study catchments, the shallow groundwater pathway occurs in the upper 10-15 m of bedrock (RPS, 2008, Moe et al., 2010). The thickness and storage in these rocks is low, flowpath lengths are typically no more than a few hundred metres, and the volume of recharge that can be accepted, stored and transmitted as groundwater flow is limited. It is assumed in water balance and recharge equations that no more than 100 mm of recharge can be accepted into Poor aquifers, and no more than 200 mm into Locally Important aquifers, with the rest being rejected as near-surface flow (Misstear et al., 2009, O'Brien et al., 2013). Shallow groundwater aquifers fill and empty relatively quickly, and springs and seeps on the surface are common reflecting the rejected recharge and return flow. This results in a high stream density and ditch network, flashy hydrographs and limited baseflow in prolonged dry periods. Poorly productive rocks such as these cover 73.5% of Ireland (O'Brien, 2013).

The productive aquifers are typically the less shaley limestones where the fractures have been enlarged through the processes of karstification and dolomitization, which has increased their permeability (Ford and Williams, 1989). The shallow groundwater pathway may be up to 30 m below the bedrock surface and groundwater flow velocities in karstic systems can be up to several hundred metres per day. These aquifers can supply significant baseflows to streams, recessions are typically long and drawn out, and major springs are common (Fitzsimons et al., 2005).

The shallow groundwater pathway in Ireland has been defined based on the expectation that it will be largely unsaturated over much of a stream's catchment during the drier summer months, with the exception perhaps, of narrow, saturated discharge zones in river valleys and flood plains close to the stream. On a catchment-wide basis therefore, the contribution of the shallow groundwater pathway is highly variable, both temporally and spatially. Moreover, in catchments underlain by the poorly productive rocks, which have low storage and short flowpaths, and where rejected recharge and return flow to the surface are common, it is probable that under certain conditions, water from the shallow bedrock may be delivered to the stream via a surface or near-surface pathway. This has implications for the hydrograph response times, and therefore the quantification of the delivery pathways.

2.6.3 Nutrient transport

The majority of the literature on nutrient transport in groundwater is focussed on nitrate. A recent national study in the United States, for example, found that nitrate delivery to streams and large rivers was primarily via the groundwater pathway (Tesoriero et al., 2009). In a range of small agricultural catchments in Brittany, Aubert et al. (2013) found that nitrate and chloride, both derived mainly from fertilizers, were transported via the shallow groundwater pathways. They also noted that since groundwater travel times through the seven study catchments were of the order of decades, there was a long lag time between the application of nitrate on the land surface and the impacts in rivers. The need to consider the lag times has also been raised as an issue in Ireland by Fenton et al. (2009a) in the context of the implementation of mitigation measures.

Traditionally, phosphorus from diffuse sources has not been associated with the groundwater pathway, but recent work has found that groundwater does play a role in eutrophication across Ireland and the United Kingdom (Holman et al., 2008). In a karst catchment in the west of Ireland, Mellander et al. (2013) found that during smaller events in winter and summer, 85-93% of the flows were delivered via small to medium sized fissures, which delivered a similar percentage (78-90%) of the total phosphorus and total reactive phosphorus. During a larger winter event, however, when conduit flow was more dominant, 70% of the water and 52-53% of the total phosphorus and total reactive phosphorus were transported via the smaller fissure network. They suggested that 40% of the total phosphorus and 46% of the total reactive phosphorus may have been retained in the fissures during this large event, which emphasizes the complexity of karst hydrogeology.

In another well-drained sandstone catchment in the south of Ireland (Timoleague), which is part of the same programme (the Agricultural Catchments Programme; ACP), phosphorus and nitrate were found to be transported via two bedrock zones, a weathered zone at 9–12 m and a deeper zone 16.5–19.5 m below ground level. While the groundwater phosphorus concentrations (0.03 mg/l phosphorus) were an order of magnitude and half an order of magnitude less than in the overland and interflow pathways, respectively, since the contribution of flow from bedrock is dominant during baseflow periods (88% of total flow), the percentage phosphorus load from groundwater was taken to be high overall (Mellander et al., 2012). It must be noted, however, that 34% of the catchment is underlain by bare rock or very thin soils, which may have had a bearing on the vertical transport pathways.

Similar findings with nitrate transport in groundwater were observed in a second well-drained ACP catchment in Wexford, although there, the phosphorus was primarily transported in the shallow permeable subsoil layer. In the two poorly drained catchments in the study, although

nitrate and phosphorus were present in small springs and weathered bedrock at depth, the near-surface ditch and tile drain pathways were found to be more important (Melland et al., 2012b).

The findings from the ACP catchments demonstrate the importance of developing a three-dimensional understanding of the hydro(geo)logical pathways that incorporates the shallow and deep pathways and considers both the soils and the bedrock.

2.7 Discussion

Much is known about contaminant sources, and increasingly more about the receptors, but typically catchment studies and CSA models have lacked a full three-dimensional assessment of the transport and delivery mechanisms along all the hydro(geo)logical pathways, particularly in relation to nitrate. CSA approaches have largely been developed for the transfer of phosphorus using surface runoff and topographical index approaches, but as nitrate is also a significant problem in many countries, including Ireland, there is a need to better understand where the highest-risk areas are for nitrate management measures. Traditionally it has been considered that nitrate is delivered via the groundwater pathway but it has recently been observed that nitrate can also be transported through a quickflow response in poorly drained catchments (Melland et al., 2012b). Similarly, although phosphorus is typically considered to be a near-surface contaminant, it is also now known to be transported via below ground pathways under some conditions. Thus, different programmes of measures may be needed in different catchments to address the same contaminant. There is a clear need to develop better three-dimensional, catchment-scale conceptual models, so that nutrient-specific CSAs can be identified and mitigation measures targeted.

Of the four pathways in the working conceptual model, i.e. overland flow, interflow, shallow and deep groundwater, least is known about the role of the interflow pathway. It is typically ill-defined as a pathway, probably because it incorporates such a range of flow, and nutrient transport processes, through the soil and subsoil horizons, which have different implications for delivery to the aquatic environment. For example, whether matrix flow or preferential flow is dominant in a poorly drained organic soil has a major bearing on whether nitrate will be denitrified or transferred rapidly to a water body. Thus, better conceptualization of how the interflow pathway functions in Ireland would further support the understanding of the nutrient transfer processes.

Cracking clays, i.e. soils that are high in swell-shrink smectitic clay minerals, are common in the United Kingdom and are present at the research sites where much of the understanding of the transport of phosphorus has been developed (Haygarth et al., 1998, Heathwaite and Johnes,

1996, Bilotta et al., 2008, Jarvie et al., 2008). However, this type of clay mineralogy is not present in Ireland. Irish clay and silt soils are substantially quartzose with much less swell-shrink (Mulqueen, 1998). In addition, Ireland tends to have higher summer rainfall, less evapotranspiration and less of a soil moisture deficit (Fitzsimons and Misstear, 2006), which means that our soils stay more saturated for longer. It is important therefore that research into the pathways through the soils is carried out in Irish catchments to determine the nature of their role in streamflow generation.

The presence of land drains, and whether or not they are effective, functioning and well maintained, may significantly alter the nature of the hydrological response. It is widely known internationally that land drains are an important delivery pathway for nutrients to streams but there is a particular need to better understand their role in nutrient transport in the Irish landscape. The evidence from the international literature suggests that they may well be significant. With the likely focus over the next few years in Ireland on developing marginal land to meet Food Harvest 2020 targets (Ibrahim et al., 2013), the likelihood that additional lands will be drained is high, so it will be important that their impacts are understood and adequately managed. There are no maps currently available of drained areas in Ireland and there is an assumption that they have followed the arterial drainage schemes, which is not considered to be the case anecdotally. There is a need for a better understanding of the hydro(geo)logical conditions in which land drains have been installed, how and where they operate and what their impacts might be on nutrient transport.

Some limited research on land drains has been completed in Ireland, but it has been predominantly carried out in the controlled conditions of small-scale test plots at agricultural research farms (Burke et al., 1974a, Watson et al., 2000a, O'Reilly, 2006). In reality, however, the artificial drainage infrastructure often receives little or no maintenance and therefore the test plots may not necessarily be representative of the typical operating scenario across most of Ireland. There is a need to carry out research on land drains and ditches as they are in their current state, so that they are as representative as possible and can be related to catchment-scale processes.

Despite a growing awareness of the importance of the bedrock groundwater in hillslope and catchment-scale hydrology, there is still very little emphasis on including groundwater (in both the fractured and competent bedrock) in catchment studies and assessing the role it may play in the transport of nutrients. There are also contrasting reports on the role of the transition zone pathway in the literature and given its broad definition in Ireland, which includes both saturated and unsaturated regimes, it is probable that it may have a complex role to play in stream flow

generation. With such a large proportion of Ireland underlain by <3 m of soils and subsoils, the role of the transition zone is likely to be significant but there are no specific studies that consider its role. The question also remains as to its role in the delivery of nutrients to streams.

3 Review of methods for assessing flow pathway contributions

3.1 Introduction

In the context of the research gaps highlighted in Chapter 2, a range of appropriate research methods are discussed in this chapter. There are a large variety of qualitative and quantitative methods, applicable at different scales, to determine the contribution of the hydro(geo)logical flowpaths to streams. Traditional methods were based primarily on the flow characteristics and response times of different flow components (physically based), but the introduction of chemical methods of hydrograph separation provided the first real insights into the significance of the subsurface contribution to streamflow (La Sala, 1967, Pinder and Jones, 1969). They were considered a breakthrough in better understanding stream generation processes at the time (Beven, 2006a) and continue to be used widely today.

Sampling stream flow and water quality at regular intervals during a storm (event sampling), or ideally continuous monitoring (Kirchner et al., 2004), has proven capability in significantly improving knowledge gained through the physical methods alone (Mellander et al., 2012). Other chemical methods include longitudinal stream profiling of flows and conductivity, which can be useful to identify significant subsurface influxes to streams (Haria et al., 2013); more intensive exploration of the spatial water quality and chemistry can provide information on the subtleties of different flow processes and pathway contributions in different parts of the catchment (Tetzlaff and Soulsby, 2008).

Many of the intensively monitored permanent research catchment studies have relied on the use of trenches or drainage collectors that separate, quantify and sample the flows from the different pathways (Freer et al., 2002, Bilotta et al., 2008, Thompson et al., 2012). Trench studies may be supported by the use of a range of other instruments to measure responses and water quality in individual pathways, such as spring flows and piezometers for groundwater (Fenton et al., 2009b), and lysimeters for soil water response (Bilotta et al., 2008). However, trenches can usually only access the upper soil layers unless the bedrock is close to the surface. It can also be difficult to separate and seal the different pathway flows (O'Reilly, 2006), and there are practical and logistical issues in asking farmers to grant continued access to deep excavations in actively grazed land. The use of trench studies was therefore not considered further in this research.

The soil water dynamics have a major bearing on the development of interflow and therefore on the transfer of nutrients through the soil profile. A range of instruments can be used to investigate the dynamics of soil moisture and flow, such as lysimeters, piezometers, tensiometers (Diamond and Shanley, 1998) and soil moisture probes (Harr, 1977). Various water balance models have also been used to estimate the interflow component, but typically only the inputs (rainfall and evapotranspiration) and the outputs (discharge) are known, and the pathway contributions are inferred. Soil water dynamic field studies have tended to involve the use of hydrologically isolated plots with very controlled conditions, including the use of rainfall simulators (Lehman and Ahuja, 1985). They are typically also only focussed on the upper soil layers, and often address the net nutrient outcomes rather than the pathway mechanisms of flow.

The methods reviewed in this chapter focus on the techniques that showed the most promise for use in this research. In particular these included chemical hydrograph separation methods at the catchment scale to determine the contribution of flow from each pathway to the stream, supported by soil water dynamic studies to try and shed further light on the interflow processes. Physical hydrograph separation methods are also included as they were used by a fellow *Pathways Project* student to inform the catchment hydrological modelling, which was in turn used by this author to inform the chemical hydrograph separations.

3.2 Physical methods

3.2.1 Physical hydrograph separation

The early methods of separating out the quickflow and baseflow contributions to the river hydrograph were based on graphical analysis of the hydrograph. Different methods such as the Constant Slope method, or Concave method, simply connected a point at the beginning of the rising limb to the end of the falling limb using different inflection points of the recession curve, with the flow above the line being considered the quickflow component. The Barnes method, for example (Barnes, 1939), distinguishes three components of flow on a semi-logarithmic plot of the log of discharge Q versus time t.

Master recession curve analysis examines the different points along an average recession curve where the trend changes and the different flow components cease to contribute. Master recession curve analysis (using the matching strip and tabulation method) was used in a major recent Irish study on groundwater and surface water interactions to distinguish the baseflow (deep groundwater) contributions to river flow (RPS, 2008).

Automated filtering separation techniques, such as the Institute of Hydrology method and the Boughton method are also widely used (O'Brien, 2013, O'Brien et al., 2014). These methods have the advantage that they provide rapid, objective and repeatable means of estimating the baseflow index, although they are relatively arbitrary and are not based on hydrological principles (Nathan and MacMahon, 1990).

Insights into flow pathway contributions can also be gained from frequency analysis of river flows, including preparation of flow duration curves (FDCs), which show the percentage of time that the complete range of flows are equalled or exceeded. Qualitative indications of the relative importance of baseflow contributions between different catchments can be gleaned from the shape of the FDCs: if the section of the FDC below the median flow (*Q50*) has a shallow slope, this indicates a continuous baseflow contribution to the river, whereas a steep curve indicates comparatively smaller contributions from groundwater storage (Smakhtin, 2001). More generally, the *Q95* flow has been used as a rule of thumb to permit comparison of baseflow regimes from different stream/river discharge monitoring points. Quantitative indices derived from the FDCs have been developed to provide descriptions of the hydrological regime. For example, the *Q90/Q50* ratio is used to indicate the proportion of streamflow contributed from groundwater storage (Nathan and MacMahon, 1990, Brodie and Hostetler, 2005); the *Q5/Q95* ratio has been used as a measure of the degree of stream flow variability or how 'flashy' a stream is (Jordan et al., 2012). Despite the wide use of FDCs in hydrological practice, the relevant literature is very limited and it has been proposed that its application potential has not been fully explored (Smakhtin, 2001).

However, all the approaches for physical hydrograph separation analysis have significant limitations (Archbold et al., 2010, Deakin et al., 2010). The primary issue is that the physical methods differentiate the pathways based on their response times, and the differentiation between the different pathway contributions is mostly arbitrary with very little basis in reality (Anderson and Burt, 1980). The methods are based on the assumption that there is a relationship between the depth of the flowpath and the response time, i.e. that the deeper groundwater pathways have the slowest response times, and the fastest pathway response time is from overland flow. This assumption may be a reasonable approximation when separation into only two pathways (baseflow and quickflow) is required. However, the relationship becomes less clear when trying to separate out more than two pathways, to include for instance, interflow, drainflow, transition zone flow and shallow groundwater flow. Several studies comparing the application of different physical hydrograph separation techniques to the same datasets have noted large differences in the resulting pathway contributions (Dowling, 2009, O'Brien, 2013,

Cartwright et al., 2014). Thus, physical methods, although they have advantages of repeatability and objectivity in some cases, and can be easily applied to readily available stream flow datasets (Brodie and Hostetler, 2005), are best used as part of a suite of tools because of the uncertainty and limitations with using any one technique.

3.2.2 Recharge estimates

A methodology for determining the proportion of rainfall that infiltrates to groundwater, versus that which runs off via the near-surface pathways, has been developed in Ireland and is useful for separating the quickflow components from the baseflow. Using readily available hydrogeological and meteorological datasets, a recharge coefficient is first determined that encapsulates the physical characteristics of the area under consideration (Misstear et al., 2009, Hunter Williams et al., 2013). The key factors that contribute to the recharge coefficient are the type, permeability and thickness of the subsoils, and the drainage characteristics of the soils (Table 3.1). The hydrologically effective rainfall is multiplied by the recharge coefficient to give a value for the potential recharge. In the poorly productive aquifers, a recharge cap is subsequently applied to reflect the ability of the underlying bedrock aquifer to accept the infiltrating water. For Poor aquifers the recharge cap is 100 mm; 200 mm is applied in areas underlain by Locally Important aquifers. The remainder of the potential recharge is assumed to be rejected as near-surface flow.

Table 3.1. Recharge coefficients for different hydrogeological settings (from Hunter Williams et al. (2013).

Groundwater vulnerability category	Hydrogeological setting	Recharge coefficient (RC)		
		Minimum (%)	Inner range (%)	Maximum (%)
Extreme	1.i Areas where rock is at ground surface	30	80–90	100
(X or E)	1.ii Sand or gravel overlain by 'well-drained' soil	50	80–90	100
	1.iii Sand or gravel overlain by 'poorly drained' (gley) soil	15	35–50	70
	1.iv Till overlain by 'well-drained' soil	45	50–70	80
	1.v Till overlain by 'poorly drained' (gley) soil	5	15–30	50
	1.vi Sand or gravel aquifer where the water table is ≤3 m below surface	50	80–90	100
	1.vii Peat	1	15–30	50
High	2.i Sand or gravel aquifer, overlain by 'well-drained' soil	50	80–90	100
(H)	2.ii High permeability subsoil (sand or gravel) overlain by 'well-drained' soil	50	80–90	100
	2.iii High permeability subsoil (sand or gravel) overlain by 'poorly drained' soil	15	35–50	70
	2.iv Sand or gravel aquifer, overlain by 'poorly drained' soil	15	35–50	70
	2.v Moderate permeability subsoil overlain by 'well-drained' soil	35	50–70	80
	2.vi Moderate permeability subsoil overlain by 'poorly drained' (gley) soil	10	15–30	50
	2.vii Low permeability subsoil	1	20–30	40
	2.viii Peat	1	5–15	20
Moderate	3.i Moderate permeability subsoil overlain by 'well-drained' soil	35	50–70	80
(M)	3.ii Moderate permeability subsoil overlain by 'poorly drained' (gley) soil	10	15–30	50
	3.iii Low permeability subsoil	1	10–20	30
	3.iv Peat	1	3–5	10
Low	4.i Low permeability subsoil	1	5–10	20
(L)	4.ii Basin peat	1	3–5	10
High to Low	5.i High predicted permeability subsoils (sand or gravels)	30	80–90	100
(HL)	5.ii Moderate permeability subsoil overlain by well-drained soils	35	50–70	80
	5.iii Moderate permeability subsoils overlain by poorly drained soils	10	15–30	50
	5.iv Low permeability subsoil	1	5–10	20
	5.v Peat	1	5	20

The recharge coefficients are a useful means of providing a reality check on the deeper groundwater flow pathways as they provide a control on the amount of recharge that is then a constraint on the groundwater flow component. The proportion of effective rainfall that gets rejected also provides a useful check on the quantity of interflow and overland flow combined. For example, where the rock lies close to the surface and the thin tills and soils are poorly drained, 15–30% of the effective rainfall is expected to recharge to groundwater, which means 70–85% is rejected as interflow and overland flow combined. Where the rock comprises a Poor aquifer, no more than 100 mm is expected to be recharged, so in high rainfall areas, a higher proportion of the effective rainfall will run off (Misstear et al., 2009). This method is less useful however, for differentiating between the different near-surface pathway contributions.

3.2.3 Numerical flow modelling

Numerical models offer a useful means of predicting catchment response but are of course highly dependent on the nature and quality of the input data. Models can be deterministic, i.e. where physical processes are represented as realistically as possible; or stochastic, where a black-box approach is adopted that uses mathematical and statistical relationships in the data to link the inputs to the outputs. Deterministic models are commonly used in hydrological modelling, and may be lumped, semi-distributed or distributed. Lumped models are often favoured in catchment studies as they do not account for spatial and temporal variations of some parameters, and are generally focussed on achieving a particular outcome rather than accurately representing the physical processes, so therefore are often considered to require less data (O'Brien, 2013). Examples of commonly used lumped models include HBV, SMAR and NAM (Archbold et al., 2010). Semi-distributed models are commonly lumped models used in subcatchments that are linked together. Fully distributed models are more complex as the catchment is divided into a grid and each cell has its own set of parameters that describe its attributes. MODFLOW and SHETRAN are both well-known industry standards in distributed hydro(geo)logical modelling.

Two lumped models were selected for use in the *Pathways Project* by fellow PhD researchers: the NAM (the Danish Nedbør-Afstrømnings-Model) as an investigative tool to determine a methodology for separating the flow hydrograph into the four pathways and identifying the primary catchment characteristics that control those pathways (O'Brien, 2013, O'Brien et al., 2013); and SMART (Soil Moisture Accounting Routine for Transport), a modification of the earlier SMAR model, as a framework for the catchment management tool which simulates both flow and contaminant pathway contributions (Mockler et al., 2013a, Mockler et al., 2013b).

A detailed description and review of the models is not provided here as the modelling work was not carried out as part of this research; the reader is referred instead to the other researchers'

work as referenced above. However, as the NAM results were used in this research, it is helpful to provide a brief overview of the structure of that model.

The NAM is a conceptual rainfall-runoff model that simulates the hydrological cycle and produces a time series of catchment runoff and subsurface contributions to streamflow. It contains four different storage zones (snow, surface, root and groundwater), although the groundwater storage zone can be divided into an upper and lower section to simulate shallow and deep groundwater flow, and the snow storage is not used in Irish simulations. The inputs to the model are rainfall and evapotranspiration, which were at 15-min intervals for the *Pathways Project* modelling, and nine constraining storage and water transfer parameters based on catchment characteristics that govern the water accounting routines. Observed stream discharge data are used for calibration and validation.

3.3 Chemical methods

3.3.1 Event sampling

High resolution chemical sampling of streamflows during rainfall events provides insights into how and when the hydro(geo)logical pathways respond to rain. It is especially helpful for determining which pathways deliver nutrients (Outram et al., 2013), turbidity (Lawler et al., 2006) or other contaminants during storms, and it is the basis for chemical hydrograph separation and assessment.

The timing and the degree of hysteresis in contaminant concentrations during the event indicates the sources and delivery pathways (Figure 3.1). Peak solute concentrations before the hydrograph peak and a clockwise hysteresis indicate sources that are close to the stream, are easily mobilized and become rapidly exhausted as the rain progresses. Conversely, contaminant peaks after the peak in flow, with an anticlockwise hysteresis, suggest a distant or more slowly mobilized source (Benskin et al., 2013).

Comparison of hysteresis loops for different solutes, and in different locations in a catchment, allows inferences to be made about nutrient transport pathways. For example, on the basis of the relationships between the concentrations of each of 13 analytes with flow, Holz (2010) identified three pathway transport groups: (a) the total phosphorus group, which included DRP, total suspended solids, total nitrogen, *Enterococcus* and *E. coli.*, was dominated by the soil surface and was transported via overland flow; (b) the NO_3 group which included total dissolved solids, Ca, Mg and Na, was associated with subsurface pathways; and (c) the NH_4 group which included K and

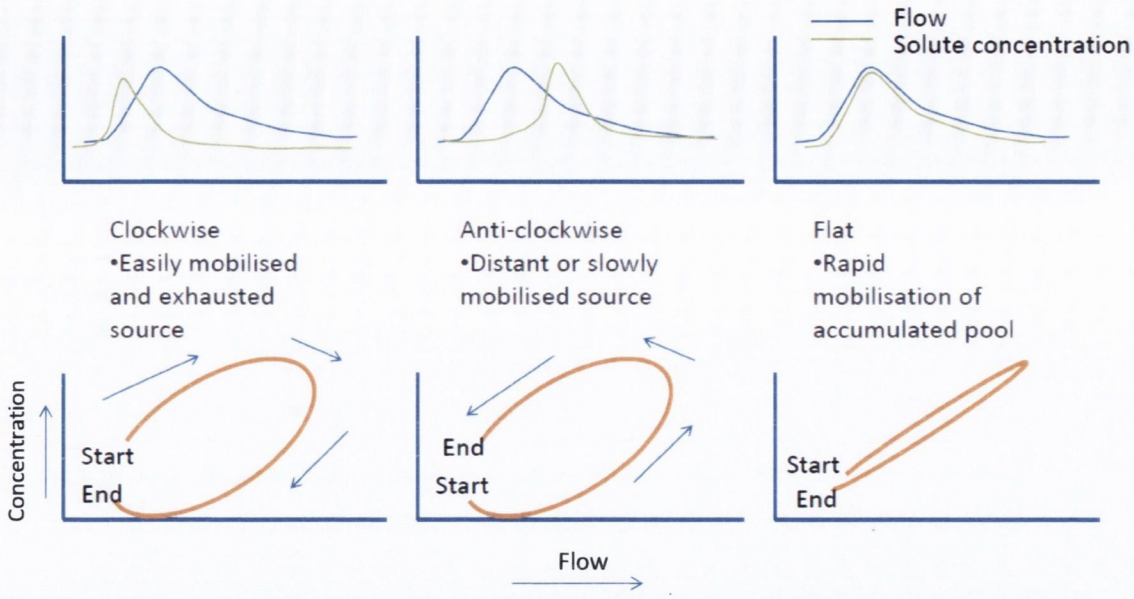

Figure 3.1. Hysteresis in contaminant concentrations during rainfall events (from Benskin et al. (2013)).

showed direct impacts of grazing activity. Although not sufficient on its own to quantify the different pathway contributions, this method is nevertheless a powerful addition to the toolbox when used in combination with other approaches.

Another approach using chemical data, the 'loadograph' approach, was developed by Mellander et al. (2012). Near continuous datasets of nutrient concentrations and flow were used to generate a continuous plot of nutrient loads for four Irish catchments. A type of recession analysis was then used to distinguish the different pathway contributions based on the assumption that the slower response times towards the end of the recession were delivered via the deeper groundwater pathways, and the quicker response times were from overland flow. A degree of validation and control was achieved by comparing stream water quality at different points in the recession with that in a series of boreholes installed at different depths in the catchment. In-stream turbidity was used to verify the quickflow response period. The method is not able to distinguish between different components of the quickflow response from, for example, overland flow, land drains, ditches, return flow or preferential flowpaths. Importantly, it also requires continuous or near continuous monitoring of the solutes being examined to calculate the loads so is a relatively expensive technique.

3.3.2 Chemical hydrograph separation

Chemical hydrograph separation approaches depend on the principle that as rainfall infiltrates through the landscape, the concentration of a selected tracer(s) increases with increased residence time and/or contact with geological materials. Variations in tracer concentrations in stream water over time, particularly during a storm event, can be used to estimate the relative contributions of the stream flow components with different origins and hydrological flowpaths

through the landscape. A number of different flow components are typically identified. In two-component models, usually pre-event and event water, or surface and subsurface flows are differentiated; three-component models introduce a third soil water component that can be satisfactorily distinguished from the other two. Occasionally up to five components have been identified (Uhlenbrook and Hoeg, 2003), but it has been observed that the larger the number of components included in the mixing model, the greater the problem of equifinality, i.e. that there may be several different, yet equally plausible solutions to the model (Beven, 2006a).

The method uses a mass balance equation to quantify the contributions of different stream flow components to the total flow (Pinder and Jones, 1969). The classic two-component mixing equation is as follows:

$$Q_{tr}C_{tr} = Q_{dr}C_{dr} + Q_{gw}C_{gw} \qquad \text{Eq 3.1}$$

where Q_{tr} is the total runoff; Q_{dr} is the direct runoff; Q_{gw} is the groundwater runoff; C_{tr} is the tracer concentration in total runoff; C_{dr} is the tracer concentration in direct runoff; and C_{gw} is the tracer concentration in groundwater. This equation can also be modified, however, to incorporate additional stream flow components, as described in (Ogunkoya and Jenkins, 1993):

$$Q_{tr}C_{tr} = Q_1C_1 + Q_2C_2 + \ldots + Q_mC_m \qquad \text{Eq 3.2}$$

where the subscripts $_{1, 2, \ldots m,}$ are the assumed components of the total runoff. The number of components to be distinguished dictates the number of tracers required: *n-1* tracers are needed to determine *n* stream flow components.

An adaptation of the early method, End Member Mixing Analysis (EMMA), was developed by Christophersen et al. (1990) and Hooper et al. (1990) and has become the industry standard. Using EMMA principles, it is assumed that stream water is derived from a mixture of soil and/or groundwater solutions, known as end members, and that the end members form the boundaries of the possible stream water observations. In this way, EMMA relates measured end member chemistry from soil samples, groundwater etc., with observed stream water chemistry. The advantage of the method is that the resulting mixing diagrams allow the user to quickly recognize when a significant end member has been missed, or a tracer is not behaving conservatively, because under those circumstances the stream chemistry will not be bounded by the end members (Christophersen et al., 1990).

Various statistical techniques are then often applied to the mixing model data to estimate the degree of uncertainty in the results. The formalized statistical approach devised for EMMA by Christophersen et al. (1990) and Hooper et al. (1990) incorporates more tracers than the

minimum *n-1* required and calculates the uncertainties associated with all possible end member combinations. Other authors have relied on Monte Carlo analyses using generated data (Bazemore et al., 1994) or field data (Joerin et al., 2002), and/or other bayesian statistical approaches (Soulsby et al., 2003a).

There are a number of assumptions that apply in carrying out hydrological mixing analyses. These include the following:

- the chemical or isotopic signatures of the stream flow components are distinguishable (Ladouche et al., 2001);
- temporal and/or spatial variations in stream flow compositions are negligible or are accounted for in the model (Eshleman et al., 1993);
- the tracer being used is conservative and is not impacted to a significant degree by chemical or biological processes at the scale or timescale of interest (Hooper and Shoemaker, 1986). Reactive tracers can be used if the associated uncertainties are integrated into the mixing models (Soulsby et al., 2003a);
- there is no significant surface storage in the system that could influence the tracer concentrations (Hooper and Shoemaker, 1986);
- where the number of stream flow components being analysed is small (e.g. two or three), the differences between potential components that are being amalgamated for the purposes of the analysis (e.g. vadose water and groundwater in two-component mixing) is insignificant (Sklash and Farvolden, 1979);
- specifically for EMMA, the signatures of the end members represent the extremes and any solution in the catchment is a mixture of those extremes or else does not contribute significantly to the stream (Hooper et al., 1990).

Several of these assumptions are difficult to satisfy in heterogeneous hydrogeological scenarios with a range of land uses, such as those present in Ireland. Some may reasonably be assumed to be met in some catchments but would not be appropriate in others, or might only be appropriate in some seasons, or at the timescale of single events. Soulsby et al. (2003a) for instance, used nitrate as a tracer and although they admit it is not completely conservative, they, and other authors (e.g. Durand and Torres (1996)) have found it can be assumed to be conservative during storm episodes where rapidly changing flow paths are the main control on stream chemistry. Many authors report that despite the challenges with the assumptions, the technique still has application, so long as the nature and extent of the uncertainties are identified (Genereux, 1998, Joerin et al., 2002, Soulsby et al., 2003a).

A recent comprehensive review by Klaus and McDonnell (2013) of over 100 studies using chemical hydrograph separation carried out since the previous major review (Buttle, 1994), confirmed that there are still deficiencies in the literature in how and where the chemical hydrograph separation method is being applied. Several of these have been considered in this research. First, the literature is dominated by studies from steep, alpine forested catchments whereas studies in low-lying agricultural catchments, especially glaciated landscapes, which are the focus of the *Pathways Project,* are still very rare. Where they have been carried out (Vidon and Cuadra, 2010, Kennedy et al., 2012), they have tended to find a higher proportion of pre-event water in the streams than in forested catchments of similar scale (Klaus and McDonnell, 2013). This suggests that the pathways delivering the pre-event event water are likely to be of greater interest in Irish catchments, for two reasons: (a) their expected dominance in the hydrograph, and (b) their propensity to deliver nitrate, which is an important water quality issue in Ireland.

Second, there is still a tendency in the literature to assume that the baseflow chemistry in the stream represents the groundwater pathway, which may not always be the case. Since the groundwater and other subsurface pathways are likely to be important in the Irish landscape, it was considered a priority in this research to use samples collected directly from those pathways, rather than make assumptions from the stream baseflow.

Third, silica was found to be the most popular tracer in the 100+ studies reviewed by Klaus and McDonnell (2013), followed by chloride, and DOC to represent the organic surface pathways. Silica has been used by a number of authors both nationally and internationally (Soulsby and Dunn, 2003, Soulsby et al., 2003a, Stewart et al., 2007, Dowling, 2009, Kane, 2009, Murphy, 2010), although it must be noted that it is not always conservative as it can be taken up by diatoms. It can also be quickly dissolved in rainfall infiltrating through soils so its applicability needs to be tested in catchments before use (Hooper and Shoemaker, 1986). Klaus and McDonnell (2013) noted that the use of δ^2H and ^{18}O isotopes was common, but they were typically used independently rather than together. They felt there was more to be learned by using a greater range of tracers and comparing the results, something that was also considered in the design phase of this research.

Fourth, consistent with other authors (Kirchner et al., 2004), Klaus and McDonnell (2013) called for greater use of higher resolution, 15-min data to better understand the nature of the pathway-stream interactions. While there are obviously cost implications surrounding this approach, it was a principle throughout this research to use as high a resolution as possible.

Chemical hydrograph separation has been widely used in the United Kingdom, particularly in Scotland and Wales (Soulsby and Dunn, 2003, Soulsby et al., 2003b, Jarvie et al., 2008) and further afield (Hooper and Shoemaker, 1986, Hooper et al., 1990, Joerin et al., 2002, Garrett et al., 2012). However, with the exception of one study by Kane (2009), plus three undergraduate student projects carried out as part of the *Pathways Project* (Dowling, 2009, Murphy, 2010, Byrne, 2011), and ongoing work in the ACP based in Teagasc (Mellander et al., 2012), the method has not been fully tested in Ireland.

3.4 Soil water dynamics

3.4.1 Introduction

As discussed in Section 2.3.2, understanding the soil water dynamics is a key aspect of determining when and how interflow is occurring, notwithstanding that there are clearly also other factors involved such as the presence of low permeability layers to generate lateral flow. The relationship between soil moisture and soil water potential (or matric potential or tension) is important as it governs the soil water retention and therefore the drainage characteristics of the soil. Measuring soil moisture is considered to be one of the most cost effective datasets that can be collected in hydrological experiments (Cuenca and Noilhan, 1991) and since gravitational drainage, rather than evapotranspiration, is the principal factor influencing soil water movement in areas north of 50°N (Kerebel et al., 2013), soil moisture is one the key parameters of interest in understanding interflow in Ireland. There are several means of measuring soil moisture in the field.

3.4.2 Measuring soil moisture

3.4.2.1 Gravimetric method

The soil moisture content can be measured manually by measuring the volume (volumetric method) or mass (gravimetric method) of water lost from a sealed, weighed soil sample on drying. Samples are taken and dried to constant mass at 105±5°C. The difference in mass of an amount of soil before and after the drying procedure is used to calculate the dry matter and water content on a mass basis (BSI, 1994). Although this method is relatively accurate and simple, it is destructive as taking the samples in the soil of interest creates new preferential flowpaths that can interfere with the processes being measured (Blonquist Jr et al., 2006).

3.4.2.2 Time-domain reflectometry

The use of time-domain reflectometry (TDR) is common practice and there are now many user-friendly meters available from different manufacturers. TDR operates on the basis that the soil

moisture content is proportional to the dielectric of the soil. The sensors emit and receive an electromagnetic signal through either two stainless steel pins that are inserted into the soil, or through a probe inserted in a tube that is in contact with the soil. The latter allows measurements at different depths.

The soil permittivity, i.e. the response to polarization in an electromagnetic field, is measured, which is proportional to the soil moisture content. However, the sensor only measures the soil moisture immediately at the stainless steel rods (Knight, 1992), and as the variability in soil moisture in the landscape is so large, issues of representivity arise. Several hundred repetitions may be required to gain a reasonable degree of confidence in the variability in the field, depending on the nature and scale of the study (Western et al., 1998). Blume et al. (2009) for example, combined the use of spatially rich and temporally poor datasets, with those that were temporally rich and spatially poor, to gain a better understanding of the relationship of soil moisture in a catchment to flow.

3.4.2.3 Other methods

Various other methods of measuring soil moisture used in the past involved the use of radioactive materials (e.g. neutron scattering) but these have been discontinued for health and safety reasons. Newer methods include airborne and satellite remote sensing techniques (Dingman, 2002, Chrisman and Zreda, 2013). Time variant electrical resistivity measurements ('4-D imaging') are now also commonly being used as they have the advantages of improvements in spatial coverage as well as temporal capabilities (Hupet and Vanclooster, 2002, Robinson et al., 2008).

3.4.3 Measuring matric potential

3.4.3.1 Electrical resistance blocks

Electrical resistance blocks, or gypsum blocks, have been widely used in soil water studies and rely on the inverse relationship between the water content and electrical resistance of a volume of porous material (e.g. gypsum). They are cheap, simple to use and have been found to be a valuable tool in arable crop management (Stenitzer, 1993). However, they measure the soil matric potential rather than the soil moisture content (Blonquist Jr et al., 2006).

3.4.3.2 Tensiometers

Soil water is subject to a number of force fields that cause its potential to differ from free water. The total soil water potential is the sum of those forces and, although additional forces may also be added, for the most part it is typically thought of as the sum of the gravitational, matric and osmotic potentials as follows (Hillel, 1982):

$$\emptyset_t = \emptyset_g + \emptyset_P + \emptyset_o \qquad \text{Eqn. 3.3}$$

where $\emptyset_t$ is the total potential; $\emptyset_g$ is the gravitational potential; $\emptyset_P$ is the pressure or matric potential; and $\emptyset_o$ is the osmotic potential. The sum of the gravitational and matric potentials is also often known as the hydraulic head, and the sum of the matric and osmotic potentials is known as the soil water potential.

The gravitational pressure at a point in the soil is given by the height of that point above an arbitrary datum, and for convenience, it is usually set to zero or considered as a positive pressure. The osmotic potential is the energy required in a solution to counter the transfer of water molecules across a semi-permeable membrane by osmosis and it is most applicable in studies of interactions of plant roots and soil water (Hillel, 1982). Thus, in hydrological studies, soil water potential is usually considered as the sum of the gravitational potential and the matric potential which is measured with a tensiometer.

Tensiometers consist of a ceramic porous cup attached with a thin plastic tube to a pressure gauge for manual readings, or a pressure transducer if the measurements are to be logged. The unit is filled with water and sealed and when it is installed in the soil, the pressure inside the tube equilibrates with the pressure in the soil through the porous cup. For practical purposes, tensiometers cannot operate at matric potential of >–85 kPa as this causes air to enter the cup, which equalizes the internal pressure with the atmosphere (Hillel, 1982).

Tensiometers have been used in several Irish studies ((Burke et al., 1974a, Ryan et al., 1998, Diamond and Sills, 2001, Premrov et al., 2010). Schulte et al. (2005) found that, for Irish conditions, the relationship between measured soil water tension and the soil moisture deficit (SMD) was close to linear for a wide range of potential parameter values, and they used this relationship in the development of an Irish SMD model, which is further discussed below. Diamond and Sills (2001) measured the tension in three different soil types (poorly drained, moderately well drained and well drained), at six depths up to 1.2 m, over 3 years. They found that the poorly drained soil was saturated for up to nearly 4 months per year at a depth of 15 cm, thereby increasing the likelihood of saturation excess overland flow occurring. The tension was found to be directly related to the drainage characteristics and the depth: the free-draining soils had the highest tension and wetness generally increased with depth.

Interestingly, although it was not commented on in their paper, the data from Diamond and Sills (2001) may also potentially provide some insights into the flowpaths (Figure 3.2). At all sites, there were changes in the hydraulic conductivity and tension at approximately 30–45 cm below ground, and again in the better drained sites below 90 cm. This raises questions as to whether

these zones represent the A/B and B/C horizon boundaries, whether the changes in hydraulic conductivity are significant enough to develop interflow zones, and whether interflow is indicated by the changes in tension?

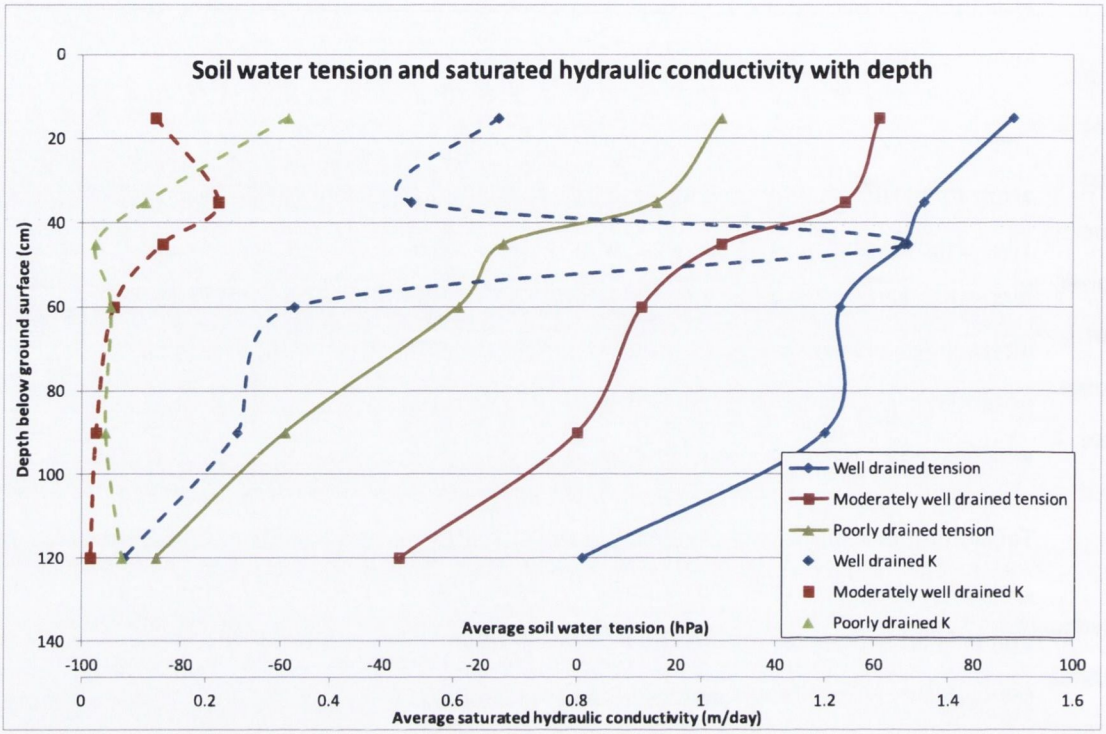

Figure 3.2. Mean soil water tension and saturated hydraulic conductivity with depth at three sites with different drainage characteristics. Data taken from Diamond and Sills (2001).

3.4.4 Soil moisture characteristic curve

As discussed in Section 2.3.2, the soil moisture characteristic curve, or soil water retention curve, describes the equilibrium relationship between the soil water potential and the soil water content for a given soil type, and it can be used to predict the conditions under which water will flow from the soil (Figure 3.3). When the soils are fully saturated, the tension is zero. As soil water potential (suction) is increased, the soil moisture is held more tightly depending on the sizes and volumes of the water filled pores. Clayey soils have higher water contents for a given suction than sandy soils, as the pores are much smaller and the capillary forces much greater. Soil structure also affects the soil moisture characteristic curve at the low suction range. Compaction of a soil decreases its total porosity and therefore its pore volume and water content (Hillel, 1982).

A hysteresis occurs in the soil moisture characteristic curve depending on whether the soil is drying under increasing tension (desorption), or wetting up following a dry period (sorption). At a given suction, the soil moisture is lower when soils are wetting up than it is when they are draining, because of the non-uniformity of individual pores and entrapped air (Figure 3.4). Partially wetted or dried soils may exhibit smaller hysteresis loops. This hysteresis means that the

wetting history of a soil can affect its hydraulic conductivity. In practice it is typically the desorption curve, or the soil water release curve, that is reported as the sorption curve is more complex to determine (Hillel, 1982).

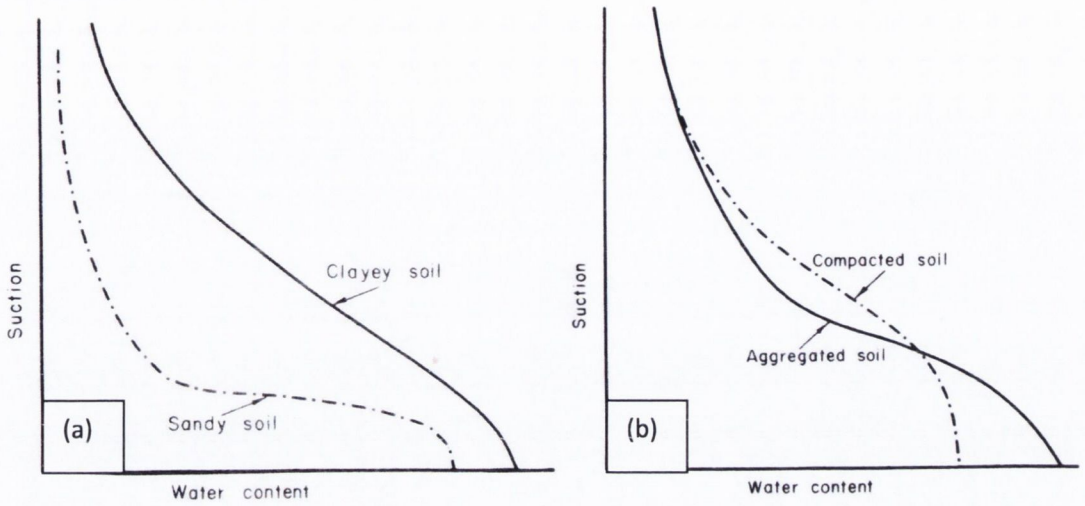

Figure 3.3. Soil moisture characteristic curves for soils with (a) different texture and (b) different soil structure (after Hillel (1982))

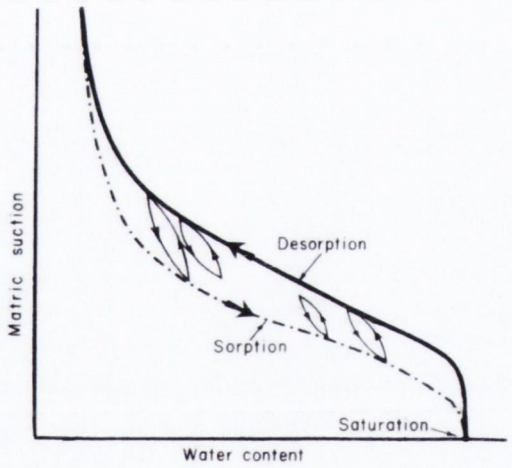

Figure 3.4. Hysteresis in the soil moisture characteristic curve under desorption (draining) and sorption (wetting up) conditions (from Hillel (1982))

3.4.5 Macropore flow

As noted in Section 2.3.2, flow through macropores or preferential flowpaths may dominate flow in some soils and can operate independently of soil moisture conditions. Measuring flow through macropores and preferential flowpaths is difficult, however. Coloured dyes are often used but the sites have to be excavated to interpret the results (Flury et al., 1994). Some authors have used the response times of tracers (Seiler et al., 2002) and inferences can also be made on the basis of whether or not particulates are present in soil water samples from depth.

3.4.6 Soil moisture deficit models

Soil moisture conditions are often assessed using soil water balance models, which quantify the inputs and outputs through the soils using a water balance approach. The basic soil water balance model as described by Rushton and Ward (1979) is:

$$P = ET + R + \Delta S \qquad \text{Eqn. 3.4}$$

Where P is precipitation, ET is evaoptranspiration, R is runoff and ΔS is change in storage. Allen et al. (1998) expanded the equation which identifies the soil water component as follows:

$$ET = I + P - RO - DP + CR \pm \Delta SF \pm \Delta SW \qquad \text{Eqn. 3.5}$$

Where ET is evapotranspiration; I and P are irrigation and precipitation, i.e. the inputs; RO and DP are surface runoff and deep percolation that recharges the water table; CR is capillary rise; ΔSF is subsurface flow in or out of the root zone; and ΔSW is the soil water content. DP, CR and SF are often discounted as they are difficult to assess especially over short time periods.

There are numerous methods for calculating evapotranspiration, but the FAO Penmann-Monteith method (Allen et al., 1998) is widely recognized as the international standard (Kennedy, 2010). The method calculates evapotranspiration for a hypothetical reference crop (ET_0), which is analogous to the potential evapotranspiration (PE), on the basis of climatic and crop resistance factors. A crop coefficient factor is then applied to take account of the actual crops growing at the site of interest.

The Penman-Grindley model, and the Aslyng method which is similar, calculate the soil moisture surplus or soil moisture deficit (SMD) from the precipitation and PE and have been commonly applied in Ireland and elsewhere (Fitzsimons and Misstear, 2006). Drainage occurs in a saturated soil until the soils reach field capacity and the water that remains is held against gravity. At this point, an SMD begins to develop but water is still readily available to the plants and actual evapotranspiration is equal to PE. Once the SMD drops below a critical level, known as the root constant (Penman-Grindley method), SMD_c (Asylng method), or Readily Available Water (RAW, FAO Penman-Monteith method), plants have difficulty transpiring and actual transpiration is less than PE.

A soil moisture deficit model has been developed for Irish grasslands by Schulte et al. (2005). The model combines two earlier models, hence is known as the Hybrid Soil Moisture Deficit Model (HSMD), and it predicts the SMD for the top layer rooting zone of Irish grasslands on three different soil types: poorly drained, moderately well drained and well drained. The model was

designed to be used with a limited number of input parameters so that it would be widely applicable, and it therefore operates as a daily time step water mass balance model that calculates the balance of precipitation, actual evapotranspiration and drainage (Eqn 5).

$$SMD_t = SMD_{t-1} - Rain_t + ET_t + Drain_t \quad \text{Eqn 3.6}$$

where SMD_t and SMD_{t-1} are the soil moisture deficits at time t and $t-1$, respectively, $Rain_t$ is the daily precipitation, ET_t is the daily actual evapotranspiration, and $Drain_t$ is the amount of water drained daily by percolation and/or overland flow. The drainage rate is dependent on the soil type and is controlled in the model by two factors: the minimum SMD and the maximum rate of drainage. In well-drained soils, the minimum SMD is taken to be zero, corresponding to field capacity, and it is assumed that drainage happens instantaneously. In poorly drained soils, the minimum SMD is taken to be –10 mm, thus allowing the soils in those conditions to saturate beyond field capacity and remain saturated for a number of days. Moderately drained soils can carry water surpluses but are expected to return to field capacity within 24 h (Kerebel et al., 2013). It is assumed that there is no drainage when the soil moisture content is below field capacity, i.e. SMD>0, and that maximum drainage occurs when the soil is saturated (SMD = –10 mm). A linear interpolation is applied to estimate drainage between these conditions. The simulation is always started in a wet period in winter when it can be reasonably assumed that the soils are saturated (Schulte et al., 2005). The SMD parameters for each soil class in the Schulte model are summarized in Table 3.2. SMD_c is taken to be 10 mm in poorly drained soils in the Schulte model, in contrast to a root constant of 30 mm typically used in the Aslyng method, and 50-76 mm for the RAW used for grassland in the FAO Penman-Monteith model (Fitzsimons and Misstear, 2006).

Table 3.2. Summary of SMD parameters for each soil class (after Kennedy (2010)).

	Well Drained	Moderately Drained	Poorly Drained
SMD_{min}	0	-10	-10
SMD_c	0	0	10
SMD_{max}	110	110	110
$DRAIN_{max}$	N/A	>10	0.5

The HSMD has been developed using extensive observations of soil water tension data from contrasting Irish soils (Diamond and Sills, 2001). It has since also been further updated and tested in a number of more recent studies. Kerebel et al. (2013) used 3 years of continuously logged TDR measurements at 10 and 20 cm depth at five field sites across Ireland to evaluate HSMD

predictions. They found that the model was accurate but that an additional soil drainage class between poor and moderate could be added. Premrov et al. (2010) slightly modified the model for well-drained arable land. The model is now widely used across Ireland and modelled outputs are available from Met Eireann for a limited number of synoptic weather station sites.

3.5 Previous Irish pathway separation studies

Several physically based studies have been conducted in Ireland to estimate the contribution of the pathways to streams, although the majority combine the shallow and deep groundwater pathways and simply provided a 'baseflow' contribution, which is presumed to be groundwater, and is separated from a quickflow component that incorporates surface and near-surface pathways. Reviews of these studies are presented elsewhere (Misstear and Brown, 2008, Archbold et al., 2010) but a summary is provided in Table 3.3. The contribution of baseflows to streams ranges from 10 to 76% of stream flow when just two pathways are defined, or 7–45% when a third intermediate flow path is included. Intuitively, it might be expected that catchments underlain by the more productive Regionally Important aquifers, particularly karst, would deliver the highest baseflow contributions, but it is apparent from the table that this is not always true.

For example, the baseflow contributions in the Monaghan Blackwater, and Maigue catchments are just 27 and 28%, respectively, which is relatively low. Conversely, the baseflow in the Dinin and the Kilkenny Blackwater catchments, which are underlain by Poor and Locally Important aquifers, is much higher at 46-76%. It is probable, therefore, that the soils and subsoils play a significant role in the transport of flow and contaminants to streams, and that the baseflow as identified through the physical response time approaches includes a proportion of flow from these materials.

Chemical hydrograph separation has been little used in Ireland with the exception of a few brief short-term student-based projects plus a comprehensive piece of research carried out in the Oona drumlin catchment in County Tyrone (Kane, *pers. comm.*, 2010), in which three end members were distinguished: overland flow, shallow soil water (~10 cm) and deep soil water (~30–40 cm), and their contributions to the stream were investigated at a range of scales. The deeper groundwater pathway was not considered. None of these studies attempted to correlate the findings with those of other methods or consider the implications at the catchment scale.

As described in Section 3.3.1, using a nutrient loadings approach, Mellander et al. (2012) found that in two Irish catchments with well-drained soils, quickflow pathways delivered just 2–8% of the flow but these were efficient in transporting phosphorus. The remainder of flow was

Table 3.3. Pathway contributions to streams based on physical hydrograph separation and modelling methods (compiled from various Irish studies).

Catchment	Km^2	Catchment characteristics	Baseflow %	Quickflow %	GW %	IF %	OF %	Reference
Owenduff	119	Poor aquifer Precambrian rocks			7	18	75	(RPS, 2008)
Allagaun		Poor aquifer, low permeability peat, exposed rock. Upland	10	90				(Aslibekian, 1999)
Dinin	153	Poor to Locally Important aquifer, low permeability subsoils. Small gravel aquifer close to river	46-65	35-54				(Misstear and Fitzsimons, 2007)
Maine and Flesk	272	Shaly limestone and pure limestone aquifers, variable till, upland and lowland	38	62				(Scanlon, 1985)
Bawn	4.9	Poorly productive in local zones			9(3)	36	55	(O'Brien, 2013)
Owenshree	35	Poorly productive in local zones			14	43	44	(O'Brien, 2013)
Ballycahalan	48	Poorly productive in local zones			7	25	68	(O'Brien, 2013)
Owendullagh	89	Poorly productive in local zones			10	28	62	(O'Brien, 2013)
Kells Blackwater	699	Poorly productive in local zones			16(9)	51	34	(O'Brien, 2013)
Fyanstown	188	Poorly productive in local zones and Locally Important			21(16)	44	35	(O'Brien, 2013)
Kilkenny Blackwater	108	Locally Important fractured sandstone, thin subsoils	60-76	24-40				(Misstear and Fitzsimons, 2007)
Ryewater	209	Locally Important limestone			32	23	45	(RPS, 2008)
Shournagh	205	Locally Important Old Red Sandstone			27	25	47	(RPS, 2008)
Bride	334	Locally Important sandstones and Regionally Important karst			24	33	43	(RPS, 2008)
Deel	285	Locally Important limestone			33	43	25	(RPS, 2008)
Deel	283	Locally Important			45(30)	27	29	(O'Brien, 2013)
Boro	174	Regionally important volcanic aquifer			35	32	34	(RPS, 2008)
Suck	1207	Karst limestone			26	55	19	(RPS, 2008)
Nore	2388	Variable aquifers including karst limestones and gravels, subsoils from all categories, uplands and lowlands	50 (41-60)	50				(Daly, 1994b)
Monaghan Blackwater	126	Regionally Important limestone aquifer, thick moderate to low permeability subsoils, upland and lowland	27	73				(MacCarthaigh, 1994)
Maigue		Karst limestone in the lowlands, Poor aquifer in the uplands	28	72				(Aslibekian, 1999)
Nore	1140	Karst limestone, moderate permeability till, gravel aquifers	58-68	32-42				(Misstear and Fitzsimons, 2007)

Notes: Poor aquifers in brown, Locally Important aquifers in green and Regionally Important aquifers in blue. Groundwater (GW) percentages are for shallow and deep GW combined. Values in brackets represent the deep GW contribution where it could be differentiated. IF, interflow; OF, overland flow.

delivered via the below ground pathways, which were effective in delivering 97% of the TON but also delivered 63% of the total reactive phosphorus and total phosphorus load overall. In two poorly drained catchments, the quickflow pathways were more dominant, delivering 55% of the flow and 88% of the phosphorus.

There have also been several plot- and small hillslope-scale studies in Ireland where attempts have been made to directly measure the contributions from the near-surface pathways, many of which have also been sampled for nutrients. These have been based mainly on the Teagasc research sites, particularly Johnstown Castle in County Wexford, and the AFBI at Hillsborough in County Down (Burke et al., 1974a, Kurz et al., 2005a, O'Reilly, 2006, Doody et al., 2010, Thompson et al., 2012, Ibrahim et al., 2013). For example, Ibrahim et al. (2013) found at Johnstown Castle that overland flow was 2.1 to 6.9 times higher than the subsurface land drain flow, but there were variations across the four plots and three events that were likely due to the differences in the depth to bedrock across the sites. O'Reilly (2006) focussed on the hydrological controls on phosphorus transport at Johnstown Castle and found that while the concentrations of phosphorus were higher in interflow than in overland flow, the loads delivered in the overland flow pathway were higher overall because of the higher flow contributions. Doody et al. (2010) measured overland flow at Hillsborough, while Watson and colleagues (Watson et al., 2000a, Watson et al., 2000b, Watson et al., 2007, Watson and Matthews, 2008) concentrated mainly on nutrient transport in 'drainage', which in the earlier Hillsborough studies comprised overland flow and land drain flow combined. None of the plot-scale studies have attempted to scale up or integrate the findings with larger scale catchment studies.

3.6 Discussion

In studies investigating the role of the contributions of near-surface pathways to streams, especially interflow, there has been an emphasis in the literature on plot- or small hillslope-scale studies, in which it is common for researchers to restrict investigations to no more than one or two of the near-surface pathways (or alternatively just the groundwater pathway), rather than consider the full depth of the hydro(geo)logical profile in an integrated way. As discussed in Section 1.5, it is the view of this researcher that this has typically been the case because of the multi-disciplinary approach that is required to take the wider view that has traditionally been lacking. Recently, the importance of incorporating geological factors and the deeper hydrological pathways has gained prominence in the hydrological literature (Melland et al., 2012a, Nasr and Bruen, 2013), and several authors have called for a more integrated approach to understanding hydrological processes, i.e. carried out at the catchment scale, using a range of techniques (McGlynn et al., 2002, Haygarth et al., 2005, Doody et al., 2012, Beven and Germann, 2013,

Bracken et al., 2013). However, there is as yet, still very little evidence of this occurring in practice in the literature.

Recent work in Ireland in the RPS study (RPS, 2008) and the on-going Agricultural Catchments Programme (ACP) has expanded to look at the catchment scale, but the RPS study quantified the flow pathways without considering nutrient transfer, and the ACP project is focussed more heavily on the relationships between land use and stream nutrient dynamics. Other studies have focussed primarily on either the nitrogen transfer pathways and processes, or the phosphorus transfer pathways, but rarely both. An integrated approach that recognizes that nutrient transfer processes are part of a dynamic hydro(geo)logical flow pathway continuum is important for a more robust understanding of catchment dynamics.

Difficulties with plot- or small hillslope-scale studies are that the processes being monitored may be scale dependent, are only representative of very small areas, and may not incorporate major subsurface field or catchment-scale features such as preferential flowpaths, variations in glacial materials, geological faults, groundwater seeps and springs, and the artificial drainage networks, all of which play a role in influencing the water quality in a stream. The scale of study is also likely to be too small to relate the results to the wider catchment, which is the scale at which monitoring takes place and ecological impacts are assessed for the WFD. For the purposes of the *Pathways Project* and this research, where the emphasis was on prioritizing areas for mitigation measures, it was considered that a catchment-wide approach where some of the hydrological variability would be averaged out, was more appropriate than a plot-scale study.

The use of isotope and chemical hydrograph separation techniques is now common, and they have been proven to provide valuable insights into the subsurface contributions to stream flow, despite the limitations of the approach. Jones et al. (2006) for example, identified that hydrodynamic mixing processes can influence estimates of the pre-event contributions. As Burns (2002) emphasized, it is no longer acceptable to rely solely on isotope and chemical hydrograph separation techniques without supporting them with other methods. Few studies have combined chemical and isotope methods with process-oriented soil moisture dynamic investigations to better elucidate the interflow pathways through the soils. This literature review found only one such study, which was carried out by McDonnell in the Maimai catchment in New Zealand as part of his doctoral thesis and subsequent research (McDonnell, 1990), and in which tracers, tensiometers and trenches were used to understand the subsurface pathways at a hillslope research site. However, the Maimai catchment is a steep-sided, forested hillslope with thin soils of high porosity, soil pipe features at the soil-bedrock surface that rapidly transfer flow, and high-intensity rainfall events. This presents an entirely different hydro(geo)logical regime than the

rolling, glaciated, grassland landscapes with low intensity rainfall in Ireland and much of Europe. The question remains whether the methods and/or findings are appropriate for Irish catchments.

With the exception of the well-established research catchments, such as Panola, Maimai, the HJ site in Oregon, Plynlimon and some of the Scottish catchments, where there are decades worth of data and a multitude of researchers, there is little reporting in the literature on the development and testing of catchment conceptual models as a framework for carrying out pathways research. Even at sites such as these, it is acknowledged that keeping the conceptual model at the core of the research programme is rare (McGlynn et al., 2002).

In summary, this literature review has found no studies, prior to the *Pathways Project*, that have considered the role of the pathways as outlined in the four-pathway model that has been adopted in recent Irish studies. In particular, the role of the near-surface pathways is poorly understood in lowland agricultural glaciated catchments. Some Irish studies have quantified some of the individual pathway contributions, and one identified an intermediate flow pathway, which was considered to be all flows in the subsurface other than bedrock groundwater. None, however, has taken advantage of both chemical and physical methods of hydrograph separation. Understanding the nature and contributions of the interflow pathway, and particularly of artificial drainage and the transition zone, has largely been ignored. Some studies have focussed on the transport of nutrients (most often phosphorus) but usually in either the near-surface or the deep pathways, and usually only at plot or hillslope scale. The ACP research has provided invaluable insights into catchment-scale stream nutrient dynamics but there has been less emphasis in that work on the delivery pathways. Some studies have characterized the soil water dynamics, but none has tried to integrate this kind of process understanding with other catchment-scale pathway determination methods, or extrapolate findings out to the catchment scale.

4 Research methodology

4.1 Research strategy

Following a review of the literature, and consistent with the objectives of the *Pathways Project*, this research was directed towards achieving a better understanding of the role of the near-surface pathways, particularly interflow, in the delivery of flow and nutrients to streams in Irish catchments. The research was carried out in the four *Pathways Project* study catchments (Figure 4.1) so that the resulting conceptual model (s) would have broad application across Ireland and would support the development of the national catchment management tools.

Figure 4.1. Location of the four study catchments (O'Brien, 2013).

The four catchments were all newly established monitoring catchments for which there were limited, if any, previous water quality or flow monitoring data. Each catchment was initially instrumented and sampled in a similar way so that comparable background datasets would be obtained for the purposes of developing the working conceptual model (Figures 4.2–4.5). Two rain gauges were installed in each catchment, one in an upland area and one in a lowland area. Each catchment was monitored continuously for water levels, electrical conductivity and turbidity at the catchment outlet and at a second location in the mid-catchment area. Approximately 6 to 8

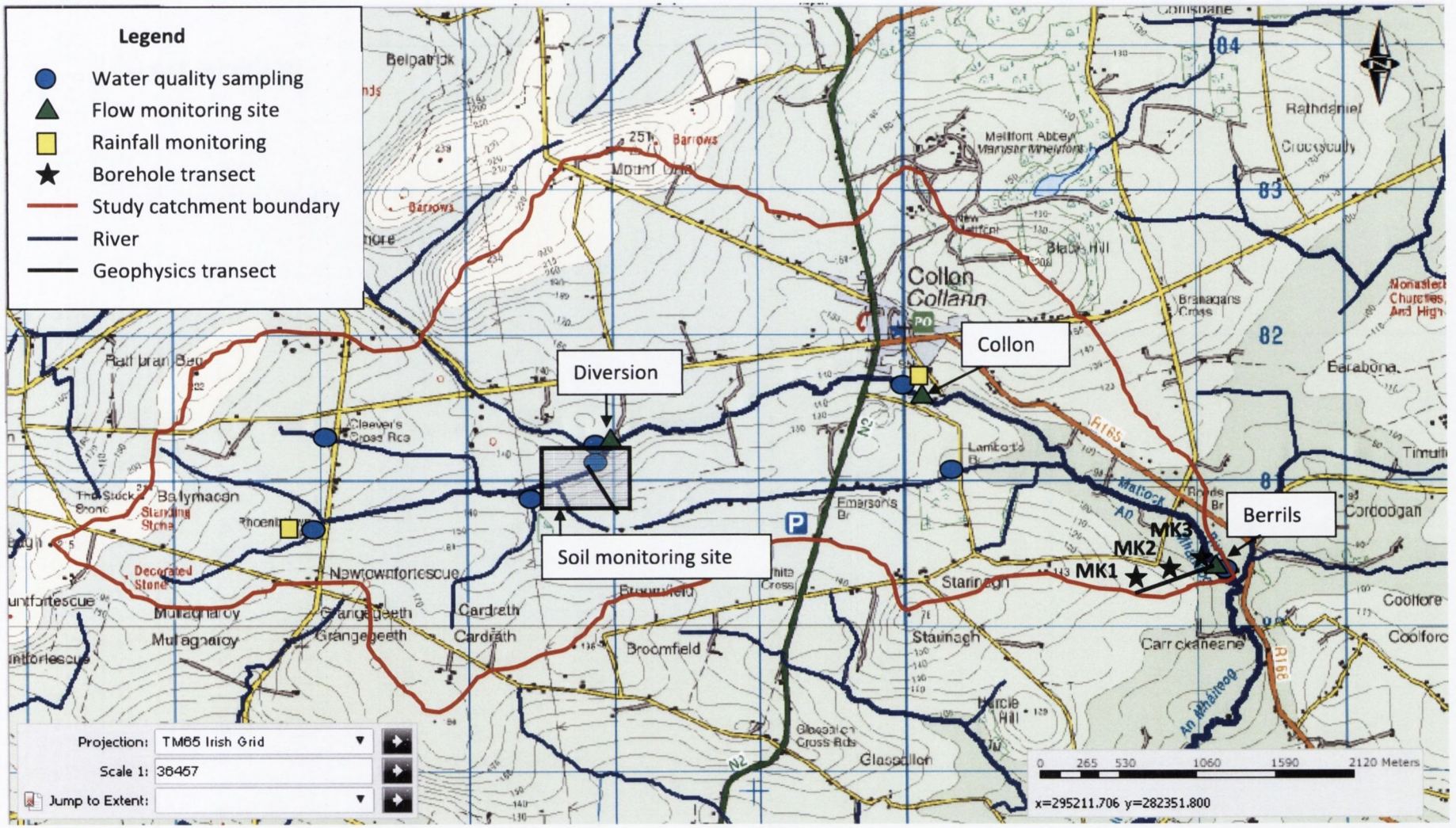

Figure 4.2. Mattock catchment with background sampling locations. The soil monitoring site is shown in the hatched area which is expanded in Figure 4.9.

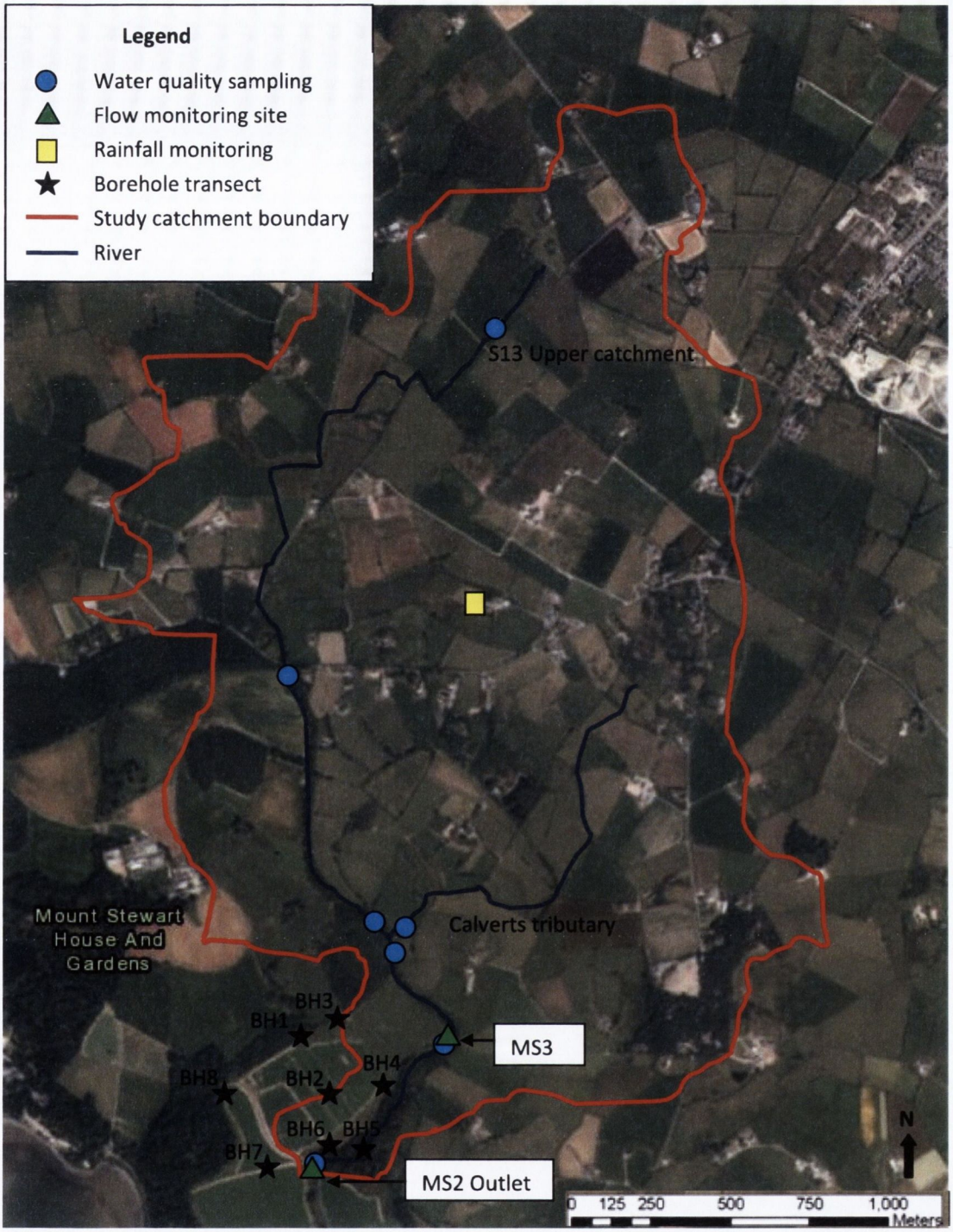

Figure 4.3. Glen Burn catchment with background sampling locations. Note that the configuration of boreholes in this catchment was different because they were installed by the Geological Survey of Northern Ireland rather than the EPA. The aerial photo was used as the basemap because the Northern Irish basemaps are different to those in the Republic.

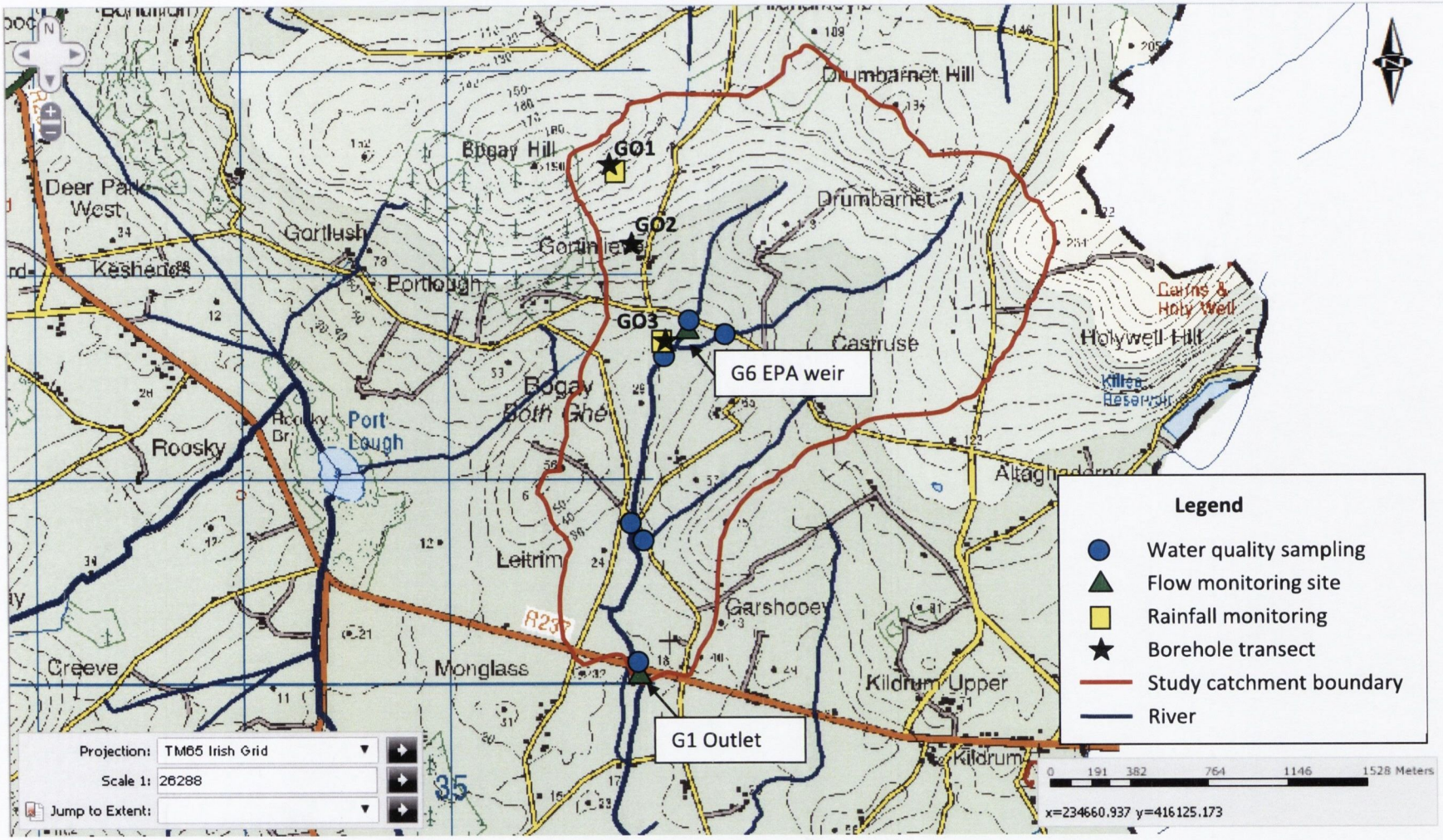

Figure 4.4. Gortinlieve catchment with background sampling locations.

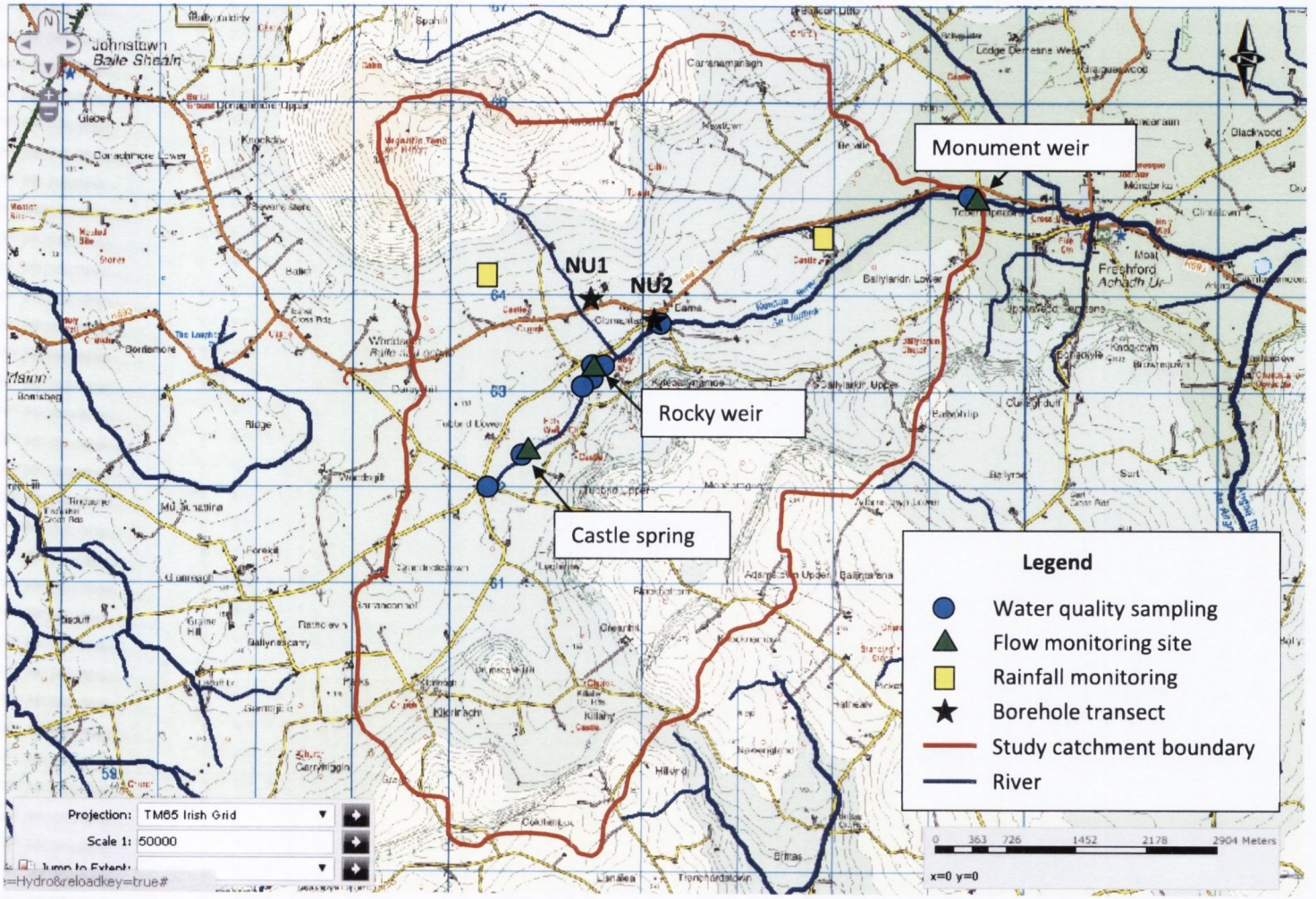

Figure 4.5. Nuenna catchment with background sampling locations.

sampling locations were selected in each catchment where water chemistry, biological assessments and spot flow monitoring were carried out at 1-2 monthly intervals over a 16 month period. Staff gauges were installed in some locations so that rating curves could be developed to aid the flow measurements. In each catchment, a suite of groundwater monitoring boreholes were installed by the EPA at different depths in one or more transects to the river, in which they carry out quarterly groundwater quality sampling. Some additional groundwater sampling was carried out by the *Pathways Project* and *Griffiths Project* teams, as well as aquifer analyses. A range of geophysical techniques was also applied by QUB to develop three-dimensional understanding.

Additional sampling campaigns were then carried out in each catchment in response to different research questions that arose and/or were tested in each catchment, often by different researchers. This resulted in the collection and interpretation of a range of datasets in different ways. Further detail on each of the experimental techniques, including the role of this author, is provided in the context of the research strategy throughout the following sections.

The data collection period was short (approximately 2 years) in comparison to some of the other research catchments worldwide, and resources were spread across the four catchments. An overall research philosophy was therefore adopted consistent with that of Blume et al. (2009) who noted: '*When investigating runoff generation processes in a previously ungauged catchment it becomes obvious from the start that the equipment we are about to install is insufficient. There will be neither enough data points in time nor in space to characterize these processes in their temporal and spatial variability. A possible way to overcome this problem is the approach where a multitude of experimental methods is applied within a relatively short time frame, producing a data set that highlights a multitude of angles and aspects of catchment functioning.*' The need to use multiple approaches, scales and methods was also one of the findings of the Prediction in Ungauged Basin (PUB) decade of hydrological research (Hrachowitz et al., 2013).

Thus, this research focussed on integrating results from a range of methods, within a conceptual model framework, as a means of limiting the dependence on any one particular method and therefore reducing the levels of uncertainty. Data and findings generated from some of the work carried out by others under the *Pathways Project* were also consequently integrated into this research. For the most part, this was raw data collected and quality controlled by others, but they were interpreted and integrated with other data and findings by this author. A clear differentiation between work carried out by this author versus that done by others is provided as appropriate throughout the text.

This research is broadly divided into three components. First, a catchment-scale approach to separating the four conceptual model pathways was used. The primary methods at this scale were the development of the conceptual model using a range of methods, event sampling and chemical hydrograph separation techniques. This work was further supported by physical hydrograph separation methods carried out by a fellow *Pathways Project* student (O'Brien, 2013, O'Brien et al., 2013, O'Brien et al., 2014). O'Brien applied a range of physical methods including master recession curve analysis, digital filtering algorithms, temperature tracer methods and the recharge coefficient approach to the four study catchments, and used the results to constrain catchment-specific NAM numerical models (refer to Section 3.2.3), which were in turn used to split the stream hydrograph into the four pathway components based on their response times. The NAM results were then used in this research to compare against the information obtained from the chemical hydrograph separation, in the context of the conceptual model, to arrive at an integrated assessment of the pathway contributions to the streams. The results of this research (as well as the NAM modelling and other parameterization techniques) were used by other project team members to constrain the newly developed SMART model that is at the core of the Pathways Catchment Modelling Tool (Mockler et al., 2013a).

Second, the Mattock catchment was selected for more intensive field-scale investigations into the soil water dynamics to determine whether there was evidence for interflow occurring at the field scale, and if so, to review how and when it was triggered, and its relationship with nutrient transport. The field-scale evidence for interflow was evaluated with the results of the catchment-scale pathway separation results for the Mattock catchment to further develop the conceptual model. This approach retained the advantages of gaining the process understanding at the plot scale, while avoiding their hydrological limitations (refer to Section 2.2.2).

Third, during the course of the catchment and field-scale work, it became apparent that artificial field drains are a significant transport pathway for water to streams in Irish agricultural catchments. Further sampling and investigations were carried out at a selected number of field drains in the Mattock catchment to better understand their contribution to flow and nutrient transport. This work was mainly carried out in the vicinity of the field-scale investigations for comparison with the soil water dynamics results, but some additional sampling was carried out at selected land drains spread more widely around the catchment to bring a spatial element to the work.

An attempt has also been made as part of this research to develop a national map of hydro(geo)logical scenarios where land drains are likely to be present. The development of the mapping approach has been supported by Tim Gleeson, a retired drainage expert from Teagasc,

who provided helpful discussions that contributed to elements of the map, and a fellow PhD researcher (Eva Mockler) who processed the GIS data and provided input into generating the final maps. The maps have been compared to results of drain surveys carried out by *Pathways Project* students as part of land holder surveys in the study catchments.

4.2 Catchment-scale approach

The catchment-scale approach comprised three subcomponents: development of the conceptual model, event sampling and chemical hydrograph separation. As discussed above, these results were then considered together with the physical hydrograph separation results and the NAM modelling, to assess the contribution of the near-surface pathways to the stream flow and to re-evaluate the conceptual model.

4.2.1 Development of the conceptual model

The working conceptual four-pathway model, as described in Chapters 1 and 2, was adopted at the commencement of the project, and this model was applied, tested and critically reviewed in each of the four study catchments as part of this research.

A conceptual model, or perceptual model as it is termed by Beven and his colleagues (Beven, 1993), serves as a framework to hold together all the pieces of scientific evidence that, particularly in a large-scale catchment study such as the *Pathways Project*, may be gathered by different researchers, at different times, in different parts of the catchment, or neighbouring catchments, using different methods. The conceptual model should be considered as a working model and should be critically reviewed, refined and updated as each new piece of evidence is obtained. Only in this way can the cumulative body of evidence contribute to the understanding of the catchment (McGlynn et al., 2002).

4.2.1.1 Desk study – GIS layers

Development of a conceptual model requires review of the available GIS layers and compilation of a three-dimensional picture of the geology, and hence the operating framework of the catchment. Publically available data layers from the EPA and the Geological Survey of Ireland were reviewed and collated using their respective web-based GIS software. Relevant information included soil drainage (EPA), subsoils (Teagasc), bedrock geology (GSI), aquifers (GSI), depth to bedrock (GSI), subsoil permeability (GSI), meteorological data (Met Eireann), stream flow (EPA), groundwater level data (EPA), and groundwater and surface water quality and hydrochemistry (EPA, local authorities, Group water schemes). The available water balance data (stream flow, rainfall, evapotranspiration) were assessed from the study catchments, or nearby geologically similar catchments, to initially gauge whether they had a rapidly responding hydrological profile (flashy)

and were therefore dominated by near-surface pathway flow (Mellander et al., 2012), or conversely, had long slow recessions that are characteristic of systems dominated by groundwater flow (Ford and Williams, 1989).

4.2.1.2 Geophysical surveys

Two-dimensional electrical resistivity surveys were carried out in all catchments in the vicinity of the EPA borehole monitoring suite (refer to Section 4.2.1.8 for further information on the boreholes), and more extensively in the three poorly drained catchments as part of the *Griffiths Project* research programme. An additional resistivity survey and a seismic refraction survey were also kindly carried out by the *Griffiths* team at the soil water dynamic experimental site in the Mattock catchment for the purposes of this research (Figure 4.6). For the resistivity survey, electrodes were spaced 1 m apart in a Wenner Schlumberger array, over a distance of 160 m in a transect perpendicular to the river. Processing and interpretation was carried out by Jean-Christophe Comte and was achievable for depths up to 10 m.

Figure 4.6. Seismic survey line (left) and resistivity survey line (right) at the Mattock soil water dynamics field investigation site.

Similar spacing was used for the seismic survey receiver array. Geophones were inserted into the soil and were used to measure the seismic or vibrational waves generated from seismic shocks induced with a sledge hammer on a steel plate at 10-m intervals. Processing and interpretation was carried out by Rachel Cassidy and was achievable for depths of up to 4 m. Interpretations were later checked and confirmed as part of this research with a series of five 2.5-m trial pits and 4-m deep boreholes drilled along the transect.

4.2.1.3 River stage and stream flow

River stage was continuously monitored in each catchment at the catchment outlet and at a mid-catchment location (Figures 4.2–4.5). A third site was added in the upper catchment in the Nuenna as the catchment was much bigger. Four of the sites had previously been established by the EPA (Gortinlieve, mid-catchment), Louth County Council (Mattock, mid-catchment) and the Northern Ireland Rivers Authority (Glen Burn, both sites), but the remainder of the sites were selected and installed as part of the *Pathways Project*, with the assistance of the EPA Hydrometric staff. Long straight stream reaches, with stable vertical banks, non-turbulent flow, a natural or artificial control structure and preferably in the shade to prevent aquatic weed growth, are optimal for the installation of robust river stage monitoring sites. These locations also naturally became the focal point for the continuously logged electrical conductivity and turbidity probes.

Stage was recorded at 15-min intervals using either an Orpheus Mini pressure transducer (Mattock and Gortinlieve, catchment outlets) as described above, or an OTT Thalimedes float and pulley logger system (all other sites) installed in a stilling well upstream of the control structure. It is reported by the manufacturer that the Thalimedes has a stage range of 19.99 m, with a resolution of 1 mm, and an accuracy of ±2 mm. Data were downloaded and quality checked by both EPA staff and other project team members using an optical reader that does not require the equipment to be removed from the stilling well which reduces the potential for disturbances.

Stream flow measurements were made using an OTT Acoustic Doppler Current (ADC) meter, and an OTT Kemptem C2 propellor current meter. The range of the ADC was -0.2 to 2.5 m/s with a resolution of 0.001 m/s and an accuracy of ±1%; the range of the C2 was 0.025 to 5 m/s, but with the same resolution and accuracy. The mid-section velocity area method (EN ISO 748, 2007) was used to calculate the flow from velocity measurements taken at regular intervals across a stream width transect (O'Brien, 2013). Rating curves were developed for the continuous stage monitoring sites by EPA staff and the project team. Stream flow measurements were also taken by the project team at the water quality monitoring sites at the same time as the water samples were being taken, so that concentrations and loads of the various determinands could be calculated.

Although these data were collected mainly by others, a high level of confidence in the data was achieved by establishing the flow monitoring sites in the Nuenna and the Mattock with O'Brien and the EPA hydrometric staff, and carrying out the first few rounds of monitoring with him. In the two northern sites where flow monitoring was difficult, the data were queried several times and cross checked with a number of subsequent dedicated sub-projects to confirm the flows. All rating curves were reviewed before use. EPA data were only used where the assigned QC rating was good.

4.2.1.4 Flow duration curves

Flow duration curves were generated by this author to evaluate the frequencies of different sized flows in an effort to gain insights into the contributions of the different pathways. The 15-min stream flow datasets were used, for one, two or three full years of data where they were available, to avoid any seasonal bias in the frequency analyses.

4.2.1.5 Rainfall

Rainfall was measured at 15-min intervals at two locations in each catchment (Figures 4.2–4.5) using ARG 100 (Environmental Measurement Ltd) tipping bucket rain gauges with AR-DT2 data loggers. Gauges were sited, fenced, managed for weed growth and downloaded by other team members. All gauges were sited in open areas with a maximum of 15° line of sight to the tops of the nearest trees (O'Brien, 2013).

4.2.1.6 Stream hydrochemistry and water quality

An initial programme of spatial water quality monitoring in different seasons and flow conditions was carried out to establish the background stream chemistry for developing the conceptual model and providing information on suitable tracers for the end member mixing analysis. Approximately eight sampling locations were selected in each catchment in the main channels and the tributaries (Figures 4.2–4.5), and each was sampled 8–10 times over the course of 14–16 months so that the seasonal, spatial and flow related variabilities in water chemistry could be assessed. This author was responsible for the Mattock and Nuenna catchments. Sampling locations were selected to include the catchment headwaters and outlet, and to capture the inputs of significant tributaries at regular intervals down the length of the stream, while avoiding any obvious point source inputs of contamination. Samples collected in the Nuenna and Mattock catchments were analysed by this author for a range of parameters, which are listed, together with the methods of analysis and references, in Table 4.1. Similar sampling campaigns were carried out by other team members in the Gortinlieve and Glen Burn catchments. Quality control procedures were jointly prepared by team members to ensure a similar approach.

Table 4.1. Water quality and hydrochemistry parameters.

Parameter	Method
Alkalinity	Titration, using Bromocresol Green indicator (APHA et al., 2005)
Nitrate	Spectrophotometer (Nova 60), using Merck test kit, Ref No. 09713 (0.1-25 mg/l NO_3)
Chloride	Spectrophotometer (Nova 60), using Merck test kit, Ref No. 14897 (2.5-25 mg/l Cl)
Sulphate	Spectrophotometer (Hach 2800), using USEPA SulfaVer 4 method, Ref 8051 (2-70 mg/l). Method adapted from Standard Methods
Ca, Mg, K, Na	Inductively coupled plasma–atomic emission spectrometry (ICP-AES) EPA method 200.7
Silica	Spectrophotometer (Nova 60), using Merck test kit, Ref No. 14794 (0.1-5 mg/l Si)
Total phosphorus (filtered and unfiltered)	Spectrophotometer (Hach DR5000), digestion method of Murphy and Riley (1962)
MRP (filtered and unfiltered)	Spectrophotometer (Hach DR5000) (Murphy and Riley, 1962)
Spectral absorption coefficient at 254 nm (SAC_{254})	Spectrophotometer (Hach DR5000) (APHA et al., 2005)
Total suspended solids (TSS)	Gravimetric analysis, BS 6068-2.54:2005
Field chemistry	Electrical conductivity, temperature, pH using hand-held Eutech meters

The sampling and quality control procedures included the following:

- Field meters were calibrated prior to sampling using standard solutions, as per the manufacturer's instructions.
- Sampling procedures were carried out in accordance with BS5667 Water Quality Sampling. Samples were kept in the dark and were transported and maintained on ice until the analyses had been completed. Samples were collected in 1 litre reusable plastic sample bottles. All sample bottles were pre-rinsed three times in the field with the water to be sampled and were scrubbed, washed and dried before reuse.
- Samples for phosphorus, major ions, silica and SAC_{254} were filtered immediately in the field using disposable 0.45-μm syringe filters. Filtered samples were transported to the lab in 30-ml disposable plastic bottles for the ions and SAC_{254}. For cost purposes, filtered sample sizes were kept to a minimum to reduce the number of disposable filters required. Samples for phosphorus were taken in 60-ml glass bottles with Teflon lids, as recommended by the laboratory technician. For samples for total phosphorus analysis, 25 ml of filtered or unfiltered sample, as appropriate, was measured directly into the glass bottles in the field with a graduated syringe so that the reagents could be added and the digestion carried out in the sample bottles directly to minimize cross contamination.
- Ten percent of samples were analysed in duplicate for major ions, silica and total suspended solids. All alkalinity samples were analysed in at least duplicate, if not triplicate, and averaged, as there is a degree of subjectivity in determining the colour change with the Bromocresol Green indicator. All SAC samples were analysed in triplicate and averaged. It was observed,

however, that the first samples in the triplicate set always returned slightly lower values than the other two, which was likely to have been due to slight dilution by the deionized water used to pre-rinse the glass cell used for the analysis. Cells were therefore pre-rinsed with some of the sample and results improved.

- As the concentrations of phosphorus were expected to be very low, and phosphorus is very susceptible to cross contamination, the additional step of sampling in triplicate for total phosphorus and MRP was taken. Separate dedicated glassware was maintained for phosphorus analyses. All glassware was rinsed three times in deionized water and three times in Millipore water immediately after analysis to minimize cross contamination. As the project progressed and confidence in the procedures and results increased, the samples were taken in duplicate to reduce costs. Results were reviewed as the analyses progressed in the lab and samples were reanalysed and/or discarded if the difference between duplicates was >0.003 absorbance units, or approximately 0.001 mg/l.
- Standard solutions (3-4) that bounded the expected field concentrations were freshly made up for each analyte for each batch of analyses and were analysed concurrently with the field samples. Calibration curves were generated to cross check and calibrate the results.
- Sample analysis was commenced on the same day as collection for alkalinity and SAC_{254}, followed by the anions. All samples were analysed well within the prescribed timeframes as per BS5667, at the very latest, ranging from 48 hours for nitrate to 28 days for total phosphorus. It was found, however, that samples kept for close to the prescribed maximum of 28 days for total phosphorus had higher MRP values than total phosphorus, which is unacceptable. This was likely due to the samples being kept in relatively small bottles, which may have led to adsorption on the glass walls and/or the phosphorus being used up by the biota. The maximum holding period for total phosphorus samples was therefore reduced to 14 days and the problem was eliminated.
- Cations were preserved using 5% nitric acid and were refrigerated for up to 3 months before analysing in large batches using inductively coupled plasma–atomic emission spectrometry (ICP-AES). Six standard solutions were used as part of the calibration routine.
- Ion balances were calculated for samples that had the full suite of anions and cations analysed. Approximately 10% of samples had ion balances greater than ±10% and were considered unreliable.
- On two occasions, duplicate samples were taken and analysed by Queen's University to cross check results. Differences were considered to be within acceptable limits, i.e. <10%.

The uncertainty in the analytical methods was quantified by calculating the accuracy, reported as the difference between the value of the standards as analysed with the samples and their true

values, as a percentage of their true values (Table 4.2). In general, the Merck test kit methods (NO3, Cl and Si) performed well, although the accuracy of the Si method was a little higher than for the other analytes. The results were therefore adjusted using the calibration curve. The ICP method varied depending on the analyte, ranging from 2.5 to 14.7%. Initially, a multi-analyte stock solution was being used to make up the standards for the four cations, but as the calcium concentrations were typically in the region of five times higher than potassium, magnesium or sodium, there were difficulties in the calibration. Results improved once the calcium was analysed separately with its own standard. The accuracy for potassium was not as good as for sodium or magnesium, which is likely due to the potassium concentrations in the samples being generally less than 50% of either sodium or magnesium. The Hach test kit method of analysing for sulphate, which relied on the use of powder pillows, proved to be very poor with an accuracy of 42%. The resolution of the method was the nearest 1 mg/l limit, and with the typically low concentrations in the catchment samples (<12 mg/l) and the inefficiencies associated with using the powder pillows, a poor level of accuracy resulted. A calibration curve was used to help improve the results but they were considered unreliable and were not used further. The accuracy for alkalinity and total suspended solids was not tested due to the difficulties in maintaining stable standards.

Table 4.2 Accuracy and precision in water quality sampling data.

Parameter	Accuracy % Compared to stds	Precision % Between replicates	Method
Silica as SiO2	6.9	0.9	Merck test kit
Cl	4.3	1.0	
NO3 as N	2.6	0.8	
Ca	3.1	3.3	ICP
K	14.7	2.6	
Na	2.5	4.0	
Mg	6.5	3.8	
MRP	3.6	1.8*	Spectrophotometer
TP	3.5	1.9*	
SAC254	n/a	0.7	
Alkalinity	n/a	1.5	Titration
SO4	42	n/a	Hach test kit
TSS	n/a	1.2	Gravimetric

*The precision for phosphorus analysis includes errors associated with the field sampling methods.

The precision, which is the standard deviation between results from replicate samples as a percentage of the mean, was also calculated to gauge the uncertainty in the laboratory methods. In general, the laboratory methods were good for all analytes. The poorest results were for the ICP analytes, which is likely to be a consequence of the machine being kept in a dusty engineering laboratory such that cross contamination from air-borne particles was somewhat inevitable. Note that the precision for the phosphorus samples includes any additional errors associated with the

field sampling protocols, which were gratifyingly low despite the low concentrations of phosphorus in the samples, and the relative ease of cross contamination.

4.2.1.7 Electrical conductivity

Manual conductivity and temperature readings were taken from watercourses, drains, ditches, springs, seeps and rainfall in all catchments using a Eutech Cyberscan Con 11 conductivity and temperature meter, which is reported by the manufacturer to have a resolution of 0.05% and an accuracy of ±1%. A YSI 556 Multiprobe System, which simultaneously measures dissolved oxygen, conductivity, temperature, pH and oxidation-reduction potential, was borrowed from one of the project partners during team sampling events. The accuracy of the YSI multiprobe conductivity measurements was ±0.5% or 1 µS/cm, whichever was the greatest. All instruments were regularly calibrated against standard solutions. In all cases, specific conductivity (the conductivity adjusted to a temperature of 25°C) was recorded.

Electrical conductivity was also measured continuously at 15-min intervals at two locations in each catchment using HOBO U24 conductivity loggers. The loggers are reported by the manufacturer to have an accuracy of ±1%. Loggers were downloaded monthly with the river stage and rainfall data by other project team members, and were cleaned weekly during the summer months to reduce the risk of biofouling. This author was responsible for installation, maintenance and quality control of data from continuous conductivity loggers in the Mattock and Nuenna catchments.

In the Nuenna karst catchment, it was found that precipitation of calcite and invertebrates taking up residence on the sensors caused problems. In general, the loggers performed reasonably well for approximately 2 years, but thereafter they became somewhat erratic, with sometimes rapid fluctuations with no corresponding changes in flow or temperature. It was also found that they were less reliable at sites where the water depth was shallow, and that they were prone to drift especially in the winter months. Adjustment of the drift was achieved using the manufacturer's calibration routine and one or both of two methods: (a) by taking manual conductivity readings with a hand-held, calibrated conductivity probe, and/or (b) from conductivity readings recorded from the start of the next dataset after the logger had been cleaned and reset. Further quality control included reviewing the data on a monthly basis against the flow and rainfall data to confirm that conductivity changes were consistent with a climatic event. Consideration was also given to whether changes might be attributable to a contamination event, i.e. a conductivity increase. Data before and after cleaning and downloads were also checked. Processed datasets and all raw data were both maintained for future reference. In view of the significant quality

control issues with the data from these loggers, the data from the two northern catchments which were collected by others were reviewed before use.

Conductivity profiling down the length of the stream channels was carried out mainly by other team members to differentiate any major contaminant inputs or changes in pathway contributions, although the technique was also used by this author on occasion to determine local-scale changes. The operator walked the length of the stream and/or tributaries taking conductivity readings at regular intervals, while recording measurement locations with a hand-held Garmin GPS. This relatively simple, quick and cheap technique has been recommended for use as a rapid assessment tool in all catchment studies (Haria et al., 2013).

4.2.1.8 Groundwater monitoring

The three study catchments in the Republic of Ireland had a comprehensive suite of monitoring boreholes installed by the EPA, in either two (Nuenna) or three (Gortinlieve and Mattock) clusters, in a transect from the catchment divide down to the river (Figure 4.7). Each cluster comprises from two to four separate boreholes, which are screened at different depths into the different hydrogeological flowpaths in the conceptual model, i.e. the subsoils, the transition zone, shallow groundwater and deep groundwater (Moe et al., 2010).

Figure 4.7. The middle borehole cluster (GO2) in the Gortinlieve catchment.

The boreholes were constructed to the highest level of professional standards which included supervision of all drilling by a hydrogeologist; logging of all drilling returns as drilling progressed; development of the holes on completion by airlifting until the water was free of sediment; installation of uPVC 2 mm slotted screens covered with 300 micron filter at the specific monitoring depths; and grouting and proper surface seals to prevent ingress of contaminants down the side of the boreholes and ensure their integrity and longevity (Moe et al., 2010). Separate boreholes were drilled at each cluster, rather than the cheaper alternative of nested piezometers, to ensure that each monitored zone was properly hydraulically isolated.

A slightly different arrangement of borehole clusters was installed in the Glen Burn catchment by the Geological Survey of Northern Ireland. There are seven clusters in the lower catchment near the stream and surrounding a drumlin. Six of them comprise two boreholes, one shallow and one deep; the seventh has three boreholes and a further borehole (BH8) stands alone.

Pumping tests and down-hole geophysical surveys were subsequently carried out by EPA consultants and *Pathways Project* students to investigate the aquifer characteristics. Water level loggers (OTT Orpheus Mini pressure transducers) were installed in each borehole and data were recorded every 15 min. The manufacturer reports a water level range of up to 10 m, with a resolution of 1 mm and an accuracy of ±5 mm. The advantage of the pressure transducer over the float and pulley system (OTT Thalimedes) used in the river stage water level loggers, is that the Thalimedes must hang vertically and freely, which is not always possible in a deep borehole.

Comprehensive full suites of groundwater chemistry and microbiological samples were taken from the EPA borehole by their consultants on a quarterly basis using standard sampling procedures, and after a rigorous quality control check including blanks, duplicates and spikes, the data were made available for this research. The level of confidence in these data is consequently very high. Sampling at the Glen Burn boreholes was carried out by other members of the *Pathways Project* and *Griffiths Project* teams in accordance with the agreed team QC protocols.

The responses in groundwater levels and chemistry were examined in relation to the responses in stream flow to rainfall, in the context of the three-dimensional geological profile, as part of this research. The aquifer characteristics calculated by others, i.e. transmissivity and hydraulic conductivity derived from the pumping test data, were used together with the gradients to estimate the contributions from the bedrock and subsoils to the stream. This provided useful insights for the conceptual understanding of how the catchment worked, as well as a means of validating the pathway contributions estimated using the hydrograph separation methods.

4.2.2 Event sampling

Event sampling was one of the major cornerstones of this research as it provides specific information about how the delivery pathways for flow and nutrients change with rainfall, which is the key hydrological pathway driver. At least two major rainfall events that were forecast to be ≥10 mm/d were selected for intensive monitoring in each study catchment over the course of the research. Stream flows and water chemistry were measured at regular intervals during the event, at the catchment outlet and the mid-catchment location to incorporate an assessment of any differences due to increasing catchment scale. A series of representative samples were taken from the near-surface pathways around the catchment that were activated during the event, including overland flow, land drains, ditches, tributaries and the main channel. The coverage over the whole catchment helped to incorporate spatial variability. Groundwater samples were taken from the monitoring boreholes to give a three-dimensional element to the pathway sampling. Replicate samples from some of the pathways were taken at different stages during the events where possible, to evaluate the temporal variability. Finally, a summer and a winter event were targeted in each catchment to capture seasonal variations and the influences of different antecedent conditions.

Two automatic samplers (ISCO 6712 Portable Sampler) were deployed at the flow monitoring sites to collect regular samples throughout the events (Figure 4.8). The samplers were typically programmed for hourly sampling for the first 24 h to capture the rising limb and peak of the hydrograph, and then reduced to 2-5 hourly intervals during the recessions for 2 to 3 days. Longer intervals and recessions were required in the karst catchment, with its higher groundwater contributions. In order to reduce costs in the later events, changes in electrical conductivity of the captured event water were used as a guide for selection of representative samples for analysis. Samples were retrieved from the sampler within 24 h to ensure that prescribed pre-analysis holding periods were not exceeded. During the summer months, the samplers were packed with ice to reduce the temperatures inside the casing. Care was taken to ensure that the suction hoses were secured in the stream bed with rocks and that the entry points were above the stream bed to reduce the risk of pumping bed sediment into the sample bottles. Groundwater sampling required the use of a pump.

As the events were very costly and labour intensive, several team members needed to be involved and samples were analysed by an accredited commercial laboratory. Results were cross checked using ion balances, duplicate samples analysed in the QUB laboratory, and review of trends in relation to other analytes and flows. Unfortunately some of the commercially analysed nutrient

Figure 4.8. Emptying the autosampler during an event in the Mattock catchment.

data had to be discarded as it was considered unreliable. Further investigation identified that the lab had frozen the samples as they had not been able to manage the volume of samples our team had delivered.

This author was responsible for carrying out the near-surface pathway sampling for all events, and for the interpretation of all the event data. A number of additional, scaled back, smaller event sampling campaigns were also carried out by this author specifically for this research, in which the focus was on the near-surface pathways in the Mattock catchment. A reduced suite of analytes was selected, restricted to those used for the end member mixing analysis (refer to Section 4.2.3), so that all samples could be collected and analysed by one person within the appropriate timeframes and at a reasonable cost.

The primary purpose of the event sampling was to understand catchment pathway dynamics and identify which pathways were dominant in the transfer of nitrate and phosphorus to streams. The data were also used for the chemical hydrograph separation methods.

4.2.3 Chemical hydrograph separation

Chemical hydrograph separation methods were applied to the results of the event sampling campaigns for the catchments underlain by poorly productive aquifers to determine the proportion of flow contributed by each of the main pathways. Two slightly different approaches were taken that recognized the differences in data availability: a traditional statistical approach that was applied in the data-rich Mattock catchment only, and a modification that was conceptual model-based and stream-focussed in all catchments. The statistical approach was useful to assess the applicability of the conceptual model approach and determine the degree of uncertainty in the results.

4.2.3.1 Statistical approach – Mattock catchment

In the statistical approach, potential end member pathways were initially selected in light of the conceptual model (refer to Chapter 5), which in the Mattock catchment included overland flow, soil water and bedrock groundwater. Appropriate tracers that best represented those end members were then identified based on the background catchment-wide monitoring results and the need, as per the basic assumptions, for the tracers to be conservative.

To identify the end member signatures, 27 baseline sampling rounds of the near-surface pathway end members were carried out between November 2011 and May 2013, at a range of flow conditions and at a number of representative sites around the catchments. For logistical reasons, the number of determinants for analysis in each sampling round was reduced to only those required for the mixing analyses (Si and SAC_{254} – refer to Chapter 6 for further discussion) as well as electrical conductivity, MRP and NO_3 for assessing nutrient transfer. A reduction in the sample size from the 1-litre and 60-ml glass bottles to 30-ml disposable plastic bottles was also required because of the need to carry up to 20 samples and field equipment around while in the field.

To determine the impact of the reduced sample bottle size on the accuracy of the results, batch tests were carried out on triplicate samples from a land drain, a ditch and the river, in 60-ml glass and 30-ml disposable plastic bottles. Results confirmed that when the samples were filtered in the lab and analysed for all parameters on the same day, the differences were small (<10%), which was deemed acceptable. All field sampling campaigns were therefore designed with these time constraints in mind.

Fourteen background groundwater sample rounds of data were available from the EPA for the monitoring boreholes from 2009 to 2012. Unfortunately, however, SAC_{254} cannot be analysed at the EPA laboratory and it was therefore not included as one of the determinands. On three occasions, it was arranged to subsample the EPA samples and SAC_{254} analysis was carried out by

this author at Trinity College. In combination with the groundwater samples by the *Pathways Project* team, in total there were 26 samples with both silica and SAC_{254} available from the bedrock boreholes to represent the bedrock end member signature.

The mixing calculations were carried out in a Monte Carlo framework to incorporate some of the uncertainty. The full range of variability in each end member signature was incorporated. Of 5000 iterations, only 395 (7.9%) were feasible separations, i.e. did not result in negative end member contributions. The median values from the feasible separations were selected to represent the contributions from each end member. The 5th and 95th percentile values were then also identified to highlight the degree of certainty in the results.

4.2.3.2 Conceptual model-based, stream-focussed approach – all catchments

A modified approach based more heavily on the conceptual model was developed for the catchments where there was limited opportunity to collect extensive water quality samples from potential end member sites, other than during the team events[2]. The full stream water quality datasets for each event in each catchment were analysed using principal component analysis (IBM SPSS Statistics 20) to determine the number of dominant contributing components, i.e. those that could account for at least 80% of the variance. The analytes that might be most suited for use as tracers to represent the pathway components were then selected on the basis of the conceptual understanding of the sources and pathways of each analyte in the catchments, the available background sampling data, and the need for the tracers to be conservative. Selection of the tracers was catchment specific and is discussed further in Chapter 6.

Mixing models of the stream chemistry during the events, as a function of the selected tracers, were plotted together with the available samples from the near surface and groundwater (refer to Figure 6.3 for an example of a mixing model diagram for the Mattock catchment). Selection of appropriate end member signatures was more difficult because of the limited dataset and so the changes in the stream chemistry during the event and the conceptual model were used to guide their selection. Mean values of the available end member samples were selected where possible. Where the data were insufficient, a best estimate was chosen based on the conceptual model and the event stream flow data, under the constraint that the end members needed to bound the stream samples. This method is far less robust than the statistical approach but as it was carried out within the constraints of the conceptual model which had been developed using a range of techniques, and it was driven by the evidence from the stream data, it was considered to be

[2] The term 'team events' is used to refer to the two large-scale event sampling campaigns that were carried out in each catchment by the Pathways Project team where full suites of analytes were analysed commercially. This is in contrast to the event sampling for a reduced suite of analytes which was carried out solely by this author.

realistic. Results were cross checked and validated against other methods, including the NAM results and calculation of the groundwater component using Darcy's Law. Further discussion is provided in Chapter 6.

4.2.3.3 Sampling the soil end member

Many chemical hydrograph separation studies that consider the interflow pathway typically adopt the approach of installing specific, new, suction cup soil water samplers as access points for sampling the soil end member. There are difficulties with the use of suction cups, however, when the research objective is to consider the interflow pathway contributions to the stream on the scale of single rainfall events. First, they only sample the pore water in the vicinity of the sampler, which may not necessarily be connected to a contributing flowpath or representative of the wider soil conditions (Addiscott et al., 2000). This is particularly pertinent where flow through macropores is dominant. Second, installed and well-established porous cups have been reported to give differing results (Lord and Shepherd, 1993). Third, it takes a number of hours or often days of applied suction to retrieve enough water sample for analysis (Ryan et al., 2005), which results in a bulk sample with no opportunity for reviewing temporal variations in water quality with rain. Fourth, the high levels of suction applied during the sampling procedure changes the total potential in the soil, which can have an impact on the concentration of nitrate in solution in the soil matrix. Hatch et al. (1997), for example, found that sampling soil solution in poorly drained clayey grassland soils (such as those prevalent in the study catchments) using ceramic cups led to up to a 10-fold underestimate in nitrate in comparison to sampling field drains and ditches, and it was therefore considered to be inappropriate for determining nitrate leaching. Fifth, even if representative soil water samples could be obtained, there would likely be little indication of which flowpath the soil water then took in its migration to the stream, e.g. overland flow, interflow, drain flow, return flow or transition zone flow.

As this research is focussed on the pathways that are delivering the flow and nutrients, rather than just the potential source of the water (e.g. soils or bedrock), a different approach was required. It was therefore decided to collect samples representing soil water from the land drains and ditches, as it was evident that, on the scale of individual rainfall events across whole catchments, they would be much more representative of the water actually arriving at the stream from the soils than the soil pore water. These were supported by samples from the subsoil boreholes from the three borehole clusters in the groundwater monitoring suites, which were also considered more likely to be representative than pore water samplers.

4.3 Soil water dynamics approach

The soil water dynamics were investigated in the Mattock catchment on a small hillslope approximately 250 m long, in a transect approximately at right angles from the river up to the subcatchment divide with the largest tributary of the Mattock to the south, known throughout the project as Lambert's tributary. Four soil and groundwater table monitoring clusters (S1 to S4) were established in a transect spanning the hillslope at distances of from 10 to 160 m from the river. A fifth site (S5) was also developed for groundwater monitoring only. The site layout, together with the associated near-surface pathway sampling locations, is shown in Figure 4.9.

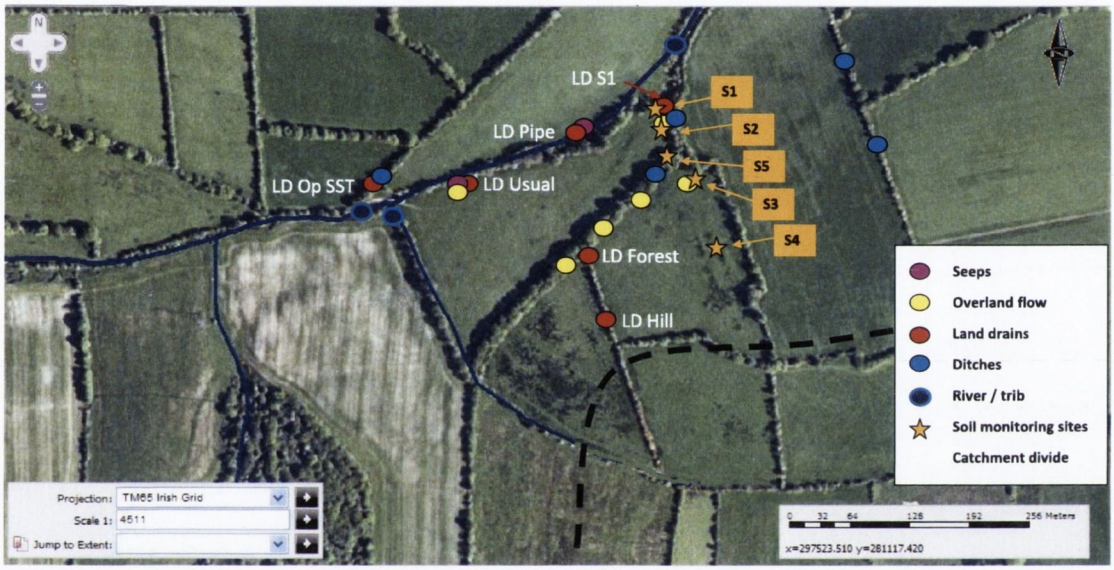

Figure 4.9. Soil water dynamics field site layout in the Mattock catchment, showing the locations of the five clusters in the transect, with the measured land drains, ditches, overland flow, seeps and river sampling sites. The land drains (LD) are labelled for reference. Note that this figure is the insert in Figure 4.19.

At each cluster location, a trial pit (Figure 4.10) was first excavated with a digger to approximately 2.5 m below ground level, at a distance of 5 m to the west of where the monitoring equipment was to be installed. The profile was logged using the Geological Survey of Ireland's standard methodology for describing subsoils which is based on BS5930:1999 (Fitzsimons et al., 2003, Swartz et al., 2003). A number of different horizons with potentially different interflow characteristics were identified for installation of soil monitoring equipment. This comprised a maximum of three horizons per cluster: an A horizon of topsoil to a depth of approximately 30 cm; a B horizon to a depth of approximately 80 cm; and a C horizon to the bottom of the holes. The holes were reinstated and equipment was purchased on the basis of the trial hole logs. Each cluster was fenced inside a 10 m x 10 m compound that was aligned with the boundary fence for the landholder's convenience.

Figure 4.10. Trial pit at S1, closest to the river. The trial pit is 2.5m deep.

4.3.1 Soil matric potential data

Three tensiometers were installed in three of the clusters (S1, S2 and S4), at each of the three measurement depths, 30 cm apart. The site design and construction are illustrated in Figure 4.11. Only one tensiometer could be installed at S3 in the topsoil, as the deeper soils were too stony. The guide holes for the shallow and mid-depth tensiometers were installed using a hand auger; the deeper depths were achieved using a small, track-mounted, drilling rig. The holes were cored inside plastic sleeves, which meant it was possible to generate an accurate site soil and subsoil log (Figure 4.12), and to recover soil for returning to the hole at the same depth from which it was retrieved. Due to limitations with the drilling equipment, the drilled guide holes were 120 mm in diameter, which was unfortunately much larger than required for the tensiometer. However, the tensiometers were inserted and pressed into the native soil at the bottom of the holes as far as possible, and the holes were backfilled with a slurry composed of depth-specific soil to at least 0.5 m above the suction cup. The remaining void was backfilled with a slurry of bentonite (Figure

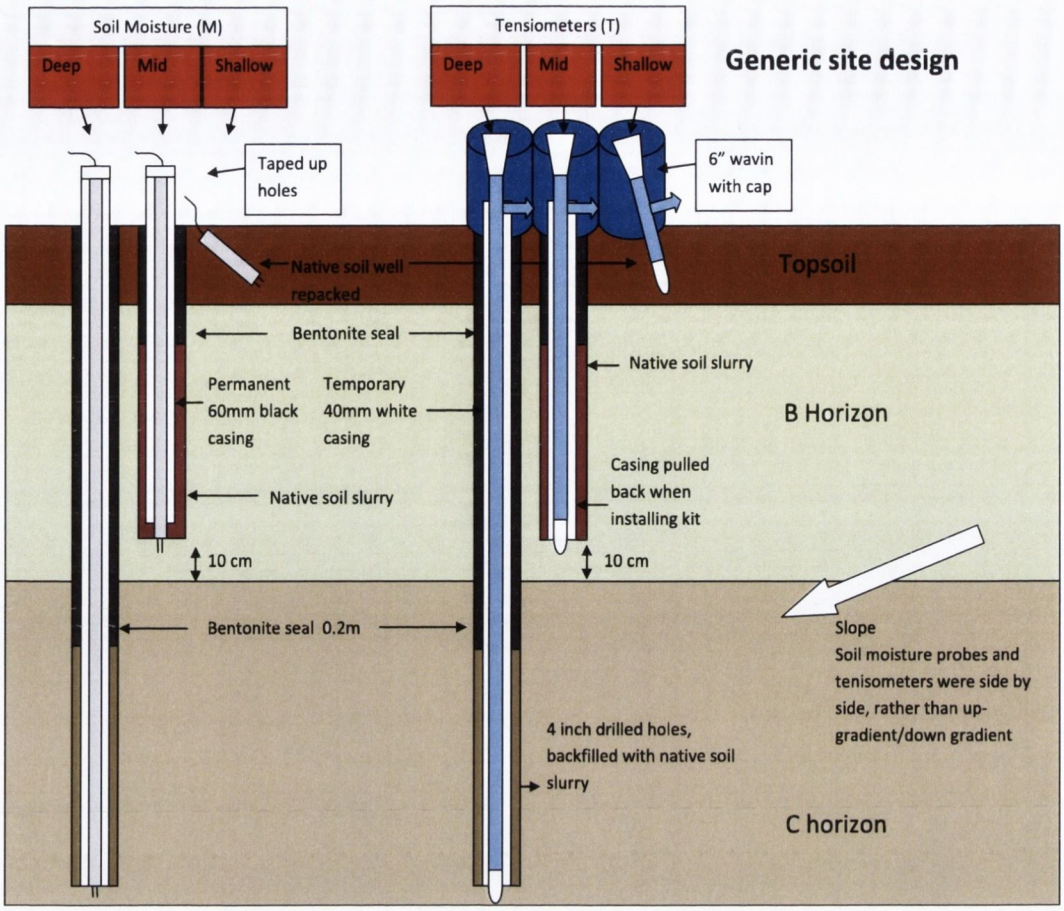

Figure 4.11. Design of the soil moisture dynamics monitoring cluster sites.

Figure 4.12. Soil core from the deep piezometer hole at S2.

Figure 4.13. Bentonite slurry ready for sealing one of the piezometers.

4.13), which was extended up to the surface to prevent ingress of rainfall. Each tensiometer top was then covered with a length of 6-inch capped wavin pipe to keep the transducers dry, and reduce the impact of cold weather and growth of algae inside the tube.

Soil matric potential data were measured using 10 Jet Fill tensiometers (Soil Moisture Equipment Corp; Model no. 2725ARL; Figure 4.14). The Jef Fill is a modular design that allows the ceramic cup to be screwed into the plastic tube, and different extension lengths to be added as required, which provides flexibility for installing different lengths in the field. The unit is sealed at the top with a jet-filled reservoir, which allows the user to refill the tensiometer from the reservoir by pumping the reservoir button, without removing the cap. All tensiometers on the site were fitted with current transducers (Soil Moisture Equipment Corp, Model no. 5301) and were wired to a LGR-5320 Series analogue 16 channel data logger (Measurement Computing; Omega Engineering). The tensiometers, transducers and logger were tested in the lab prior to installation in the field, by applying suction with a hand pump and checking against a manual gauge. Onsite, the logger was stored in a home-made logger box located in the middle of the site (Figure 4.15). All wires were either buried or pinned back behind the boundary fence to avoid being interfered with by grazing animals. Data were recorded at 15-min intervals. Power to the site was maintained using two alternated 12 V car batteries supplemented by a 100 W solar panel and trickle charger.

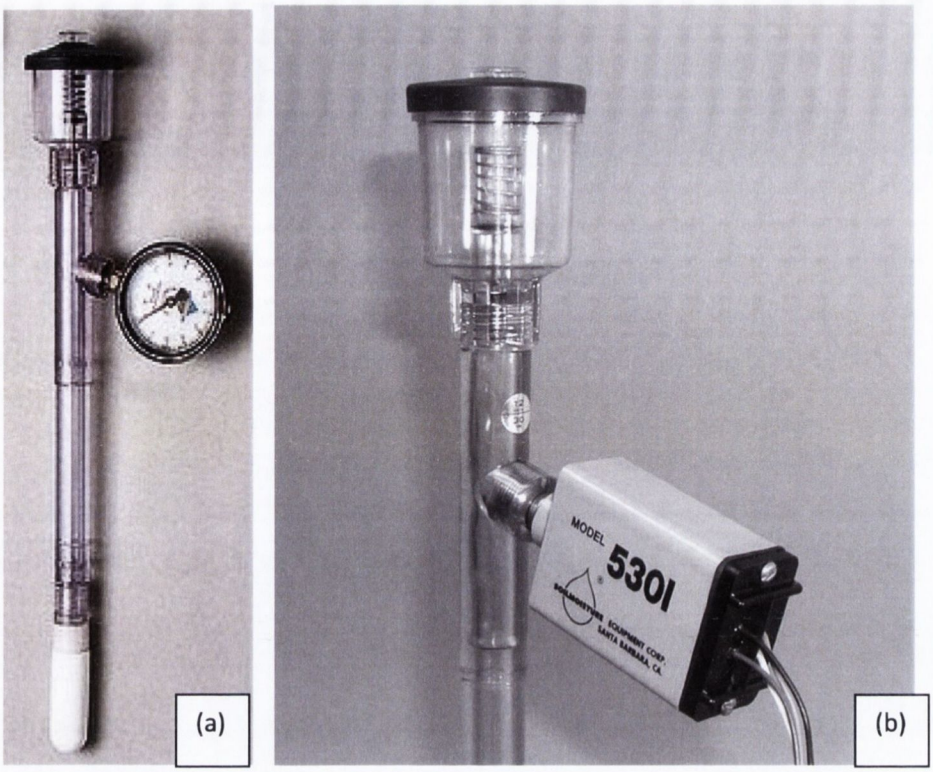

Figure 4.14. (a) Jet-filled tensiometer showing the ceramic porous cup, the plastic tube and the jet-filled reservoir with the manual gauge attached. (b) A closer view of the jet-filled reservoir cap and the manual gauge replaced with a transducer for logged readings (pictures from Soil Moisture Equipment Corp).

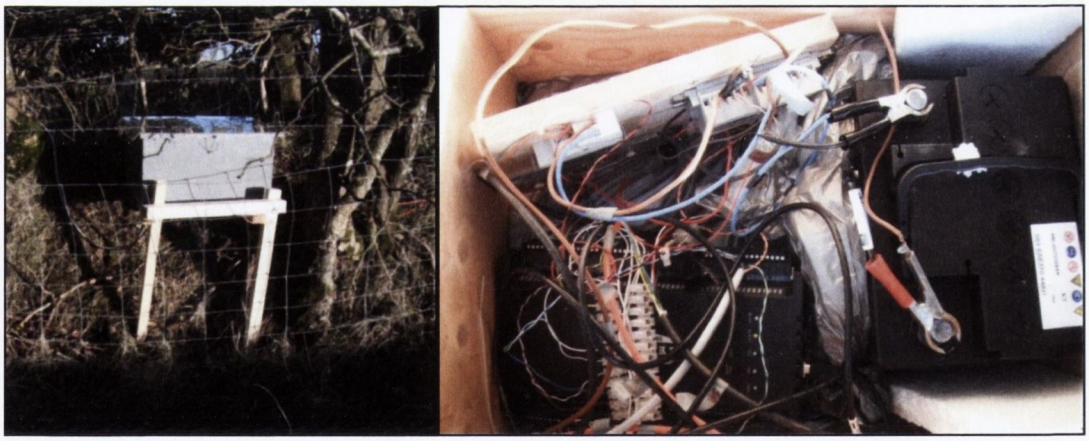

Figure 4.15. Home-made logger box with logger and battery inside.

4.3.2 Soil moisture data

Three soil moisture TDR sensors (Delta-T Devices Ltd., Model no. SM300-UM-1.1) were installed within 30 cm of the tensiometers at the three monitoring depths at S1 for the first year, before being moved to the equivalent positions at S2 for the second year. The TDR sensors were much more expensive than the tensiometers so just three were purchased with a view to moving them around to each site once relationships with the tensiometers had been established. It became apparent, however, during the course of the study, that S3 was underlain by an artificial fill (likely to be an old farm track) and therefore was unrepresentatively well drained, and difficulties with

the power supply and tensiometers at S4 meant that it was not clear if it would be possible to keep the site running long enough to establish a relationship between soil moisture and tension. It was therefore decided to maintain the TDR sensors at S1 and S2 for a period of 12 months each.

The TDR sensors comprise a sealed plastic body attached to two 51-mm long stainless steel sensing rods (Figure 4.16). Guide holes were augered and cased with plastic casing, and the rods were pushed firmly into fresh soil at the bottom of the holes using extension tubes. The holes were backfilled outside the casing with a slurry of the soil that had been removed and then sealed to the surface with bentonite to prevent vertical infiltration of surface water along the preferential flowpath created. The casing was sealed at the top. The upper sensor, which was positioned at 20 cm below the surface, was installed horizontally in a shallow trench pointing in an upgradient direction to minimize the risk of generating preferential flow to the sensor. The unit was completely buried so that accurate soil temperature measurements could be taken. Bentonite was not used for the shallow sensor as it has very high water retention properties and there was a risk that it might penetrate into the soil being measured and interfere with the results. The orientation of the sensor, however, was such that preferential flow was considered unlikely. The sensors were wired to a Campbell Scientific CR23X 16 channel logger as differential individually powered sensors. Measurements were recorded at 15-min intervals.

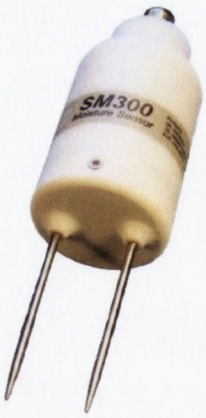

Figure 4.16. SM300 TDR sensor from Delta-T Devices Ltd.

The manufacturer's polynomial calibration curve for mineral soils was used to calibrate the output voltage of the sensors. An accuracy of ±2.5% over 0–50% volume and 0–60°C is reported in the manual and it is claimed that the standard calibration curve is appropriate for use (and has been tested) for the majority of mineral soils. A separate curve is available for use in organic soils. However, as soil moisture is dependent on the site-specific properties of soils such as hydraulic conductivity and porosity, additional validation tests were carried out to cross check the results.

Soil samples were taken from within 1 m of the installed soil moisture probes, at each of the monitored depths, and were returned to the lab for gravimetric soil moisture analysis for comparison against the logged SM300 data. The samples were collected in September 2013 at the end of a long dry summer, and again in November 2013 after an extended period of rain. This validation process was left to the end of the research period to avoid creating additional preferential flow paths on the site.

During the September round, the soils were so dry and hard that penetration and collection of samples with the hand auger was very difficult. Four samples were collected at 20 cm depth, and two at 60 cm. The average soil moisture content using the gravimetric method was 11.9–16.4%, which was in the same range as that recorded by the SM300s at the same time (11.4–19.8%), suggesting that the manufacturer's mineral soil calibration curve was adequate.

During the wetter November round, 10 samples were taken for gravimetric analysis but, unfortunately the results were surprisingly low at 10.9–29.6% moisture content, in contrast to the SM300 values which were much higher at 41.8–57.5%. Review of the other available water balance data for the same day, and the evidence that the soils were visibly wet in the field, suggests that the gravimetric analysis was inaccurate. This is likely to be because the samples had to be left overnight before weighing and they not been adequately sealed prior to the analysis, so some of the moisture content had escaped before the samples could be weighed. Regrettably, there was no further opportunity to repeat the test. Although the absolute values of soil moisture at high moisture contents could not therefore be checked, nevertheless, the relative changes in soil moisture content with depth are of greater interest in this research than the absolute values.

4.3.3 Piezometers

As part of the soil moisture dynamics study, five piezometers approximately 4 m deep were drilled at each of the four soil monitoring clusters, and an additional site S5, using a track-mounted, down-hole hammer drilling rig (White Young Green PLC, Figure 4.17). Each hole was finished into a coarse sand/gravel layer which, at the time of drilling in November 2011, was saturated or at least wet. Slots were cut into the bottom 1 m of an appropriate length of 60-mm plastic tubing, which was used as casing, and the holes were backfilled using first the native gravelly material until just above the slots, followed by a slurry of the native soil and a bentonite cap. Water levels were measured manually at each field visit with a Van Walt water level meter fitted with a measuring tape graduated in centimetres. Water level measurements were therefore accurate to ±0.5 cm. The groundwater level data were a useful measure of the antecedent conditions and provided context for the soil moisture readings.

Figure 4.17. Piezometer being drilled at Site 4 using the track-mounted down-hole hammer rig

4.4 Artificial field drainage

In order to investigate the role of artificial field drains in more detail, a number of land drains and ditches were included in the 27 rounds of sampling near-surface pathways as described in Section 4.2.3.1 (Figure 4.18). The majority of the sites were located in the vicinity of the soil moisture dynamics field site (Figure 4.9) to correlate with that aspect of the research, but some additional sites were also added to bring a spatial dimension to the research (Figure 4.19). Land drains are typically installed to solve a particular drainage problem, so in plot-scale studies, which have been the most common in Ireland to date, the drains are only representative of one drainage process. This study selected existing land drains at different parts of the catchment that had different drainage characteristics to determine how that impacted on the delivery of nutrients. Two ditches and a land drain on the northern side of the river, in a different hydro(geo)logical setting, were regularly sampled with those at the soil moisture dynamics site. A series of seven additional ditches and two land drains in the upper catchment were also sampled on occasion, including during one of the team events. Easily accessible sampling sites were selected in view of the analysis time constraints with using the smaller sampling bottles, as described in Section 4.2.3.1.

Figure 4.18. Sampling S1 land drain, Mattock catchment.

Regular flow measurements were taken from five of the land drains that were discharging through open pipes, using either a 1 litre, 500 ml or 30 ml bottle, and a stop watch. As the method is highly dependent on the reaction time of the operator, the size of the measurement vessel used was adjusted to try to maintain a filling time of at least 20 seconds, so that the measurement error could be kept to no more than 2.5%, i.e. assuming a reaction time of ±0.5 s. Flow measurements were taken three times and averaged.

The purpose of this aspect of the work was to gauge the spatial and temporal variability in flow, chemistry and nutrient concentrations in land drains and ditches around the catchment. Some preliminary work has also been carried out by this researcher to delineate a national map of the hydro(geo)logical environments in which land drains are likely to be present. As described in the following chapters, this research has helped to show that artificial drainage does have a significant bearing on the transport of flow and nutrients to streams, and a map is consequently required as a contributing input layer for the *Pathways Project* catchment management support tool. A set of rules, i.e. GIS algorithms, dictating the scenarios where drainage is likely to be present was generated based on discussions with other practitioners and a review of the literature. A drainage map was then generated for each of the four study catchments and was tested against land drain surveys carried out by other *Pathways Project* students in interviews with landholders. The results were used to refine the GIS algorithms.

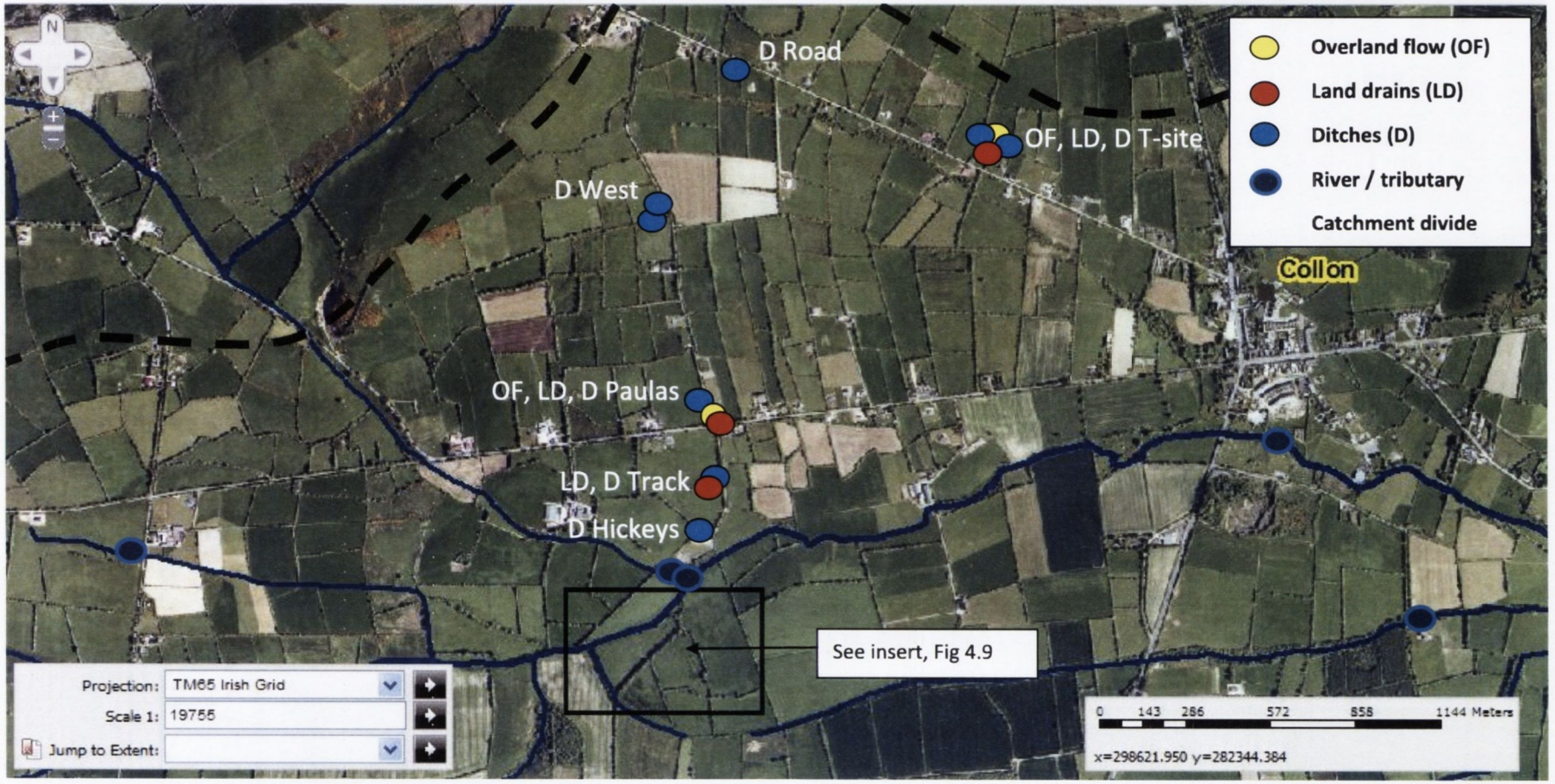

Figure 4.19. Spatial sampling of the artificial drainage network. Note the insert is presented in Figure 4.9.

4.5 Summary

The data collected in the three elements to this work were used to address the role of the near-surface pathways in the transfer of flow and nutrients to streams, as in general, and specifically in Irish soils, they are poorly understood. It is clear from the literature, however, that the hydro(geo)logical pathways in a catchment are in fact a continuum, and that the near-surface pathways must therefore be investigated in a whole-of-catchment context considering the full three-dimensional geological profile. This is particularly pertinent in this research as the context of the work was to contribute to the development of a set of national catchment management support tools. In addition, the study catchments were new research catchments with very limited data available, in contrast to the many, long-established research catchments worldwide. Thus, the overall research strategy was to apply a range of investigatory techniques in all the catchments, so that the resulting conceptual model had as broad an application as possible. Temporal and spatial variability were both important within the constraints of the available resources. A catchment focus was therefore dominant, but it was supported by site-scale dynamic, process studies in the Mattock catchment. As 70% of the land surface in Ireland is underlain by poorly productive rock aquifers and poorly drained soils, the Mattock was considered to be representative of the majority of the Irish landscape.

5 Catchment conceptual models

This chapter presents consolidated conceptual models for each of the four study catchments, based on interpretations of the available catchment data, using a range of techniques. It is not intended to present all the available catchment information here, rather just the data and methods that support the conceptual understanding of how the pathways function in the delivery of flow and nutrients to the stream, particularly the near-surface pathways. A strong conceptual understanding of stream flow generation processes was found to be essential as a basis for implementing the hydrograph separation techniques, as outlined in Chapter 6.

A section on each study catchment commences with a brief description of the geological framework and land use, followed by a discussion on the pathways as supported by stream flow, groundwater level and electrical conductivity data. Assessment of the water chemistry and quality data is also included where it has a specific bearing on the interpretation of the pathways. An assessment of the nutrient transport pathways based on the event sampling and other data is then presented. A final section summarizes the conceptual model for the catchment. This chapter concludes with a brief discussion of pertinent issues for consideration in carrying out the hydrograph separations (Chapter 6).

Insights from this chapter, and Chapters 6–8, have been used to critique and improve the generic conceptual model in Chapter 9. Much of the sections detailing the catchment conceptual models has been duplicated in the *Pathways Project* catchments field report (Deakin et al., 2014). Where analyses and interpretations have been made by others, references are provided as appropriate; otherwise the work is that of this author. Although data collection in the Glen Burn and Gortinlieve catchments was the primary responsibility of staff and students from Queen's University as part of the *Pathways Project*, the analysis and interpretation of the data was carried out by this researcher as a contribution to the overall project and for the purposes of this research. A location map showing the four catchments is provided in Figure 4.1.

5.1 Mattock catchment

The Mattock catchment straddles the Meath/Louth border and covers an area of 17 km^2 with the village of Collon at its centre. The catchment outlet is at an elevation of approximately 85 m OD and the catchment rises to an elevation of approximately 250 m OD on its northern flank to the northwest of the village.

5.1.1 Geological framework

The catchment is underlain by Silurian greywackes, mudstones and siltstones to the west and east and there is a central core block of Ordovician volcanic rocks and metasediments. All the rocks are classified by the Geological Survey of Ireland as either Poor aquifers which are generally unproductive (Pu) or generally unproductive except for local zones (Pl) (Figure 5.1), which is similar to the aquifer classification in Gortinlieve and Glen Burn. Estimates of the hydraulic conductivities in the deep boreholes in the EPA monitoring borehole suite in the lower catchment (see Figure 4.2 for borehole locations) were one and two orders of magnitude higher than in the Gortinlieve and Glen Burn catchments, respectively. Consistent with the other two catchments, fracture analysis showed that there were a limited number of fractures in the bedrock that were hydraulically active (Nitsche, 2013, *unpublished data*).

The transition zone was not formally identified when the monitoring boreholes were being drilled. However, it is clear from the water level data in the subsoil borehole at MK1 (refer to Section 5.1.3.2), there was sufficient permeability at the junction between the subsoils and the bedrock to maintain a responsive water level in this zone for at least 6 months of the year. The question remains as to whether there is sufficient weathering in this zone to create the transmissivity to contribute significant flows to the stream hydrograph. If not, water from the saturated soils is likely to discharge at the surface when the profile is fully saturated; these environments are typically suited for the installation of artificial drainage networks. While the transition zone may not have been observed in the monitoring boreholes in the lower catchment, it is probable that it is present in other parts of the catchment. For example, the Geological Survey of Ireland's well database includes three dug wells and two drilled wells that are completed into the upper 3–6 m of weathered bedrock.

The subsoils in the catchment are predominantly poorly draining tills derived from these Lower Palaeozoic rocks ranging from <1 m deep on the higher ground to >10 m deep in some parts of the valley. This results in the full range of groundwater vulnerability categories from Extreme to Low (Figure 5.1). Alluvial deposits are present along the river channel. The soils across the catchment are typically poorly drained, except in the areas where rock is close to the surface or there are underlying permeable gravels (Figure 5.1).

Five resistivity profiles perpendicular to the river, and a sixth at the soil water dynamics research site, all carried out by researchers at Queen's University Belfast, have shown that there are two deep palaeochannels along the axes of the main river channel and the parallel tributary to the south (Lamberts tributary), which are infilled with a chaotic mixture of sands, gravels and tills

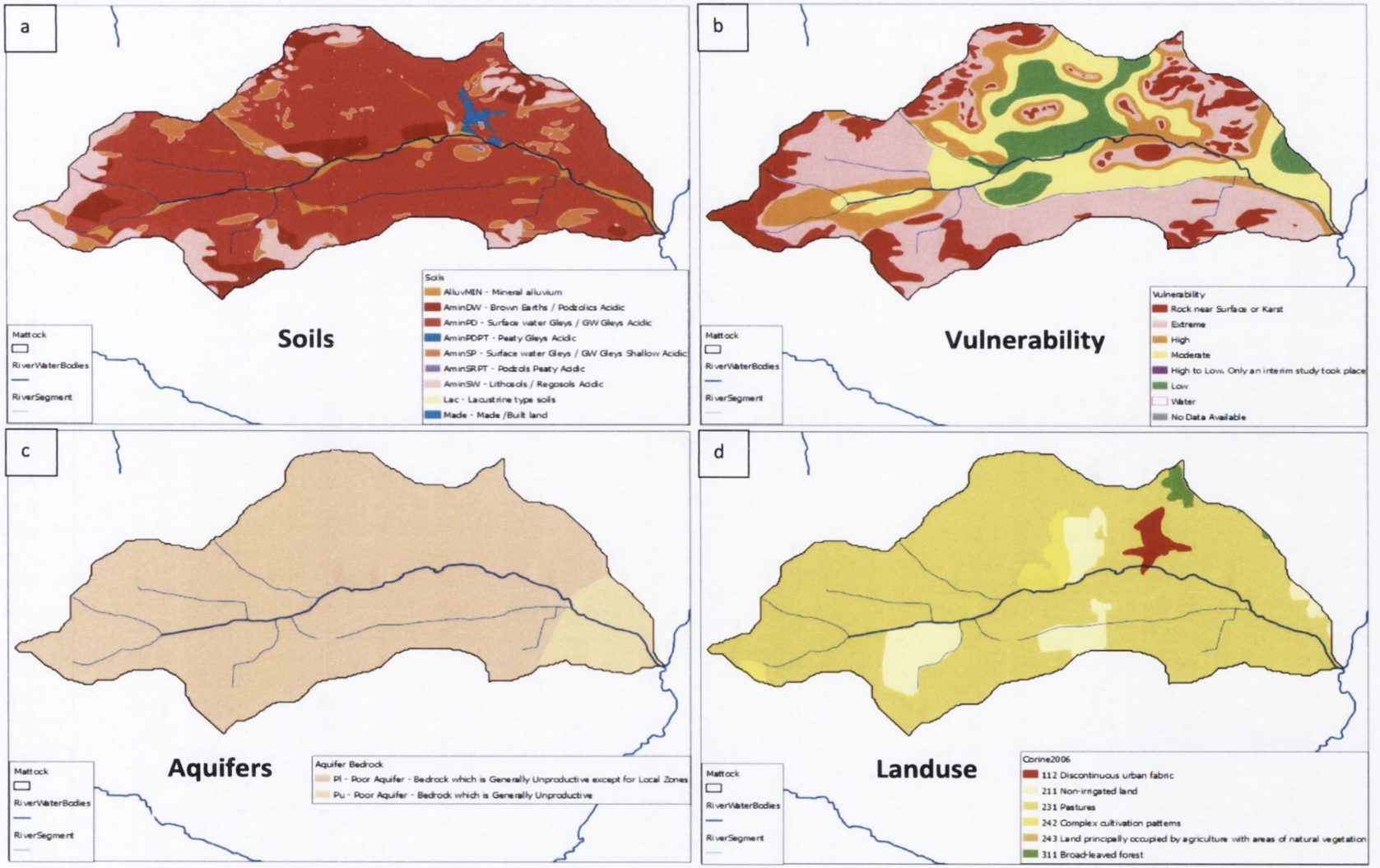

Figure 5.1. Mattock catchment soils (a), groundwater vulnerability (b), aquifers (c), land use (d) (Deakin et al., 2014). See Figure 4.2 for sampling locations and local features.

(Wilson et al., 2012). In the vicinity of the borehole transect, the palaeochannel is 40 m deep and is overlain by a 5 m sequence of finer grained, less permeable alluvial deposits (Figure 5.2). The channel has a significant impact on groundwater-surface water interactions in the catchment as described in Section 5.1.3.

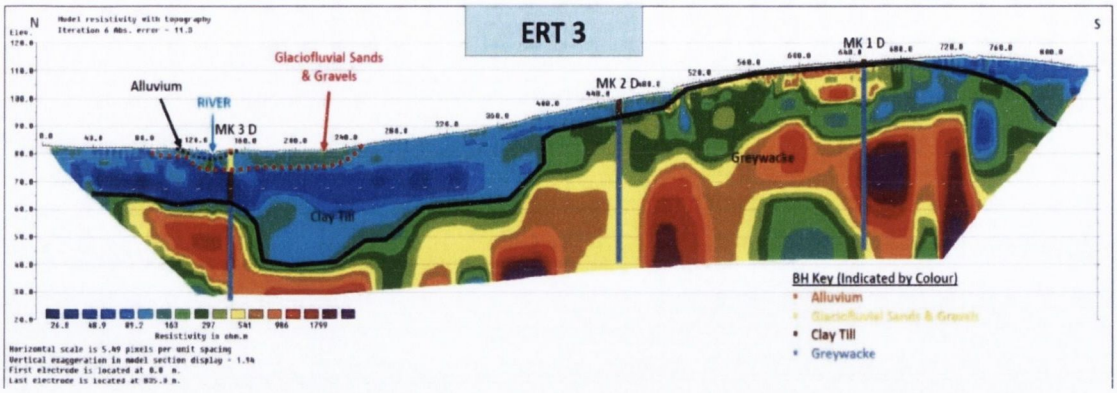

Figure 5.2. Resistivity profile through the EPA borehole transect in the lower catchment showing the major palaeochannel (from Wilson et al. (2012)). The location of the profile, together with the boreholes, is marked on the map in Figure 4.2.

5.1.2 Land use

A detailed land-use survey found that there was approximately 83% pasture (dairy, cattle, sheep, with some horses) and 7% arable for cereals and maize, with the remainder a mixture of woodland, scrub, urban and other categories (Crockford, 2009). Application of organic and inorganic fertilizers was reported as being common. The rural population is approximately 1850, just over half of which is presently served by a modern wastewater treatment plant (WWTP) with a high level of phosphorus treatment (EPA, 2005). The town's drinking water supply is provided by three boreholes located in the gravels and upper bedrock adjacent to the WWTP site (Groves, 2010)[3]. The remainder of the population is rural and is serviced by private wells and domestic waste water treatment systems (mainly septic tanks).

5.1.3 Pathways

5.1.3.1 Stream flows

Flow in the Mattock catchment is very responsive to rainfall as would be expected in a poorly productive aquifer setting, and there is very little baseflow during the summer months. Between February 2011 and February 2013, the range in flow at the catchment outlet was large, from 0.002 to 15 m^3/s, and the mean flow was 0.14 m^3/s. Much of the agricultural land is artificially drained and rushes and other vegetation indicators of poor natural drainage are prevalent where

[3] The WWTP and the abstraction boreholes are located in the same Council owned compound, which is also the site of the rainfall gauge in Collon. Refer to Figure 4.2 for their location.

they have not been managed (Figure 5.3). The geological setting and the hydrological regime are therefore indicative of a highly responsive flashy catchment in which the near-surface pathways are dominant.

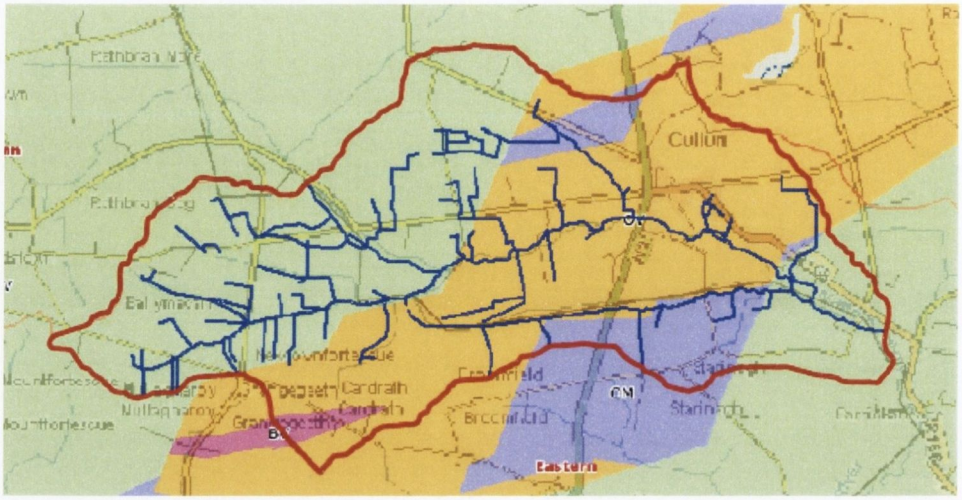

Figure 5.3. Land drainage based on a land-use survey and bedrock geology in the Mattock catchment (Quigley, 2012). Pale green, Silurian greywackes, mudstones and siltstones; orange, purple and pink, Ordovician volcanic and metasediments.

5.1.3.2 Groundwater levels

Reliable groundwater level data were limited to the EPA borehole transect in the southeastern corner of the catchment (Figure 4.2). The groundwater level data (Figure 5.4) showed that at MK1, close to the catchment divide, the average groundwater levels in the subsoils, shallow bedrock and deep bedrock boreholes were 1.8 m, 3 m and 2.8 m below ground level, respectively, indicating that the upper shallow bedrock was the primary bedrock discharge pathway. The subsoil and shallow bedrock water levels also responded to rain consistent with the stream hydrograph; there was little direct response in the deep borehole. This is representative of typical hydrogeological conditions in a poorly productive aquifer but it is very different to the water level regime at MK2 and MK3.

At MK2 Deep, the average depth to the water table was 24 m bgl, and the shallow bedrock borehole (22.9 m depth) was consistently dry. At MK3 close to the river, the water tables in the shallow and deep bedrock boreholes were some 12–14 m below ground level, did not respond to rainfall and showed evidence of an earth tide effect. There was an upward gradient from the deep bedrock into the shallow bedrock which was confined by 10 m of clayey till. Above the clayey till, the alluvium (MKSubs1) and glaciofluvial gravel (MKSubs2) boreholes responded to rainfall, although the response in the gravel borehole was more muted than in the alluvium due to the 1-m thick clay horizon separating them. During rainfall events, the groundwater head in the

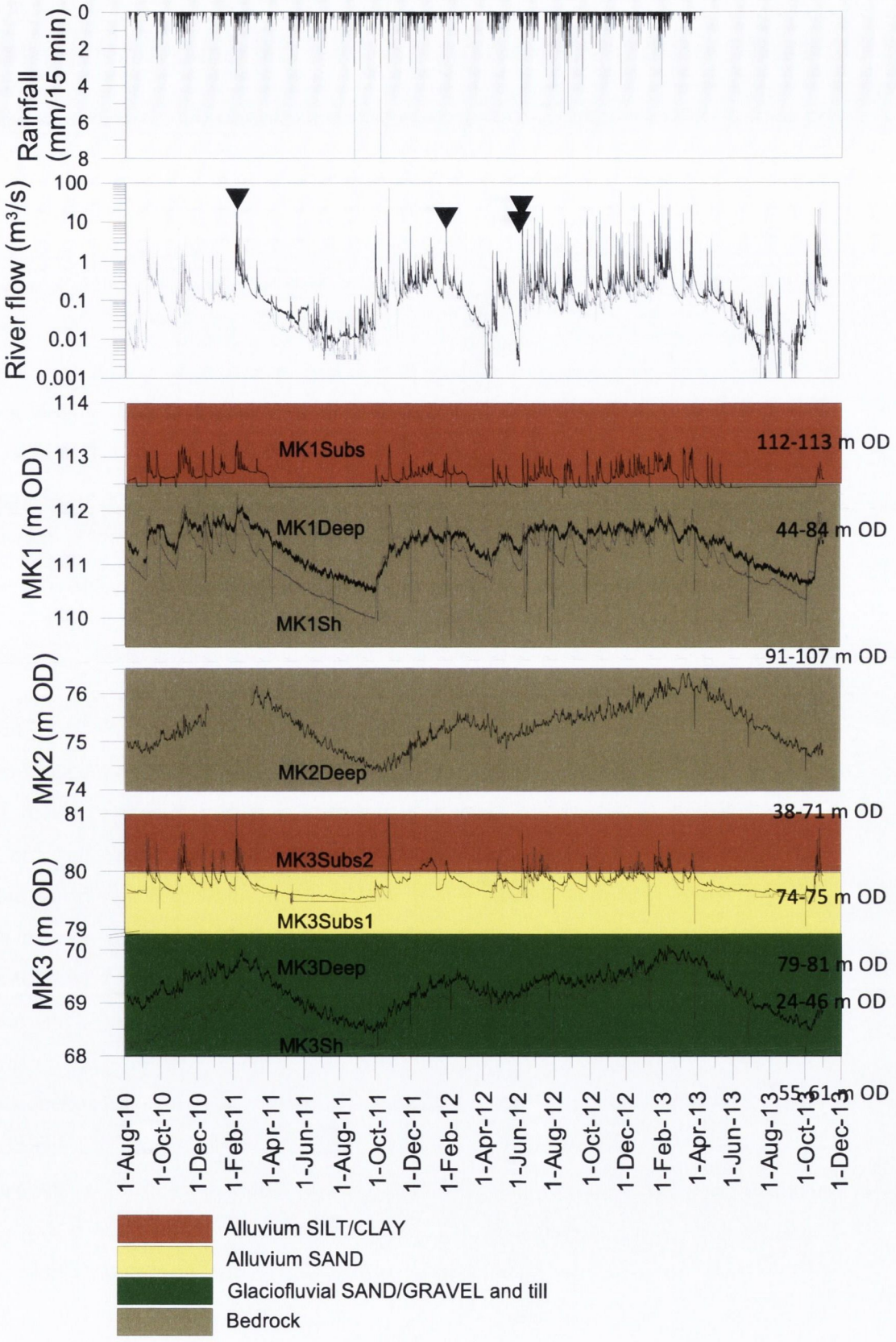

Figure 5.4. Mattock groundwater levels with the geological profile, Collon rainfall and stream flows (Berrils, black and Collon, grey) in the Mattock catchment. The screened intervals in the boreholes are listed to the right of each hydrograph. Black triangles, event sampling dates. Boreholes located on Figure 4.2. Note boreholes with the same prefix, e.g. MK1 Subs, MK1 Shallow and MK1 Deep, are all located within a few meters of each other and are marked on Figure 4.2 as one location.

alluvium was higher than in the gravels, but otherwise there was a small upward gradient from the gravels. The river is therefore disconnected from the bedrock groundwater in the valley floor.

The boreholes at MK2 and MK3 were affected by the presence of the palaeochannel which was lowering the deeper water table. A similar scenario occurred at the soil water dynamics research site where the palaeochannel in the adjacent Lambert's tributary valley has resulted in a 4-m borehole close to the catchment divide being dry for much of the year. Further evidence is provided at a large disused quarry just south of Collon that has been excavated to approximately 30 m below ground level into the volcanic rocks; despite numerous field visits, there has never been any evidence of a water table observed. Such deep water tables are unusual in rocks such as these, which are classified as poorly productive. An interpretation of the available evidence in the context of the glacial history in this catchment by Dr Robert Meehan (*pers. comm.*) suggests that there is a high likelihood that there are interconnections between the sand and gravel deposits at depth in the palaeochannel, and that water may discharge below the ground surface into the major Boyne River terrace gravels several kilometres further south and downstream of the catchment.

5.1.3.3 Electrical conductivity

Sampling of the electrical conductivity in the river from the groundwater monitoring boreholes and from representative examples of rainfall, overland flow, land drains and ditches around the catchment was carried out and is shown in Figure 5.5. The results show, as expected, that the near-surface pathways typically had lower electrical conductivity values than the deeper pathways, reflecting shorter residence times and less interaction with the geological substrate. The signature of the ditches aligned quite closely with that of the river. It is evident in the field and from the data that ditches are essentially an extension of the river network, and that they are a mixture of water from the deeper pathways with higher conductivity on the one hand, and water from the near-surface pathways and rainfall that is lower in conductivity on the other. Equally, it could be hypothesized that the land drains comprise a mixture of soil and subsoil water, which is higher in conductivity, and overland flow and rainfall, which is lower. Further discussion on the origin of the water in the land drains is provided in Section 8.4.1. The very high conductivity values in MK3 Deep and MK3 Shallow (together with the hydrochemistry) reflected the much longer residence time in the confined system and emphasized their disconnect from the river, as confirmed by the groundwater levels.

Despite the groundwater-surface water disconnect in the valley floor, it is apparent from the electrical conductivity measurements in the stream that bedrock groundwater must contribute to

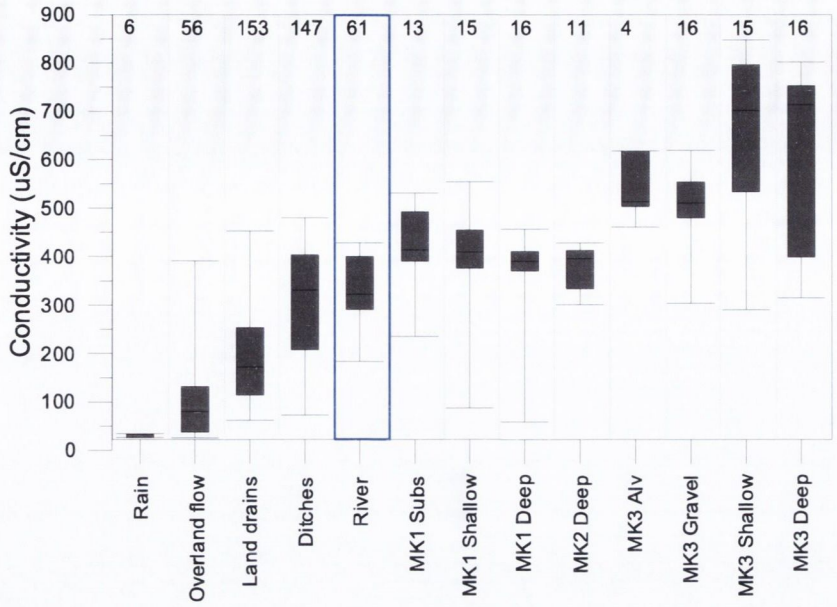

Figure 5.5. Electrical conductivity measurements from pathways. The numbers at the top of the plot indicate the number of samples. Samples from rain, overland flow, land drains, ditches and the river comprise samples from each pathway type taken from all over the catchment, as shown in Figures 4.2, 4.9 and 4.19. The remainder of the samples were taken from each specific named borehole (Figure 4.2).

provide the higher values to counter balance the near-surface contributions. There is evidence in the field from bedrock exposures in the bottom of ditches, from the fact that they flow all year round, and from the hydrochemistry of ditch water, that bedrock groundwater does contribute to the stream, but that it does so via numerous seeps and springs that discharge into the headwaters of the drainage ditches. The ditches commonly start high up in the catchment where the shallow rock gives way to increasingly thicker tills as one moves down into the valley. This results in quicker apparent response times for the groundwater contribution to the streams than might otherwise be expected, which needs to be taken into account in the pathways separation (refer to Section 6.5.2). Further discussion of the origin of the water in the ditches is provided in Section 8.5.2.

Electrical conductivity values >1000 µS/cm, with very high ammonium or nitrate, were measured in MK3 Alv (the borehole into the shallow alluvium close to the stream) on two occasions and so those data have been removed from this analysis as the water was contaminated. There were fewer samples from the monitoring boreholes than from the river, especially those that were dry on occasion such as MK3 Alv, which means that the datasets are not comparable statistically. Nevertheless, they do provide an indication of the differences between the water in the river and its likely contributing pathways.

5.1.4 Nutrient transfer

The spatial river water quality sampling data demonstrated a uniform increase in nitrate loads with distance downstream, which suggested that the sources were relatively uniform across the

catchment and were therefore largely diffuse, with the exception of the Collon area where the load increased eight-fold during low flows. The stream profile showed less uniform contributions of phosphorus in the catchment, especially in the lower part of the catchment at moderate flows, which suggested the influence of point sources (Deakin et al., 2014).

5.1.4.1 Pathways sampling

Review of all the available data from the EPA borehole network, i.e. fourteen rounds of quarterly sampling from 2009 to 2012, showed that at MK1 in the upper catchment, where the soils and subsoils are thin, all the contaminant indicators were higher in the subsoils and the top of the bedrock than in either of the deeper boreholes (Figure 5.6). When considered with the upward gradient and the higher transmissivity, this suggested that the upper bedrock/transition zone was a significant nutrient transport pathway.

The deep borehole at MK2 had an unusually large unsaturated zone because of the palaeochannel, which has resulted in high nitrate at depth, but not phosphate or coliforms[4]. In the lower catchment at MK3, the alluvium was the most contaminated of all the boreholes with high nitrate, ammonium and phosphate, but no coliforms, which may suggest a travel time long enough for bacteria to die off. Contaminants were typically much lower with depth, although elevated phosphate was found in the gravel on occasion. Water quality in the shallow and deep bedrock was generally good, although ammonium was elevated in the shallow groundwater pathway on occasion.

A nutrient mixing model was generated which presents nitrate and phosphate concentrations for the river during the monitored events, with those from spot samples from the different contributing pathways, including overland flow, land drains, ditches, and the bedrock and subsoil boreholes (Figure 5.7). The results show that during the events, the river almost always had higher concentrations of phosphate than the 0.035 mg/l as P threshold limit between Good and Moderate status. The concentrations of phosphate were often high in overland flow and the ditches, suggesting that they were contributing pathways. The mixing plot also shows that the river was often at a higher nitrate level than the interim ecological surrogate level of 8 mg/l as NO_3; it was only diluted below this level at peak flows. The land drains, subsoil boreholes and bedrock boreholes were the main pathways which had high nitrate levels, although the ditches were also high on occasion.

[4] Coliforms are included in the routine quarterly groundwater monitoring carried out by the EPA. Although coliforms are not a focus of this thesis, their presence in groundwater provides additional information to support the conceptual model, so they have been included in the discussion.

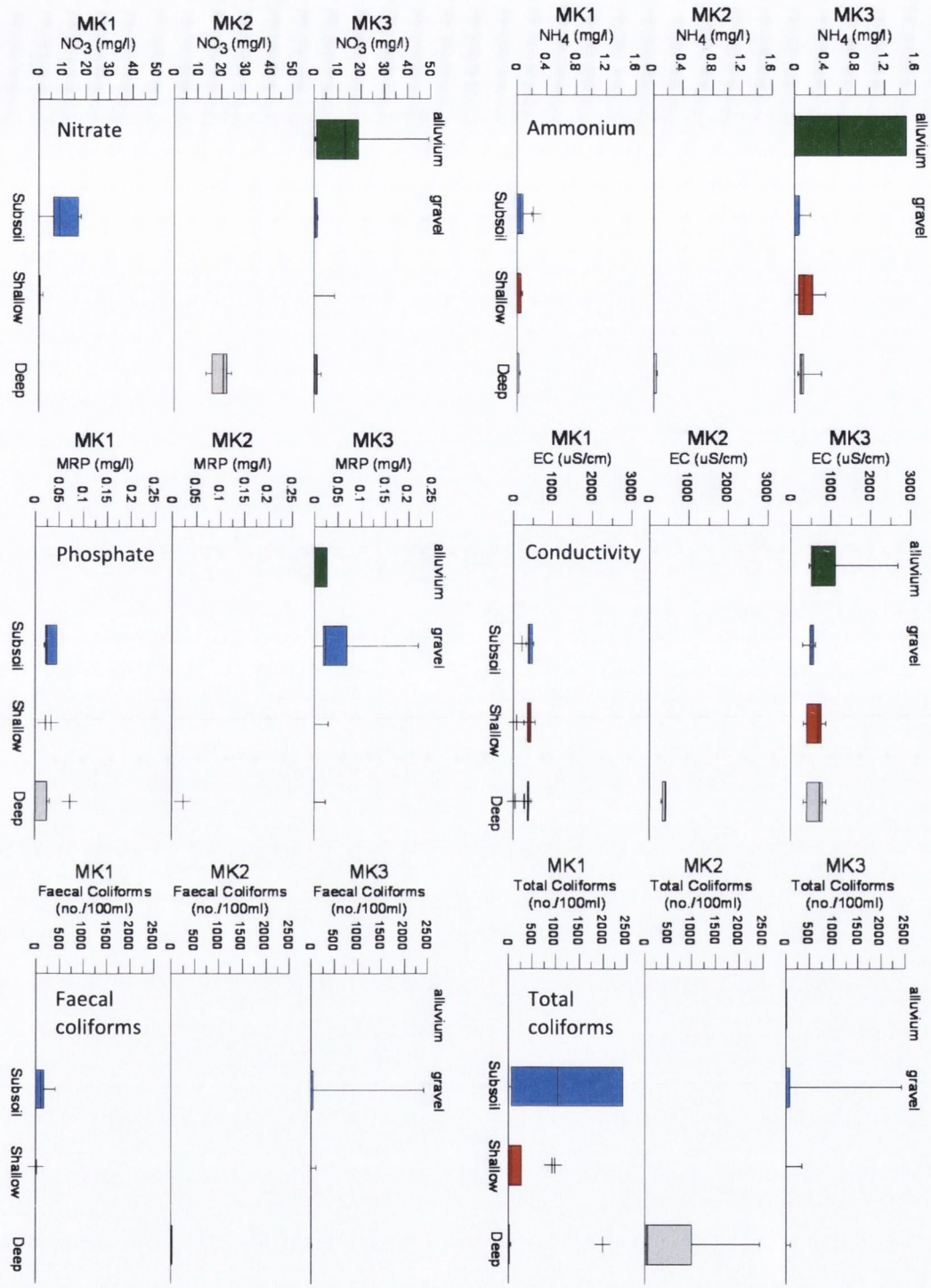

Figure 5.6. Contaminant indicators in the subsoil and bedrock groundwater pathways in the EPA monitoring cluster. (Figure based on a template drawn by A. Orr and reported in Deakin et al. (2014)). Based on quarterly sampling carried out by the EPA between June 2009 and July 2012. n = 14 for all boreholes except those that occasionally dry up, including MK1 Subsoil and MK2 Deep (n = 10); and MK3 Alluvium (n = 6).

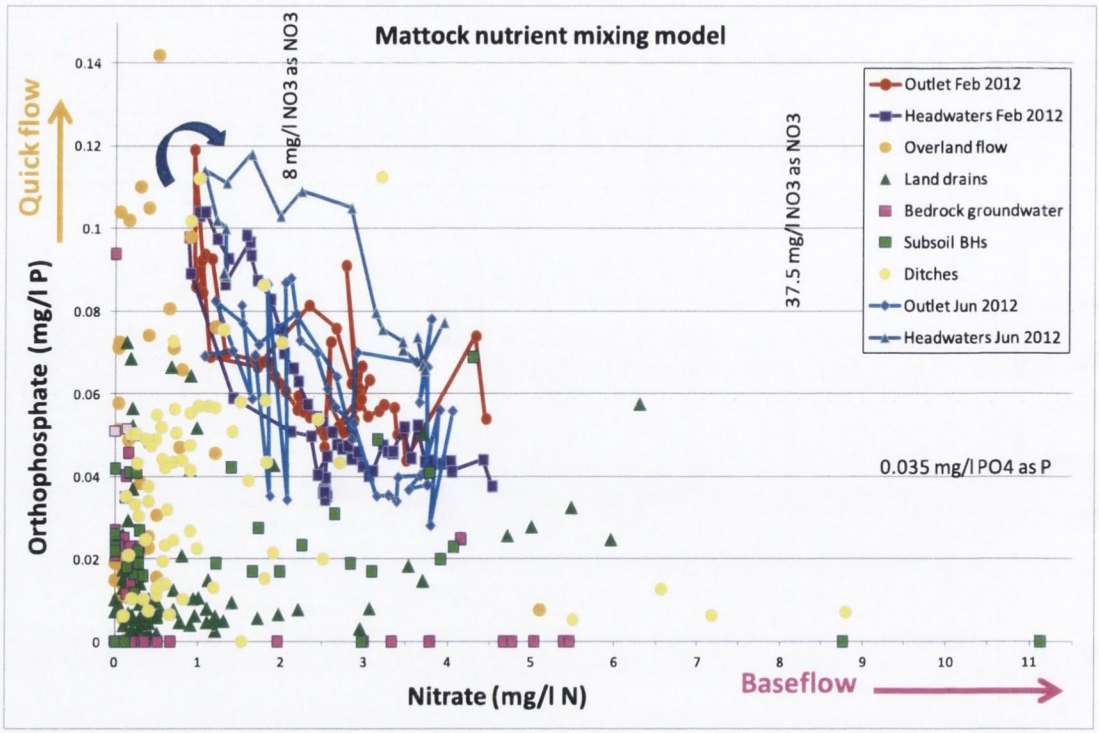

Figure 5.7. Nutrient mixing model showing the primary delivery pathways for nitrate and phosphate to the river. Dashed lines highlight environmental management thresholds. River samples connected by the same line were collected at hourly intervals during the same rainfall event. The semi-circular arrow indicates the direction of the progression of the events, and hence the hysteresis.

A box and whisker plot (Figure 5.8) suggested that over the longer term, the pathways sampled may not have provided sufficient phosphate to deliver the observed concentrations in the river, which supports the hypothesis of a contribution from point sources. Nitrate was sufficiently high in the subsoils and deep bedrock at MK2 to account for the nitrate in the river, but hydrological pathway links to the river need to be present in order for them to provide viable sources. This is unlikely at MK2 because of the drainage to the palaeochannel, and in the subsoils a link via artificial drainage and/or the shallow bedrock/transition zone would be required.

5.1.4.2 February 2011 event

Five rainfall events that occurred over a 6-day period in February 2011 were sampled hourly in the river at Collon.[5] The total rain over the period was 67 mm with a maximum rainfall intensity of 5.97 mm/h. A plot of nitrate versus flow during the five events provided a number of insights into the nitrate, and consequently the flow delivery pathways in the upper catchment (Figure 5.9).

[5] A sixth subsequent event was also sampled but the nutrient data did not meet quality control standards. The samples were frozen in an effort to preserve them but the nitrate data were unfortunately unsatisfactory as a result.

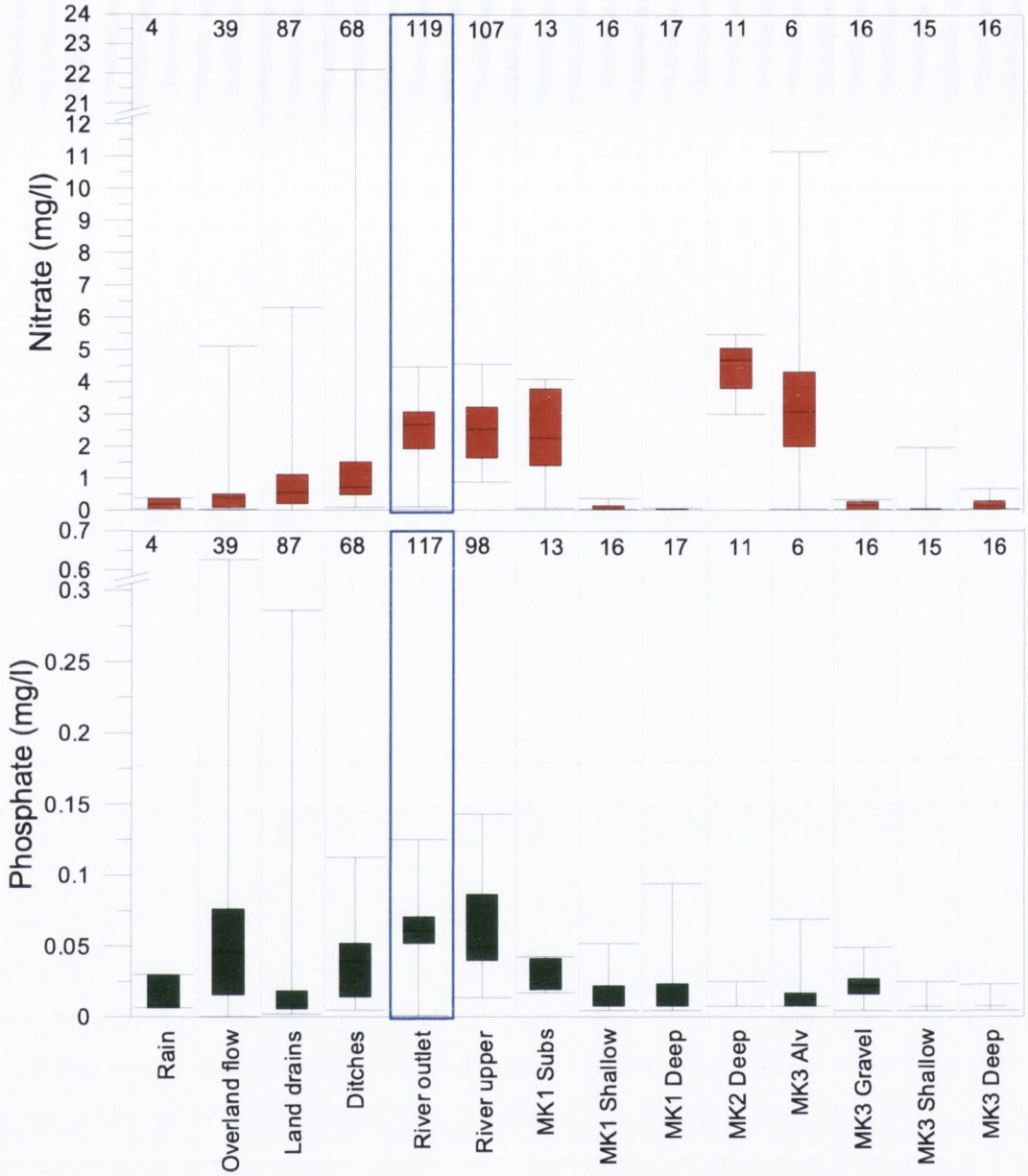

Figure 5.8. Concentrations of nitrate (mg/l as N) and phosphate (mg/l as P) in the main pathways in the Mattock catchment. The numbers at the top of the plots are the numbers of samples. Near-surface samples were taken regularly over a 2-year period from October 2011 to September 2013; borehole samples were taken by the EPA between June 2009 and July 2012. River samples were taken during background sampling, event sampling and sampling during collection of near surface spot samples, which is why the river category has the greatest number of samples. Refer to Figures 4.2, 4.9 and 4.19 for sample locations.

First, with the exception of the first event when there may have been some incidental, first flush losses, nitrate decreased in concentration during rainfall events, which suggested it was delivered via a subsurface pathway, and that the contribution from that pathway was diluted with overland flow.

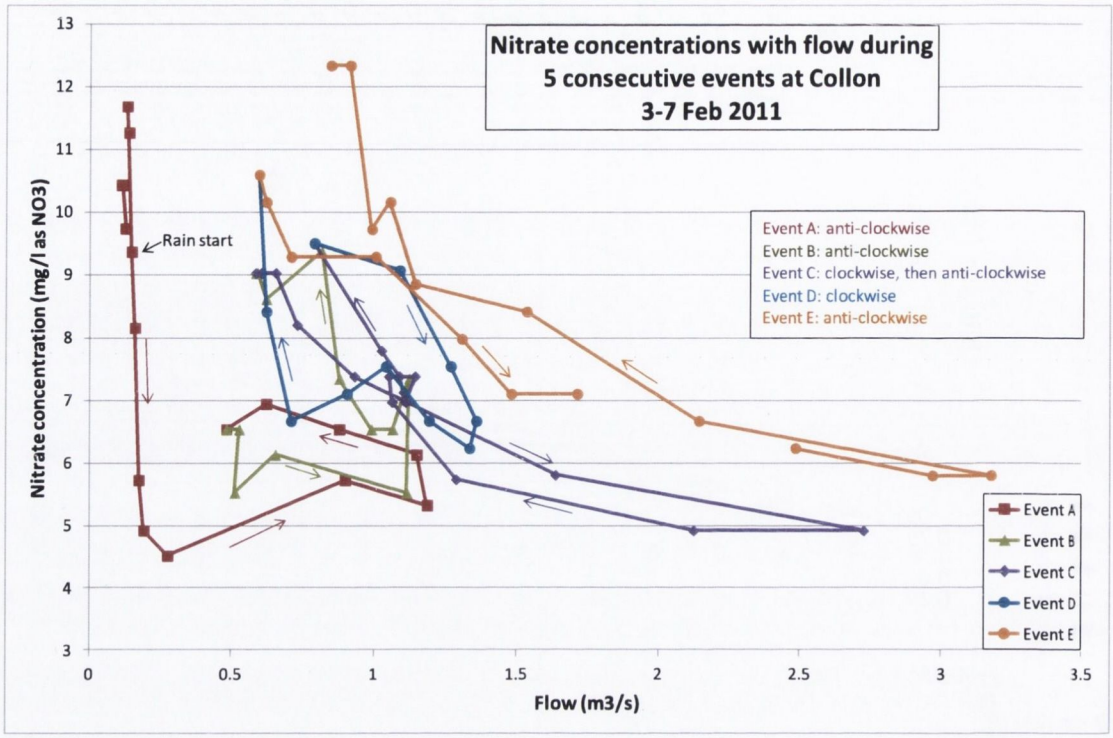

Figure 5.9. Changes in nitrate concentrations with flow during five successive rainfall events at Collon in February 2011. Arrows show the direction of the hysteresis for each event.

Second, nitrate concentrations were higher at the end of each successive event than they were at the end of the previous one, despite increases in flow and potentially therefore dilution. This suggests that new sources were being mobilized overall as the events progressed. The groundwater level data for the same period (Figure 5.10) showed that the water levels in the bedrock and subsoils in the upper catchment away from the palaeochannel (MK1), and in the gravel and alluvium close to the river at MK3, all increased during the event. As the subsoils at MK1 and MK3 were sources of nitrate and ammonium (Figure 5.7), the rising water levels in the subsoils during the event may have mobilized the additional nitrate sources.

Third, the nitrate–flow relationships also showed hysteresis effects during each of the events, which changed under different antecedent and flow conditions. Events A and B progressed in an anti-clockwise direction, consistent with the mobilization of new sources. Event C, which was larger, commenced in a clockwise direction during the high flood peak suggesting that the sources were being depleted or rapidly diluted with the influx of fresher water. After the peak had receded, it reverted to the anti-clockwise direction once more. Event D was smaller in size and showed a clockwise hysteresis; Event E, which was the largest event, was slightly anti-clockwise but more linear overall. The depleting source response during Event D followed the wetter

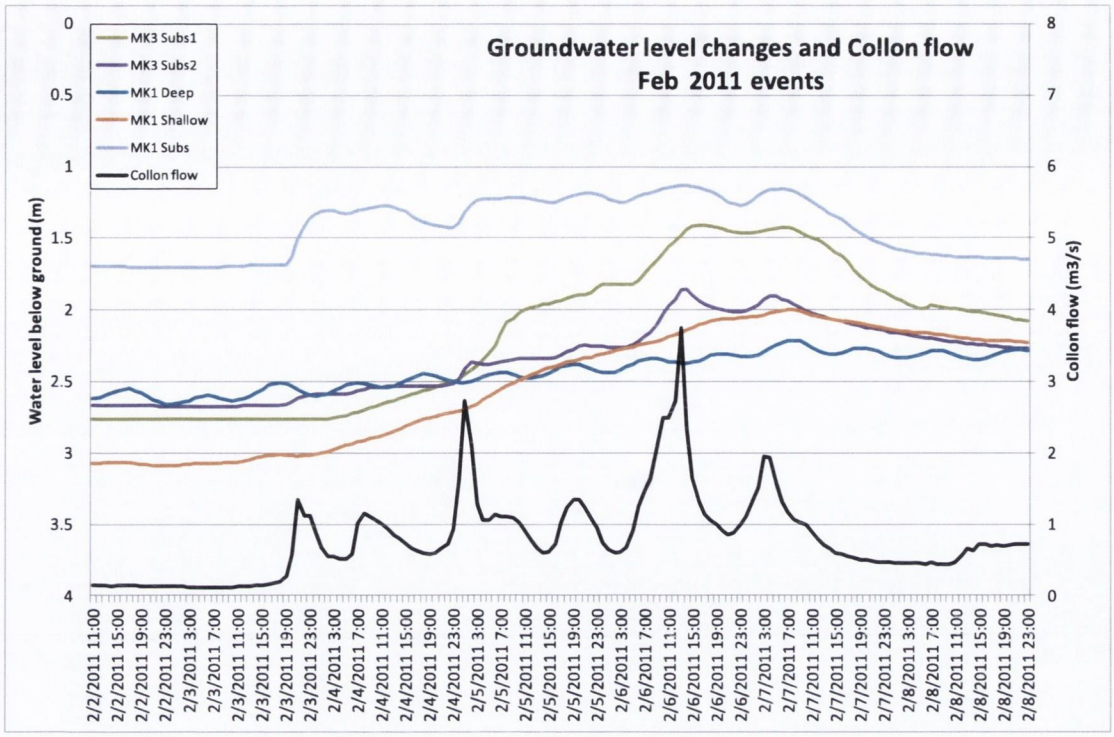

Figure 5.10. Groundwater levels and flow at Collon during the February 2011 series of events. Data are hourly. Water levels for MK2 Deep unfortunately were not available; water levels for MK3 Deep and MK3 Shallow have been omitted as they did not respond during the event.

antecedent conditions of the previous larger event. One possible explanation is that the subsurface flow paths delivering the nitrate became overwhelmed with the influx of rainfall suggesting that they may have been subsurface pathways that were close to the surface and within reach of the effects of the rainfall, rather than from the deeper groundwater pathways.

This would be consistent with the alluvium and subsoils being the sources. However, achieving adequate flow rates through these deposits to contribute to the river over the time scale of a rainfall event would depend on there being either (a) sandy/gravelly units within the alluvium; (b) land drains and/or ditches present; and/or (c) return flow leading to rapid discharge via the overland flow pathway.

During the larger events when the flow at Collon was greater than approximately 1.2 m^3/s, the nitrate–flow relationship became much more linear, reflecting the dominance of a simple dilution process with overland flow. The groundwater level data show that at this stage in the lower catchment, the sandy alluvium was fully saturated and confined under the SILT/CLAY which, assuming it was representative of the alluvium elsewhere in the catchment, would support the dominance of overland flow processes at that flow level. A similar change point was identified in the Glen Burn (refer to Figure 5.24).

5.1.4.3 January 2012 event

The January 2012 event was a project team sampling event during which the total rainfall was 27.7 mm with a maximum rainfall intensity of just 2.2 mm/h. There were three flow peaks that generated corresponding increases in the loads of most of the indicator parameters (Figure 5.11). The relationships between the timings of the flow peaks and the points of maximum contaminant load delivery varied, however, and provided insights into the transport and delivery mechanisms. As the stream began to rise, total phosphorus and ammonium loads peaked first, before the maximum flow. These parameters responded with the rain rather than with the stream hydrograph, became depleted quickly and are likely due to wash-off from point sources, potentially farmyards and other high-risk, hard stand, runoff areas. These peaks were followed by peaks in phosphate and potassium loads, which reached a maximum at approximately the same time as the maximum flow. These contaminants are likely to be transported to the river via the overland flow pathway and may represent a broader interaction with diffuse sources.

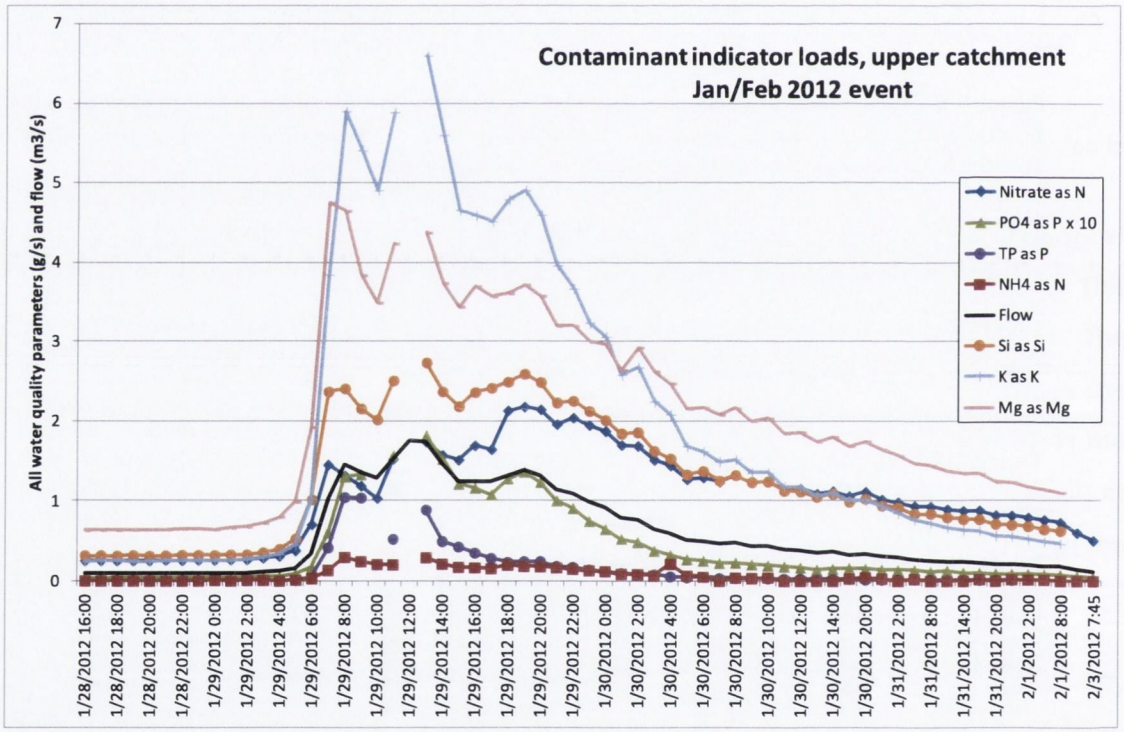

Figure 5.11. Increases in contaminant loads with flow during the January 2012 event, Mattock catchment.

The nitrate concentration in the river decreased during the event, but the total nitrate loads increased. Nitrate loads peak after the maximum flow and are correlated very well with silica loads ($R^2 = 0.95$), which suggests that nitrate is transported via a subsurface pathway with a lag in the time of maximum delivery to the stream. The relationship between nitrate and silica is strong because they are both mainly delivered via the subsurface pathways. The relationship between phosphorus and other parameters is much weaker as there are multiple sources and pathways for its delivery.

5.1.4.4 June 2012 event

The total rainfall during the June event was 40.6 mm and it came in six small events ranging in intensity from <1 mm/h to >4 mm/h. The concentrations of the parameters of interest generally behaved in the same way as during the winter event, i.e. the solutes associated with the subsurface pathways were diluted during the rainfall event and the surface pathway contaminants increased in concentration. The first increase in flow also invoked a flushing response that delivered relatively large nutrient loads in comparison to the subsequent flow peaks (Figure 5.12). The first flush was important for the delivery of ammonium, phosphate and potassium, but the highest peaks in load were coincident with the third flow peak. For total phosphorus, the second flow peak appears to be the most important period of delivery, whereas the nitrate, silica and potassium loads all behave similarly and peak with the flow. This suggests that during the first peak, there were initial flushes of small point sources adjacent to the stream, possibly from cattle access areas. As the rain progressed, overland flow developed and delivered both soluble and particulate contaminants to the stream. All the soluble contaminants continued to increase with the third flow peak, reflecting a likely increase in the contributions from both the surface and subsurface pathways as the saturated areas continued to expand.

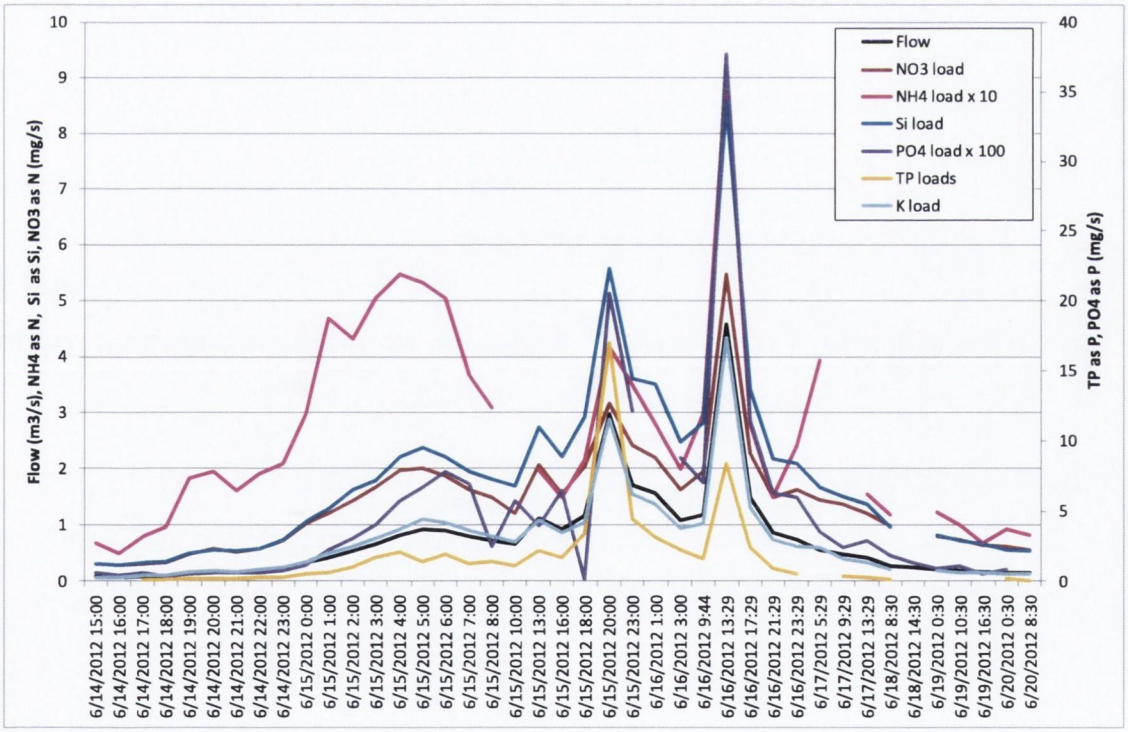

Figure 5.12. Increases in contaminant loads with flow during the June 2012 event, Mattock catchment.

The apparent lack of a third increase in total phosphorus may be simply due to the infrequency of sampling, which by that time had been reduced to every four hours. It has been observed in this catchment and elsewhere that the maximum response in total phosphorus can often lag behind

the soluble contaminants, presumably because the travel time for particulate phosphorus takes longer than for soluble phosphorus (Deakin et al., 2014).

5.1.5 Conceptual model summary

It is considered that the dominant flowpaths in the Mattock catchment are the near-surface pathways, including overland flow, and soil and subsoil water that is delivered through the artificial drainage networks, the transition zone and the shallow bedrock. In the groundwater recharge areas, the water level data showed a downward gradient, and the aquifer parameter data indicated that the upper bedrock/transition zone was the most transmissive horizon capable of moving nutrients laterally. Flow and contaminants in this zone have had greatest interaction with the soil layer. Moving down into the valley, the subsoils become thicker and low permeability soils dominate. Surface drainage networks are common to relieve poor infiltration capacity and drain high water tables, and they can deliver relatively high levels of nutrients where there are linked pressures. Bedrock groundwater is disconnected from the river in the valley floor but contributes via the drainage networks from higher up in the catchment.

Nitrate increases proportionally to the catchment area suggesting that the primary source is diffuse, although impacts from point sources, especially domestic wastewater treatment systems, have also been observed and measured in the field. The borehole data show that shallow subsoils are a key nitrate subsurface store.

Phosphorus sources are both point and diffuse with the primary diffuse delivery pathway being overland flow, although ditches are also important. The contribution of phosphorus from small point sources such as farmyards and poorly functioning domestic wastewater treatment systems, which discharge throughout the catchment into ditches, tributaries and directly into the main channel, is evident from field surveys (Finn, 2012).

5.2 Glen Burn catchment

The Glen Burn catchment, also known as the Mt Stewart catchment, is a small (5 km^2), low-lying, drumlin catchment located on the Ards peninsula in Co. Down.

5.2.1 Geological framework

The bedrock comprises greywackes and shales of Silurian age that are classified as a poorly productive aquifer, which is generally unproductive, except in local zones (Pl). Pumping tests using packers (carried out by students from Queens University) suggested that the bulk hydraulic conductivities in the bedrock decreased significantly with depth (Figure 5.13), from 10^{-1} m/d in the highly weathered zone at the top of the bedrock, i.e. the transition zone, to 10^{-2} m/d in the

shallow fissured bedrock, and 10^{-3} m/d in the deep, poorly fissured to massive bedrock (Comte et al., 2012). Geophysical borehole logging and well dilution tests suggested that only a small number of steeply dipping, discrete fractures in the bedrock were water bearing and that they were unlikely to act as a hydrological pathway link between the nutrient sources in the catchment and the Glen Burn River (Nitsche and Flynn, 2011).

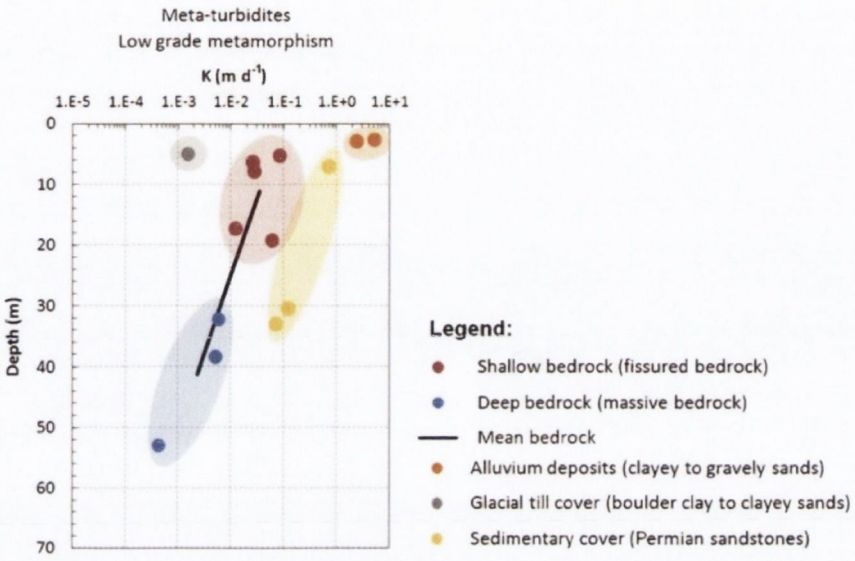

Figure 5.13. Bulk hydraulic conductivities with depth in the Glen Burn catchment based on pumping tests with packers (from Comte et al. (2012)).

The most permeable bedrock groundwater pathway in the catchment is therefore the upper weathered bedrock, although resistivity surveys found that there was strong spatial variability in the degree of weathering (Comte et al., 2012). Lateral hydraulic gradients were of the order of 0.05 to 0.07 based on the borehole data, and the direction and orientation was not found to vary significantly between seasons (borehole locations are shown in Figure 4.3).

Drumlins comprising low permeability soils and glacial till 15–20 m thick, overly the bedrock. The hydraulic conductivity of the till is similar to the deep bedrock at 10^{-3} m/d (Figure 5.13). In the inter-drumlin areas, the rock is close to the surface and the thin soils and subsoils are poorly drained (Figure 5.14). The groundwater vulnerability, mapped using the Geological Survey of Ireland methodology, ranges from Low vulnerability on the drumlins to Extreme in the inter-drumlin areas (Meredith, 2010). The presence of groundwater gleys in the catchment area of the main tributary, known throughout the project as Calvert's tributary, indicates that soils and subsoils in the inter-drumlin areas are often saturated. Peat and organic alluvial deposits are present in the upper part of the catchment, and there is an important area of alluvial sands and gravels that is connected to the stream in the lower catchment (Figure 5.14).

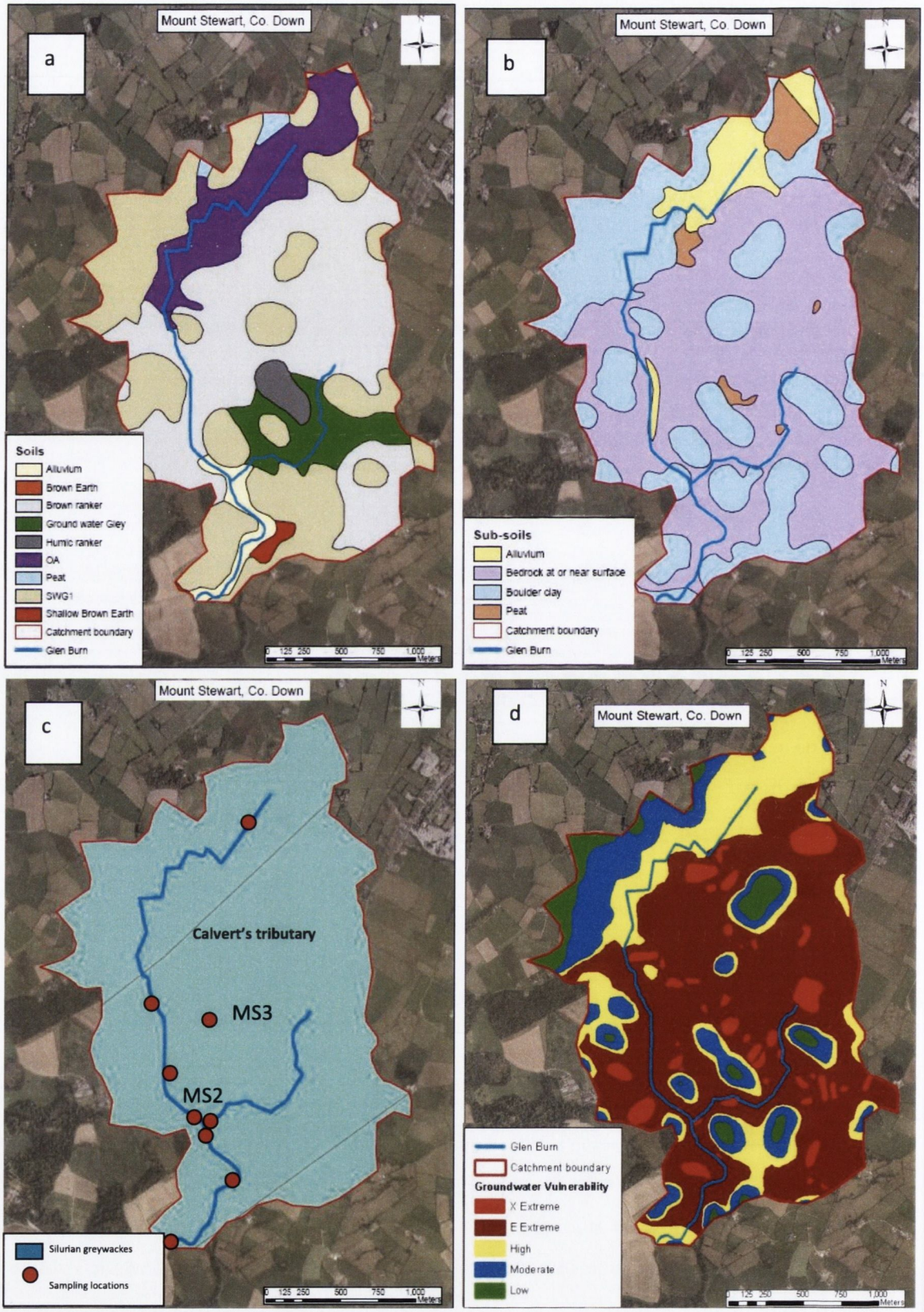

Figure 5.14. (a) Soils; (b) subsoils; (c) bedrock and river sampling locations; and (d) groundwater vulnerability using the Geological Survey of Ireland mapping scheme (Meredith, 2010).

5.2.2 Land use

Land use in the catchment comprises approximately 82% intensive pasture with some areas of tillage (10%) and small areas of woodland (5%), with the remaining area consisting of diffuse rural settlement and roads (Meredith, 2010). Septic tanks and farmyards are common, and cattle have direct access to the stream, particularly in the lower catchment, although they are housed in winter (Finn, 2012). Many of the small farmyards do not have slurry storage and faecal matter is soaked in bedding which is then stored before land spreading. Three applications of slurry is common practice in the headwaters, decreasing to one or none in the lower catchment (Meredith, 2010). Nutrient sources are spread widely around the catchment and are from both point and diffuse sources, although there are typically larger nutrient management risks in the upper catchment.

5.2.3 Pathways

5.2.3.1 Stream flows

Stream flows in the Glen Burn were monitored for 2 years (2011–2013), at two locations, MS2 at the catchment outlet and MS3 downstream of Calvert's tributary (Figure 4.3). Flows at the catchment outlet ranged from less than 0.001 m^3/s to greater than 1.11 m^3/s, based on the available data. The mean recorded discharge was 0.07 m^3/s and the median discharge was significantly lower at 0.037 m^3/s. The large difference of greater than 47% suggests that the stream responds quickly to rainfall and is 'flashy' (O'Brien, 2013). The stream has been heavily modified (Figure 5.15) and it is known on the basis of two different surveys (Meredith, 2010, Finn, 2012) that some 7.2 km of land drainage works has been undertaken.

There was a strong power law relationship ($R^2 = 0.86$) between the flows in the upper catchment headwaters, just downstream of the organic alluvium and peat deposits, and those at the catchment outlet (Figure 5.16). The upper catchment (see Figure 4.3 for location) contributed more than 60% of the flow to the stream when the flows were <10 m^3/s at the catchment outlet, which has important implications for understanding the fluxes of nutrients in the stream in the summer months.

5.2.3.2 Groundwater levels

Groundwater levels were monitored over the same period in five boreholes within the monitoring suite, which is identified in Figure 5.17. At BH6, which is completed in the bedrock close to the stream, groundwater was confined beneath the low permeability clayey till in all seasons, as it was at BH2, which is located on a drumlin. In contrast, at BH5, which is also in the river valley but

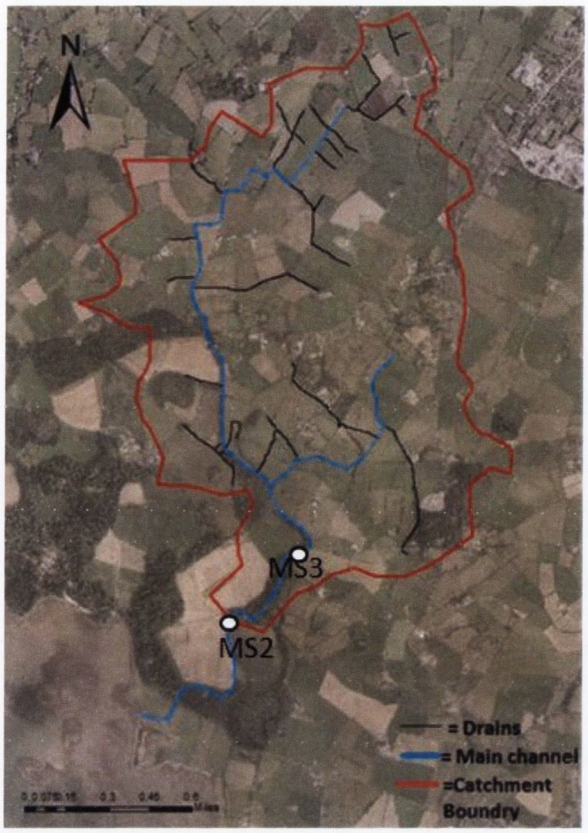

Figure 5.15. Presence of mapped artificial drainage in the Glen Burn catchment (Finn, 2012). MS2 and MS3 are the two main catchment sampling points (refer to Figure 4.3).

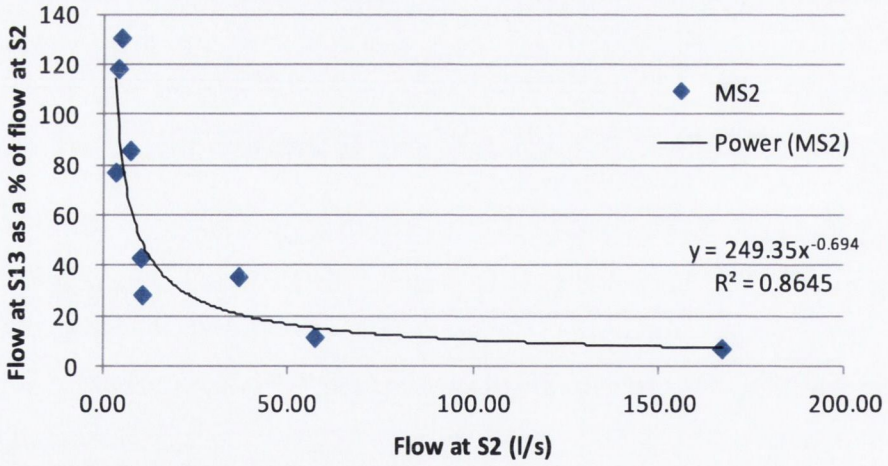

Figure 5.16. Comparison of flows in the upper catchment (S13) with those at the catchment outlet (MS2).

completed in the alluvial sands and gravels, it is evident that although the alluvium was fully saturated during the winter, it was partially dewatered in the summer for at least some periods. A similar response was apparent in the weathered bedrock in BH1 near the catchment divide. Thus, groundwater confined beneath the low permeability glacial tills is likely to be protected from nutrients applied at the surface, whereas the alluvial deposits and the shallow unconfined bedrock are likely to be transport pathways where there are source pressures present.

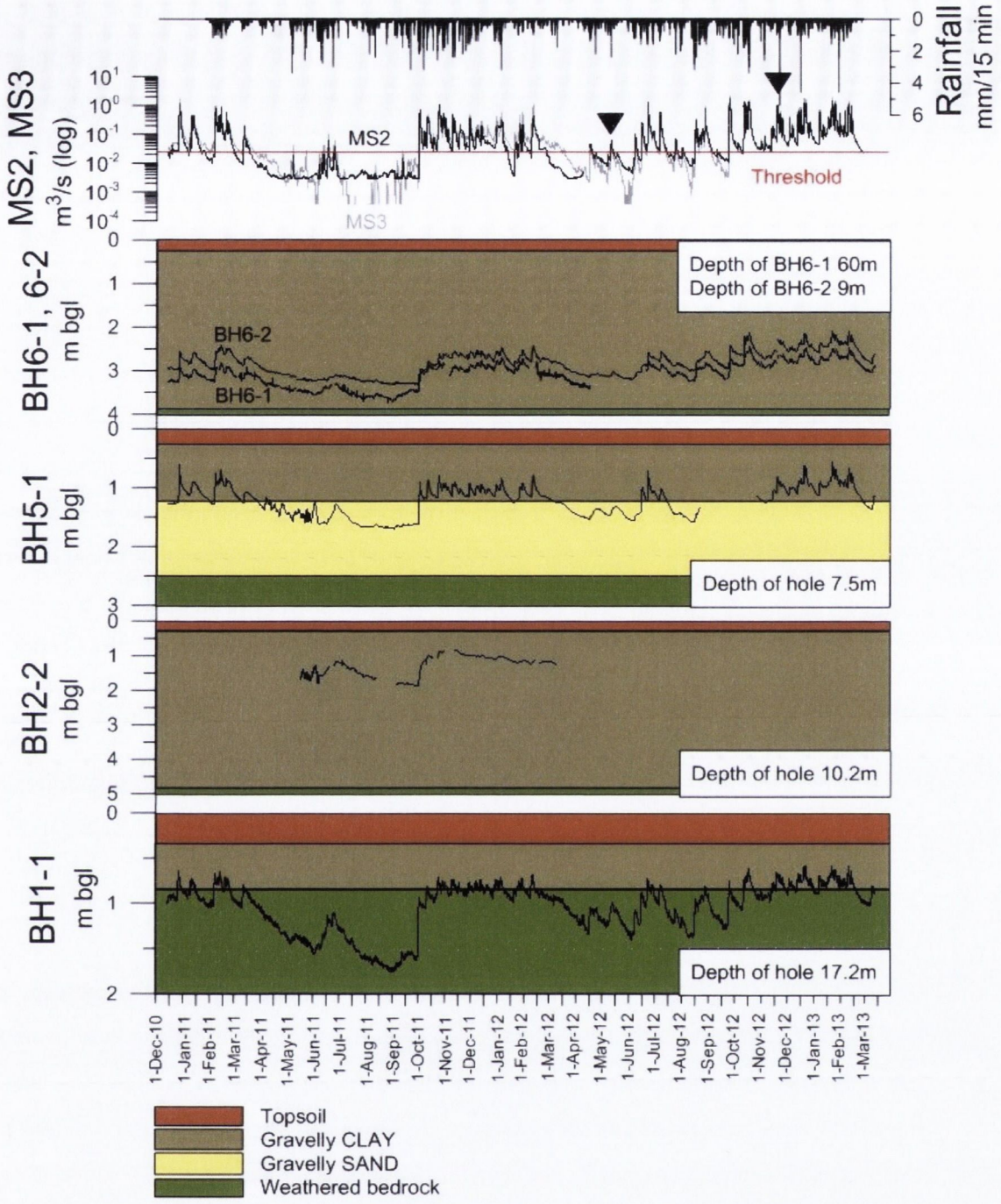

Figure 5.17. Groundwater level hydrographs in relation to the geological profiles at four of the monitoring boreholes. The river flow hydrographs for the two flow monitoring stations (MS2 and MS3) are also shown for the same period. The black triangles indicate the dates of the event sampling. The dashed lines highlight a period of high groundwater levels which resulted in high baseflows in the stream above the threshold level.

Comparison of the river flow hydrographs with the groundwater level data and the geological profile (Figure 5.17) revealed that there was a significant increase in the flow in the stream when the weathered bedrock (BH1) and alluvial aquifers (BH5) became fully saturated, and that the flow remained above a threshold until the groundwater levels fell to below the clays once more,

despite a decrease in rainfall. For example, in October 2011, a significant rain event resulted in the water levels in BH1-1 and BH5-1 rising sufficiently to become confined under the clays. As BH1-1 is near the catchment divide in the shallow weathered bedrock, and BH5-1 is in the alluvium in the stream channel, this suggests that these highest permeability geological units were likely to have been saturated throughout the catchment. They are unlikely to have been confined throughout the catchment however, particularly in the inter-drumlin areas where subsoils are shallow. The flow in the stream during the period when these units were full increased dramatically from 0.010 m^3/s to just less than 0.030 m^3/s. The stream flow remained above that threshold level until late February 2012, when the water levels in BH 1-1 and BH 5-1 dropped beneath the level of the clays again and were no longer fully saturated. This period is highlighted between the dashed lines in Figure 5.18. This suggests that the shallow groundwater pathway in the upper weathered bedrock, i.e. the transition zone, and the alluvium deposits play a significant role in generating stream flow when they are fully saturated, not only in terms of a direct contribution through taking advantage of the full depth of transmissivity when water tables are high, but also indirectly: when the storage in the shallow bedrock layers is already full, there is no opportunity for any further recharge, and therefore more will be rejected via the overland flow and drainage flow pathways. The dominant pathways contributing flow to the stream are therefore likely to be different above and below the threshold point when the aquifers become saturated. This threshold point corresponds to a flow of approximately 0.027 m^3/s at the catchment outlet (Figure 5.17).

5.2.3.3 Flow duration curves

Log-normal flow duration curve plots, for both MS2 and MS3, highlight the pathway changes (Figure 5.18). Different rates of change in flow are represented by the changes in slope on the plot and reflect the contributions of the different pathways. The steeper the slope, the less storage there is and the quicker the pathway response. Six periods of stream flow with different pathway characteristics can be identified for the Glen Burn.

The flow data suggested that the flow at MS3 was usually higher than the catchment outlet at MS2. Additional flow measurements carried out at both sites, and elsewhere throughout the catchment, confirmed that this was not due to a problem with the rating curves (Gregory, 2012). The shape of the contours on the 5 m digital elevation model, and a gravel pit marked on the old 6-inch sheets, suggest that there may be a palaeochannel or a major fault to the east of the stream between the gauges that takes water out of the catchment via a different route at the mid-range flow levels (Deakin et al., 2014). Discharge may also be bypassing the MS2 gauge through the gravels at the catchment outlet.

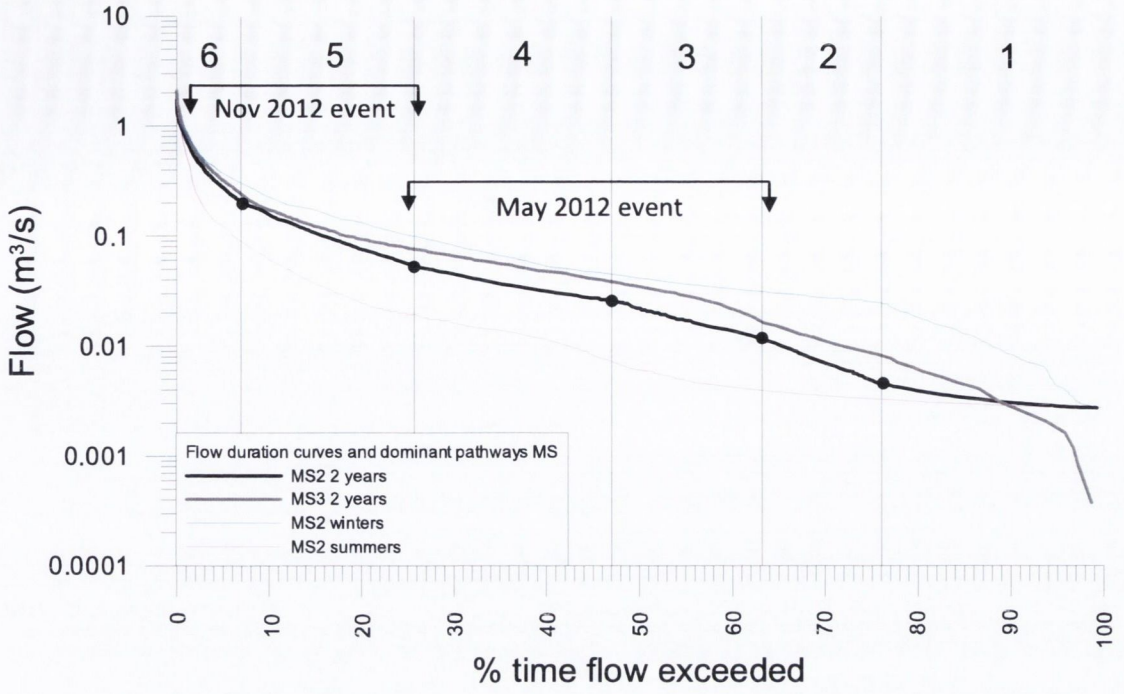

Figure 5.18. Comparison of flow duration curves (15-min data) for 2 years of data for the subcatchment at MS3 and the catchment outlet at MS2, with the winter and summer flow duration curves for the catchment outlet. Flows are typically higher at MS3 than MS2 because of the loss of water from the lower catchment. The closed circles indicate significant changes in slope, which divide the curve into six flow segments. These are considered, based on the flow and chemistry data, to represent flow periods with different pathway characteristics. The range of flows captured during the two events is indicated by the arrows.

5.2.3.4 Electrical conductivity

Analysis of the continuous electrical conductivity measurements in the stream and spot measurements from the boreholes and near-surface pathways at different flow levels provided supporting evidence to characterize the six stream flow bands[6]. There was a general decrease in electrical conductivity in a downstream direction, and also with increasing flows. There were also seasonal relationships and different relationships depending on whether or not the aquifers were fully saturated (Figure 5.19). Electrical conductivity tended to be higher in summer for the same given flow than in winter, possibly reflecting impacts of higher land-use pressures. When the aquifers were fully saturated, stream flows were higher and electrical conductivity were consequently lower because in the wetter antecedent conditions, catchment runoff had less interaction time with the soil. In contrast, in the drier conditions when the aquifers were not fully saturated, there was greater infiltration of rainfall, more mixing within the pathways and longer lag times in flow transport, which resulted in higher electrical conductivity. The larger variations in electrical conductivity in summer 2011 in comparison to summer 2012 when the aquifers were

[6] Different approaches to utilising the electrical conductivity data were taken in the three catchments due to the availability of data, the usefulness of the approaches given the nature of the hydro(geo)logical conditions in each catchment, and the questions to be addressed in developing the conceptual model.

not full, may be a result of the wetter summer in 2012, which maintained surface land-use pressures at generally more dilute concentrations overall.

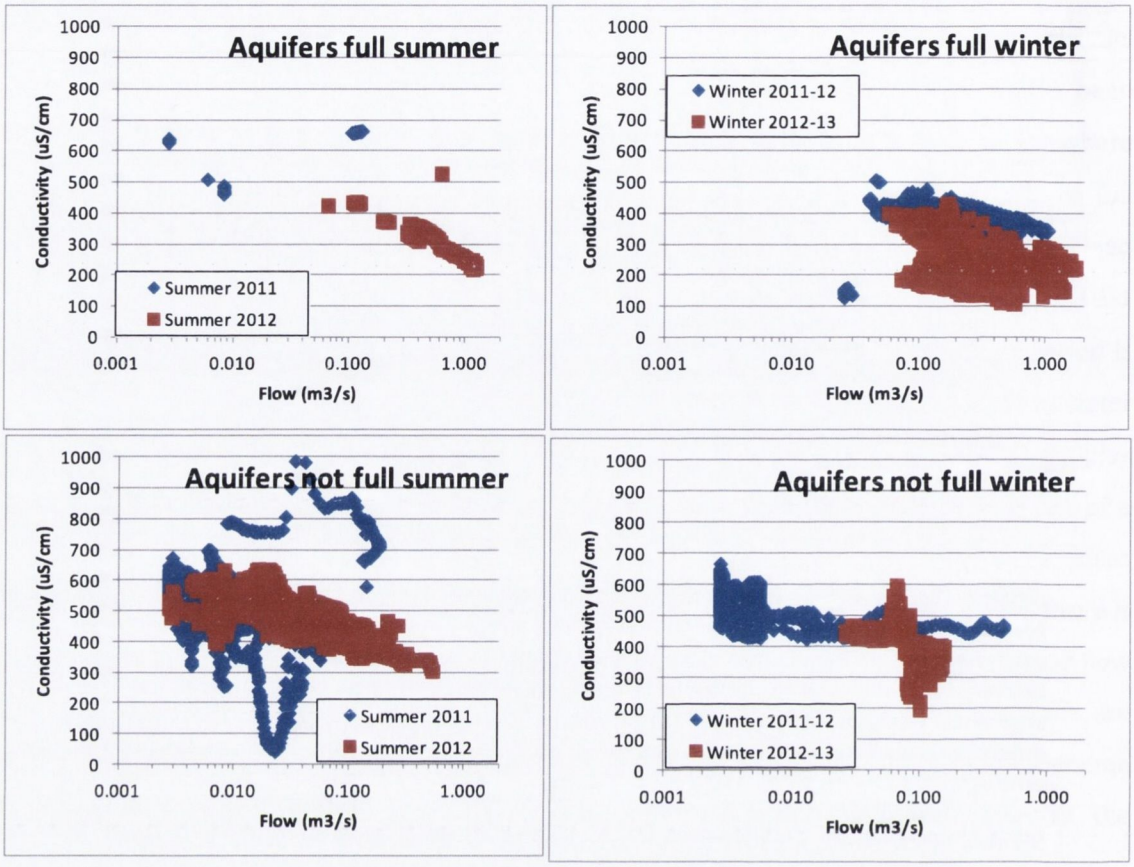

Figure 5.19. Relationship between flow and electrical conductivity at the catchment outlet under different aquifer and seasonal conditions.

Comparison of the 15-min electrical conductivity data for the stream at the catchment outlet during each of the six flow bands described in Figure 5.18, highlighted the different patterns in electrical conductivity responses (Figure 5.20). Electrical conductivity was at its highest (Table 5.1) in bands 1 and 2 during the low flows (<0.012 m^3/s) when water from the upper catchment and bedrock was dominant. The greatest fluctuations in electrical conductivity were seen in bands 3 and 4, between 0.012 and 0.055 l/s, when the lower flows were significantly diluted with rainfall during events. At the highest flow levels in bands 5 and 6, the electrical conductivity was at its lowest and it decreased more uniformly with flow. This reflects periods when the near-surface and shallow groundwater storage is full and the quick overland flow pathways are dominant. High peaks in electrical conductivity were observed on occasion during most of the flow bands and are likely to reflect flushes of contaminant-rich water. This finding is supported by the catchment-wide biological and water quality sampling carried out as part of the *Pathways Project* (Deakin et al., 2014).

Spot measurements of electrical conductivity were taken from groundwater in the boreholes on a number of occasions over the 2-year period, whereas the near-surface pathways were sampled

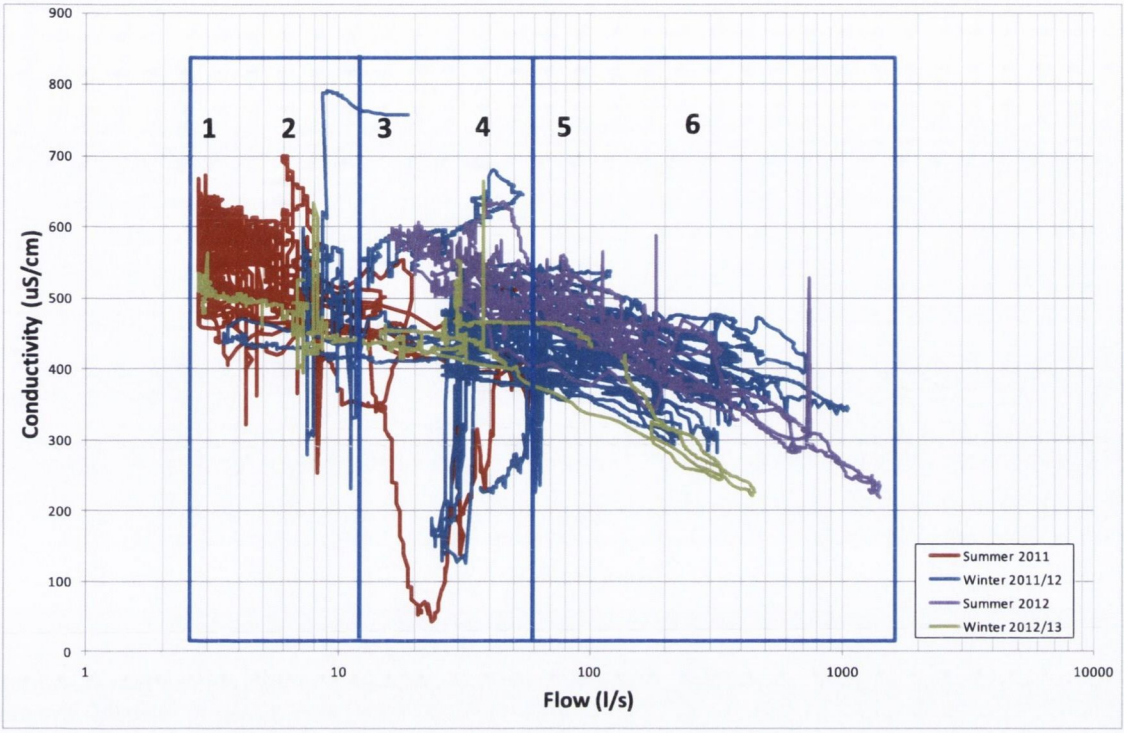

Figure 5.20. Seasonal changes in electrical conductivity with flow in the six different flow bands at the catchment outlet, based on 2 years of 15-min data from 2011 to 2013. Summer, April–September; Winter, October–March. The most important changes in electrical conductivity occur between pairs of flow bands which are marked with the solid blue lines.

Table 5.1 Electrical conductivity in the stream at the catchment outlet in each of the six flow bands. Based on 2 years of 15 min data from 2011 to 2013.

Flow band	Type of flow	Flow m^3/s	Electrical conductivity (µS/cm)				
			Mean	St Dev	No.	Summer*	Winter*
1	Very low flow	<0.0045	569	47	11659	581	498
2	Low flows, upper catchment dominates	0.0045–0.012	491	55	3101	543	473
3	Low flows, below threshold, aquifers not fully saturated	0.012–0.027	502	97	3688	540	463
4	Medium flows, aquifers saturated	0.027–0.055	483	67	10672	518	456
5	High flows, aquifers saturated, near-surface pathways dominant	0.055–0.2	448	59	8526	469	427
6	Very high flows, overland flow dominant	>0.2	370	59	2437	361	374

*Mean values in summer, April to September inclusive; and winter, October to March inclusive.

during the events. The electrical conductivity was found to increase with depth (and longer residence times based on the transmissivity values), from a median of 356 µS/cm in the shallow transition zone boreholes where the flow is typically more transient, to 544 µS/cm in the deep bedrock (Figure 5.21).

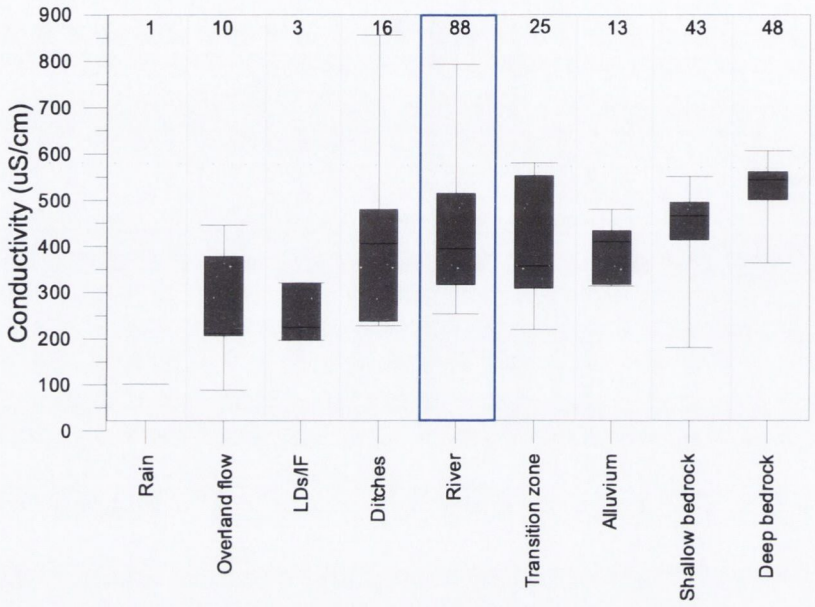

Figure 5.21. Electrical conductivity characteristics of water from the different pathways, based on spot measurements in the boreholes over a 2-year period and in pathways during the events. The numbers at the top of the plot are the number of samples for each pathway. Electrical conductivity values for the river are from grab samples taken at the catchment outlet (MS2) concurrently with the other samples, rather than the logged values presented in Figure 5.21. LDs/IF = land drains/interflow.

In the near-surface pathways, the mean electrical conductivity of overland flow was 244 µS/cm, although the range from 89 to 446 µS/cm suggests that some of the flow on the land surface was in fact flow from deeper depths. This was supported by the major ion chemistry (Deakin et al., 2014) and was also reflected in the relatively high mean electrical conductivity of 370 µS/cm in the very high flows in band 6, when overland flow would be expected to dominate. There were few land drains located for sampling in the catchment; it was observed that drainage ditches were the favoured type of drainage works. This may be due to the high water tables in the inter-drumlin areas and the gentle gradients. Nevertheless, the mean electrical conductivity in the few land drains that could be sampled was 239 µS/cm, whereas the ditches had a signature closer to the alluvium and transition zone (406 µS/cm). This suggests that the land drain signatures, and some of the overland flow samples, were those of soil water, whereas the ditches were generally draining shallow groundwater/transition zone water. The latter was corroborated by field observations of outcrop in the ditches, particularly in the upper and mid-catchment areas. The inter-mixing of water from different pathways, particularly the near-surface pathways, is therefore quite important in this catchment where the depth to bedrock is shallow. This has implications for the hydrograph separation techniques that are discussed further in Section 6.2.2.

5.2.4 Nutrient transfer

Two events were intensively sampled in the Glen Burn catchment in May 2012 and November 2012. The events were similar in magnitude (~20 mm) and maximum intensity (3 mm/h), but the duration of the May event was more than twice that in November, which meant that the average rainfall intensity was much lower. The peak flow level of the May event was also approximately the same as the baseflow level before the November event (Figure 5.18); consequently, the November antecedent conditions were much wetter and the response in the river was therefore much greater. The responses of the nutrients in the river during the two events were different, reflecting the different hydrological pathways and land-use activities prevalent at the time. An initial section presents the background and event nutrient data for each of the pathways. This is then followed by a discussion on the pathways transferring nutrients during the events.

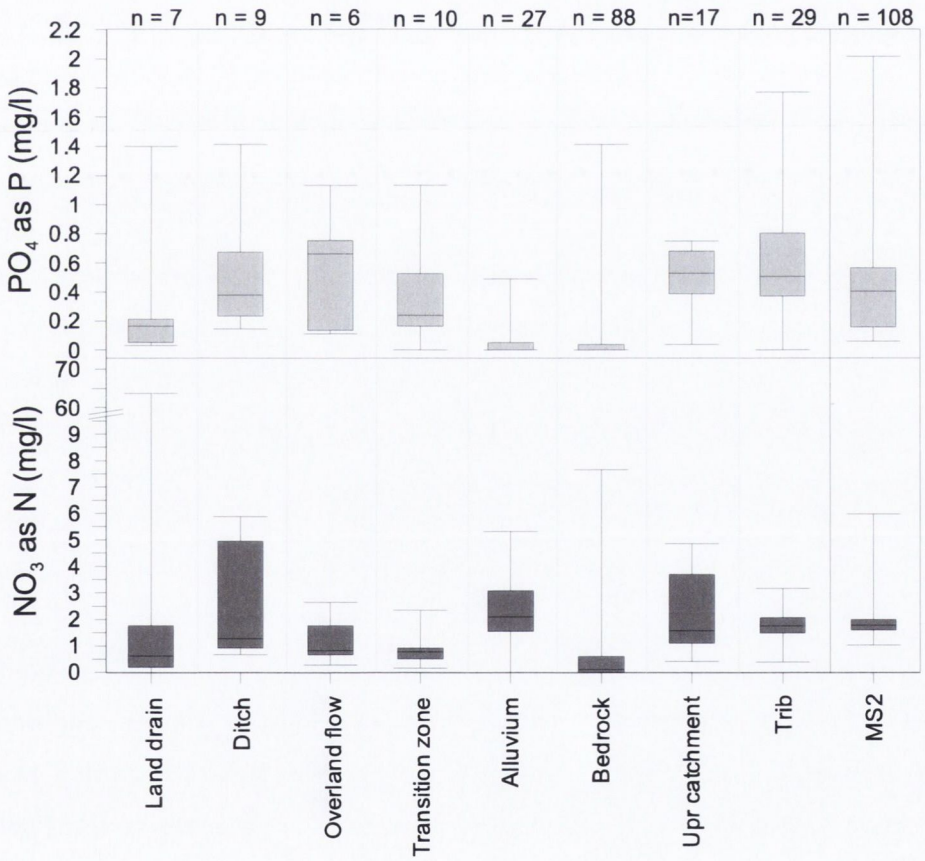

Figure 5.22. Pathways as sources of nutrients in the Glen Burn catchment. The data presented represent all the available data from each pathway. Sampling in land drains, ditches and overland flow pathways was opportunistically carried out throughout the catchment during events (and so was limited). Data for the transition zone, alluvium and bedrock were collected from the monitoring boreholes during events and background groundwater sampling campaigns. Data for the upper catchment, tributary and at MS2 were all taken from the river and were collected during events and background sampling campaigns. Refer to Figure 4.3 for borehole and river sampling locations.

5.2.4.1 Pathways sampling

The available nutrient data for the different pathways and the river at the catchment outlet, the upper catchment and the tributary provided insights into the most important nutrient delivery pathways (Figure 5.22). The upper catchment and Calvert's tributary were relatively high in nutrients which confirmed the results of the land-use surveys that suggested that those areas had higher pressures. The bedrock groundwater (shallow and deep combined) was not typically a source of nutrients although the transition zone was important for phosphorus, whereas the alluvium was high in nitrate. Overland flow was a key contributor of phosphorus, and the ditches often contained nitrate and phosphorus. Few land drains were sampled but the available data suggested they were not a dominant nutrient source. However, there was one land drain sampled that was very high in both nitrate and phosphorus but it is suspected that it is directly connected to a farmyard upgradient.

5.2.4.2 May 2012 event

During the summer event, there were three separate increases in contaminant concentrations and loads, which reflected different combinations of sources and pathways (Figure 5.23). At low flows prior to the event, nitrate concentrations at the catchment outlet were low (5 mg/l as NO_3) but phosphorus concentrations were very high at 0.14 mg/l total phosphorus as P. A small spike in most of the contaminant indicators (nitrate, ammonium, total phosphorus, molybdate reactive phosphorus (MRP), total suspended sediment, chloride, potassium and electrical conductivity) but not in flow or silica, was evident in the stream in the early evening, prior to the rain starting. This may be due to the impacts of small point sources without dependencies on hydrological flowpaths, such as domestic wastewater treatment systems, consistent with findings in other studies in similar catchments (Jordan et al., 2012).

A second, much larger spike occurred as the river began to rise in response to the rain. There were increases in concentrations and loads of all the contaminant indicators, but there was also a decrease in electrical conductivity and in many of the major ions, and a gentle increase in silica. Peak contaminant concentrations occurred before the first peak in flow and were much larger at the catchment outlet than at a second sampling point in the mid-catchment upstream of the tributary. This emphasizes the importance of the reach between the sampling points and Calvert's tributary as a source of nutrients. This spike represents the delivery of source-limited contaminants to the river via a quickflow pathway as the rain started and the river began to rise. Higher levels of ammonium could potentially be consistent with incidental losses of manure at cattle access points, for example. The low ion concentrations point towards a limited, but gradually increasing, contribution from the subsurface at this stage.

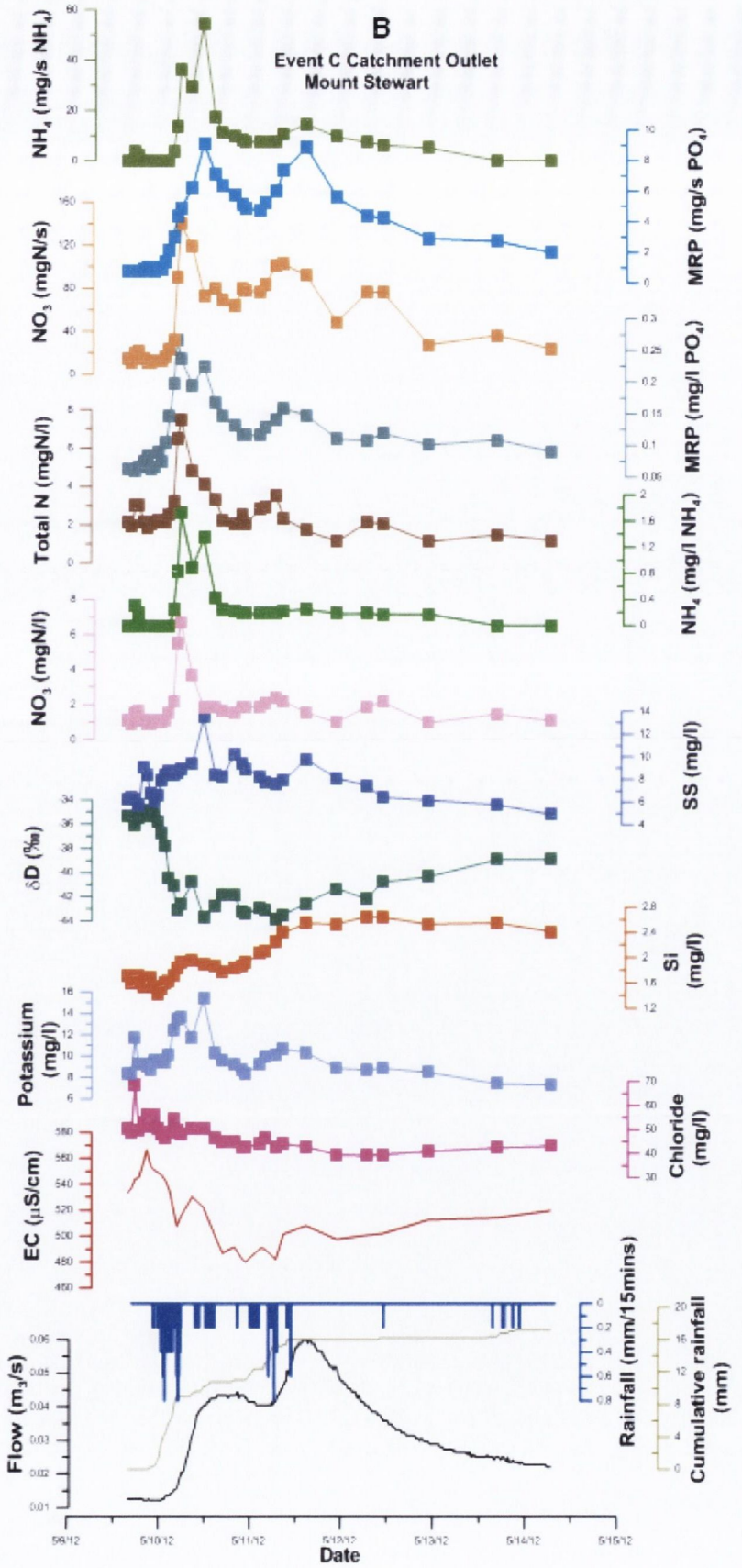

Figure 5.24. Changes in chemistry and flows with rainfall at the catchment outlet during the May 2012 event (Deakin et al., 2014).

Two days after the initial rainfall event, a second pulse of rain and subsequent increase in flow up to 0.06 m^3/s, delivered a third spike that had lower contaminant concentrations, but still relatively high contaminant loads. It was also associated with slight increases in electrical conductivity, a gradual increase and then stabilizing of silica concentrations and significantly higher silica loads. The increase in ion concentrations suggests that the shallow groundwater pathway was having more influence at this flow level. The relationship between flow and nitrate concentration also changed to a linear increase and decrease with flow, rather than the hysteretic effects seen at lower flow levels (Figure 5.24). This may be because the shallow groundwater inputs became more significant and delivered more distal diffuse sources of nitrate, which became dominant, reducing the relative impacts of small point sources. The concentration of phosphorus increased slightly during this last peak, and the load increase was similar in size to that previously observed in the second spike. It is suspected that this was due to expanding saturated areas adjacent to the river and drainage network channels that brought in additional nutrient sources.

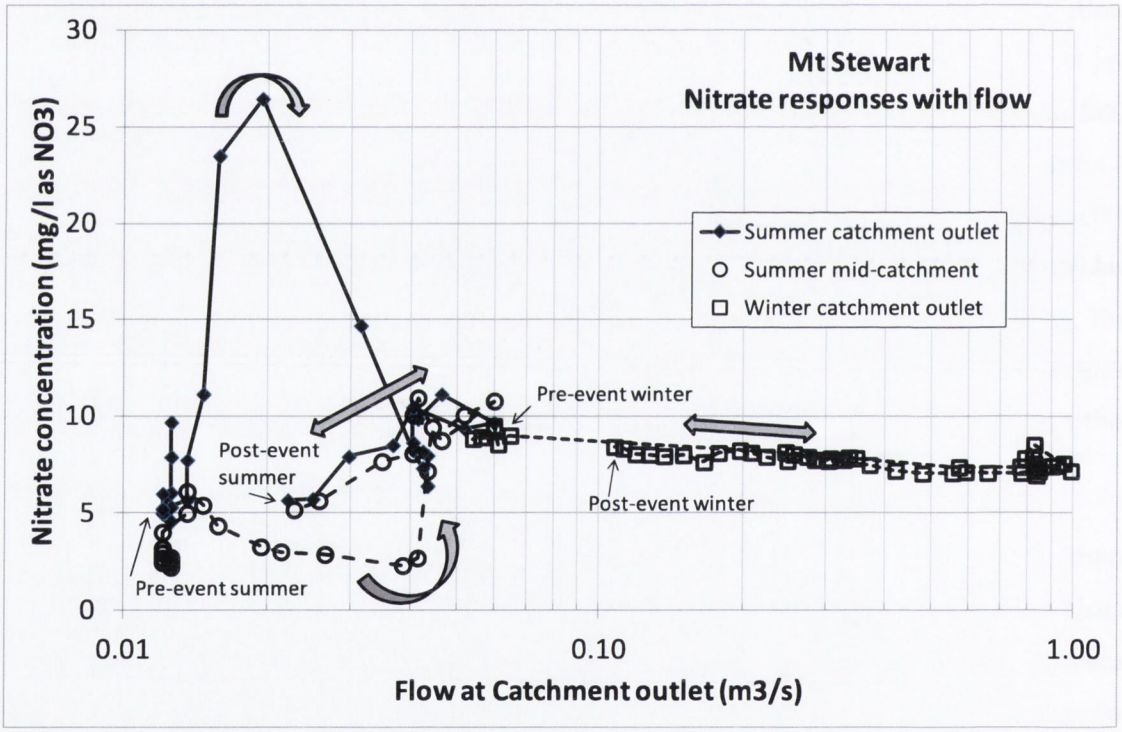

Figure 5.24. Changes in nitrate concentration with flow at the catchment outlet and a mid-catchment location upstream of Calvert's tributary and sampling locations during the 2012 summer event. Grey arrows indicate the directions of progression of the events. Double-ended arrows indicate the periods when the relationship between nitrate concentration and flow became linear.

5.2.4.3 November 2012 event

During the November event, the flow and chemistry relationships reflected more uniform dilution with rainfall (Figure 5.25). This is because there was no soil moisture deficit (Devlin, 2012), the

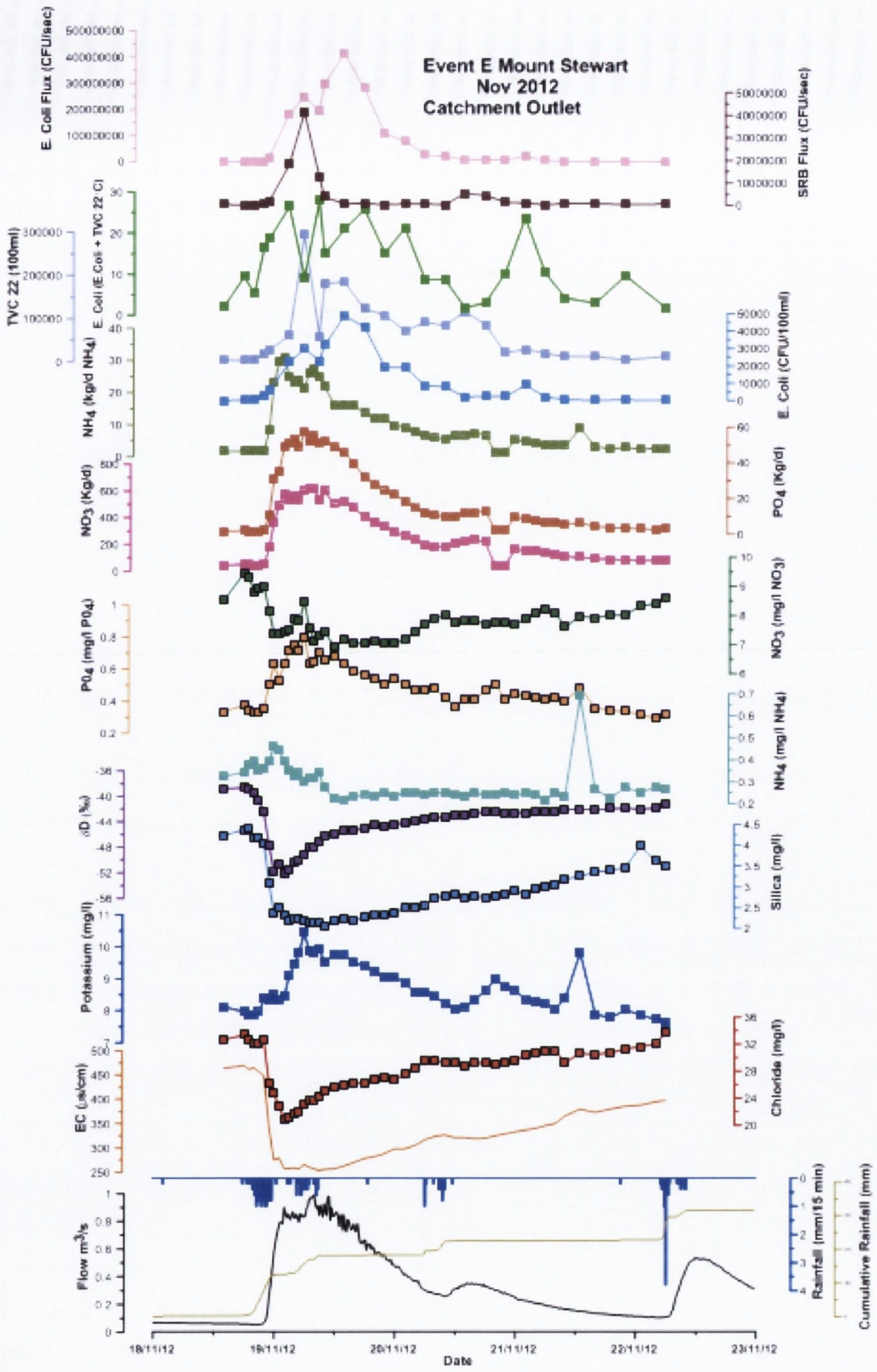

Figure 5.25. Changes in chemistry and flows with rainfall at the catchment outlet during the November 2012 event (Deakin et al., 2014). CFU, colony forming unit; SRB, sulphate reducing bacteria; TVC, total viable count.

shallow bedrock, subsoils and soils were fully saturated, the water table and river discharges were higher, and the nearer-surface pathway contributions were likely to have been important. A slight early increase in nitrate concentrations, as well as in phosphate, chloride and ammonium, was again observed in the evening just as the rain was starting. The concentration increases were smaller than during the summer event as they were diluted by the higher baseflows, but the nitrate load was five times higher than during the first summer event spike. The presence of point sources in both seasons was supported by principal component analysis carried out on each dataset (further described in Chapter 6) that showed that there was at least one distinct contamination signal comprising NH_4, P, NO_2 and/or NO_3 in each event.

As the stream began to rise, a second pulse of high ammonium occurred briefly, before it became diluted with the high flows and remained at a lower concentration for the rest of the event. The load also decreased as the event progressed, which again suggests a source that was depleted with the rainfall. Phosphate and potassium concentrations and loads increased with the high flows and reduced during the recession, peaking 6 h later than the ammonium. Nitrate concentrations showed broadly the opposite trend with a close relationship between increasing flow and gently decreasing nitrate concentration (Figure 5.24), although there were small increases in concentration close to the peak flow that matched the increases in phosphorus and potassium. The nitrate load also increased with flow overall and there were no threshold changes evident. This suggests that the nitrate and phosphorus were largely delivered via different pathways. It is likely that the nitrate was derived from soils, subsoils and the transition zone, and released via the drains and ditches, whereupon it was diluted by overland flow. The phosphorus and potassium increases with rain are likely to be due to increases in the extent of the saturated area, which mobilized new nutrients via overland flow. Silica, chloride and other major ion concentrations, as well as electrical conductivity, all decreased during the event, consistent with a soil and shallow groundwater/transition zone source diluted by overland flow.

5.2.5 Conceptual model summary

The geological framework, being generally poorly drained and low permeability, lends itself to a predominance of flows via the near-surface pathways. Based on the hydraulic conductivity data, apart from the alluvium, which is geographically constrained, the most permeable subsurface geological horizon is the transition zone at the junction between the rock and the overlying soils. This horizon is close to the surface in the inter-drumlin areas and it is in these areas that the extensive network of drains and ditches has been developed to try and alleviate the often saturated conditions (Figure 5.26).

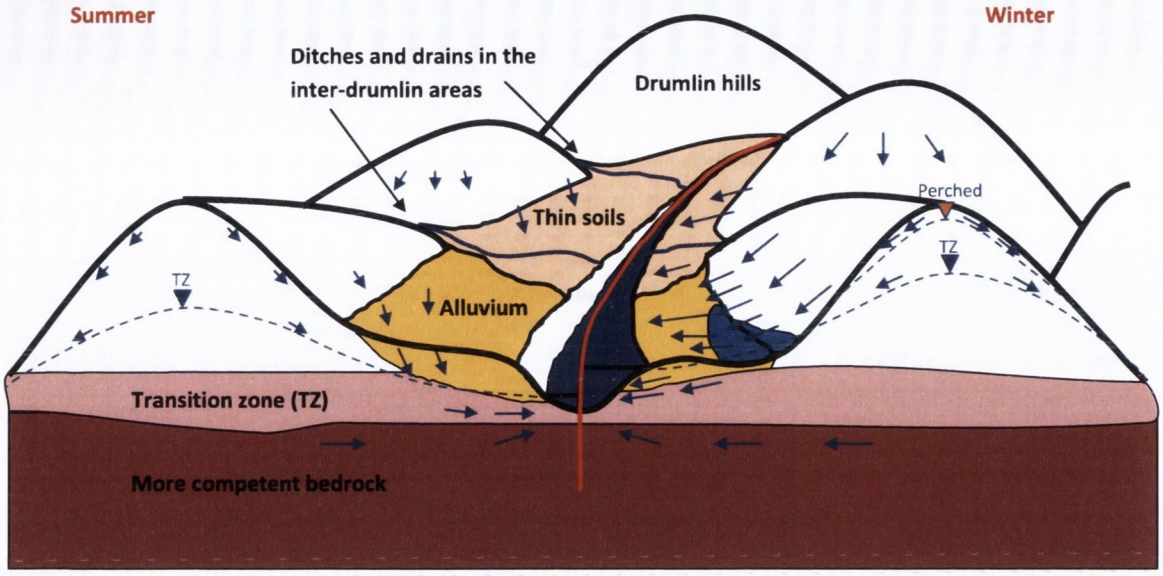

Figure 5.26. Conceptual model of flow pathways in the drumlin topography in the Glen Burn catchment. The pathways to the left of the diagram are present in summer when the groundwater table is low; to the right the nearer-surface pathways are more dominant when the water table is higher.

When the discharge at MS2 is greater than 0.027 m^3/s, the aquifers are typically full, there is a larger contribution of shallow groundwater and transition zone water to the stream, and overland flow responds quickly. Below the threshold, the aquifers are unsaturated, there is greater infiltration and mixing in the shallow subsurface, baseflow contributions are low and there is very little overland flow.

The available nutrient data suggest that the river is affected by small point sources, in particular with respect to phosphorus, which is evident in the stream at very high concentrations for a large portion of the year including in dry weather. This finding is supported by background and event microbiological sampling carried out in the catchment by others (Deakin et al., 2014). The key diffuse pathway for the delivery of phosphorus is overland flow. The ditches are also important, which is likely to be due to a combination of direct inputs from small point sources (e.g. domestic wastewater treatment systems, animal access points and farmyards) as well as diffuse inputs from the drained transition zone under thin soils in the inter-drumlin areas.

The alluvium, and the shallow bedrock and transition zone, where they are intersected by the ditch network, are the key nitrate delivery pathways. This is notwithstanding the results shown in Figure 5.22 which suggest the transition zone and shallow bedrock have low nitrate concentrations. This apparent contradiction is because the boreholes that have provided the groundwater nitrate data have all been installed in one part of the catchment, on or around a

drumlin, where the shallow groundwater is confined beneath the low permeability tills. These environments present favourable conditions for the attenuation of nitrate. In contrast, in the inter-drumlin areas over the majority of the catchment, where the shallow bedrock and transition zone are unconfined under thin soils, there is likely to be greater throughput of water throughout the year. There is a higher likelihood that the ditch and field drain network in these areas drain nitrate-rich waters. Further specific investigatory field work in these areas would be beneficial.

5.3 Gortinlieve catchment

The Gortinlieve catchment is a small (4.3 km^2) subcatchment of the River Foyle, located near Newtown Cunningham in Co. Donegal. The upper part of the catchment is steeply dipping to the south and southwest, from the most north-easterly point at 234 m OD, to 40 m OD in the mid-catchment at the river flow gauging station, a gradient of 0.15. The lower catchment has a much more gentle gradient of 0.007 to the catchment outlet at 17 m OD. This gives rise to different hydrological regimes in the upper and lower catchments.

5.3.1 Geological framework

The catchment is underlain by Pre-Cambrian quartzites, gneisses and schists that are classified by the Geological Survey of Ireland as a Poor aquifer that is Generally Unproductive, except for Local Zones (Pl). Research carried out as part of the *Griffith's Project* (Comte et al., 2012) has found that in contrast to the greywackes in the Glen Burn catchment, the decrease in bedrock hydraulic conductivity with depth observed at Gortinlieve is only approximately half an order of magnitude (Figure 5.27), which is attributed to the deep weathering profile, as observed in resistivity profiles. The weathering is also responsible for the larger spatial variation in lateral hydraulic conductivity within the shallow bedrock zone, which was found to increase by a factor of four to five from the catchment divide to the valley bottom (Comte et al., 2012).

Two dominant fracture sets were previously identified but geophysical borehole logging and well dilution tests suggest that only a small number of discrete features were water bearing in the secondary set corresponding to a NE–SW/NNE–SSW trend (Nitsche and Flynn, 2011). The two tributaries in the catchment also follow this same orientation, so their alignments may be being controlled by the hydrogeological structure.

The subsoils in the catchment are mainly low permeability glacial tills derived from the Pre-Cambrian rocks, which increase in thickness from <1 m on the higher ground, to more than 5 m in the valley floor (Figure 5.28). There are localized areas of alluvium present along the river valley, which comprise clay, silt, peat and thin horizons of clayey gravel and have a bulk hydraulic

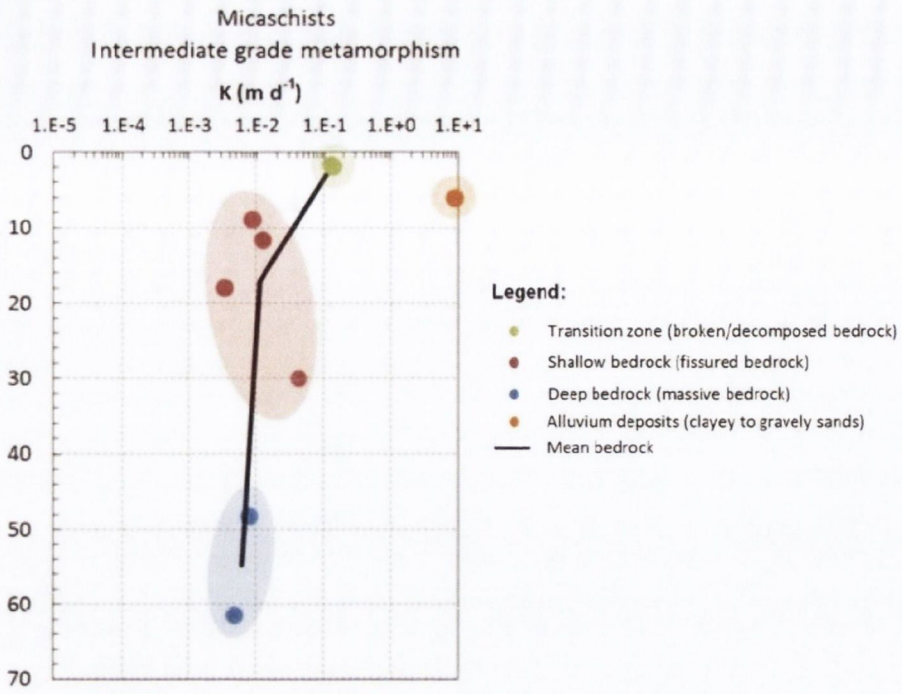

Figure 5.27. Comparison of hydraulic conductivity in the transition zone, alluvium, shallow bedrock and deep bedrock in the Gortinlieve borehole transect (modified from (Comte et al., 2012)). Y-axis is depth (m) below ground surface.

conductivity of the order of 10 m/d, based on borehole pumping tests (Comte et al., 2012). Hydraulic conductivity data were not available for the tills, but they are likely to be comparable with those in the Glen Burn, i.e. at least three orders of magnitude less than the alluvium.

5.3.2 Land use

Landowner interviews and a walkover survey conducted in 2011 found that the catchment comprised less pasture (63%) and more arable (23%) land than in the Glen Burn, with 7.5% forestry, 3.5% peat bog and 3% artificial surfaces such as farmyards and single dwellings (Mackin, 2011). The rural catchment population of approximately 120 people is served by domestic wastewater treatment plants. Discharges of farm/silage effluent into the river have been observed on a number of occasions during the summer months (Deakin et al., 2014).

5.3.3 Pathways

5.3.3.1 Stream flows

Similar to the Glen Burn, the stream at Gortinlieve is flashy, with a median flow of 0.065 m^3/s and a much larger mean flow of 0.113 m^3/s based on the available data. In contrast however, the Gortinlieve catchment has higher effective rainfall and the catchment is much wetter; the actual evapotranspiration is almost the same as the potential evapotranspiration, which highlights that

there is rarely a soil moisture deficit (O'Brien, 2013). Land-use surveys (Mackin, 2011) have found that the catchment is extensively drained, particularly in the lower catchment (Figure 5.29). Stone and piped land drains are in place within the fields and drain directly to the stream, tributary or drainage ditches. Deep drains have been excavated at the major break in slope.

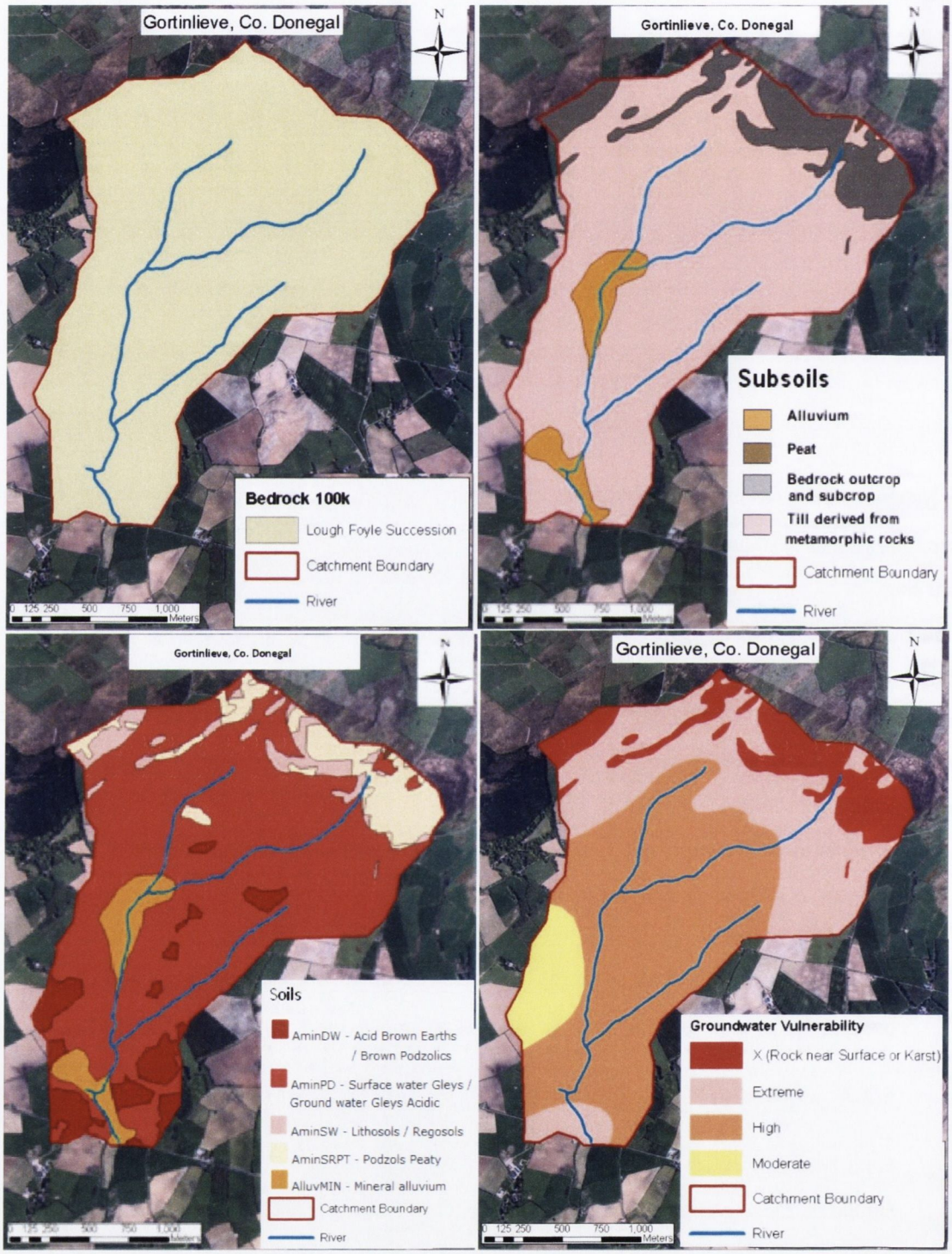

Figure 5.28. Gortinlieve catchment maps: (a) Bedrock; (b) subsoils; (c) soils; and (d) groundwater vulnerability (Deakin et al., 2014).

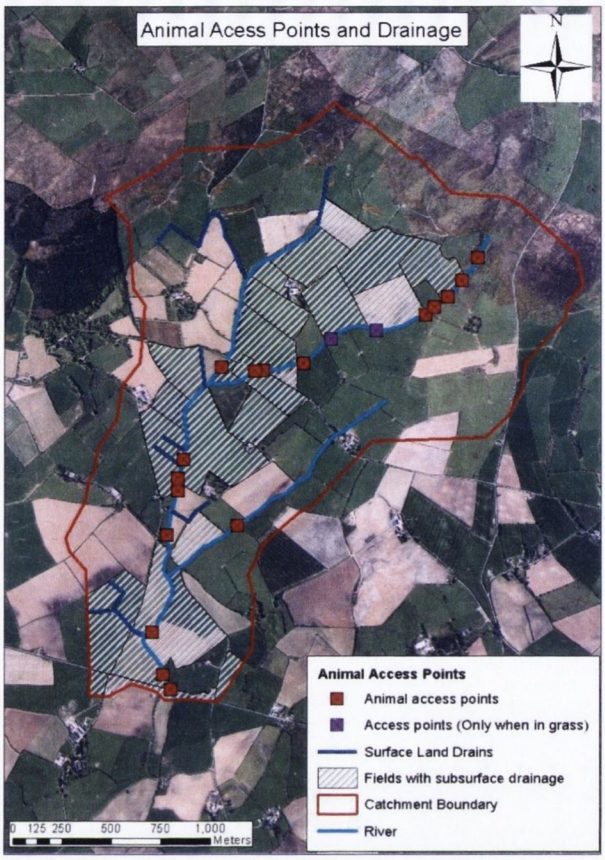

Figure 5.29. Drainage in the catchment, with observed cattle access points to the streams (Mackin, 2011). Note that 'surface land drains' as mapped by Mackin are referred to as ditches here.

5.3.3.2 Groundwater levels

Groundwater level data were available at a 15-min timestep for the EPA boreholes from November 2009 to February 2013 (Table 5.2). The data show that there was typically a downward gradient to the deep bedrock in the upper (GO1) and middle clusters (GO2), and while the transition zone water levels responded to rainfall, there were no such responses in the shallow and deep bedrock. At GO3, however, which is in the lower catchment where the topographic gradients are less steep, there was typically an upward gradient from the shallow and deep boreholes into the transition zone, and a downward gradient from the subsoils into the transition zone (Figure 5.30). The relationship between the water levels in the subsoil and in the shallow groundwater varied with antecedent conditions. In wet conditions, the subsoil head was higher, whereas in dry conditions the reverse was the case, although the difference was small at <10 cm. The piezometric levels in all boreholes responded to rainfall. The range in water level fluctuations was greatest in the transition zone at GO2, followed by the shallow bedrock and transition zone at GO1, and the subsoils at GO3. There was very little fluctuation in water levels in the deeper horizons at GO3 close to the river.

Table 5.2. Groundwater level data (m OD) for the EPA boreholes. 15-min data from November 2009 to February 2013.

	GO1			GO2			GO3			
	Trans	**Shallow**	**Deep**	**Trans**	**Shallow**	**Deep**	**Subs**	**Trans**	**Shallow**	**Deep**
Min	173.24	172.45	169.56	82.49	83.14	76.91	31.16	31.13	31.25	31.93
Max	175.02	174.46	171.16	89.58	85.45	79.04	32.74	32.09	32.09	32.86
Range	1.78	2.01	1.60	7.09	2.31	2.14	1.58	0.96	0.84	0.93
Mean	174.16	173.92	170.49	88.90	84.54	78.04	31.70	31.49	31.64	32.39
Stdev	0.36	0.41	0.32	0.31	0.50	0.42	0.26	0.14	0.15	0.15

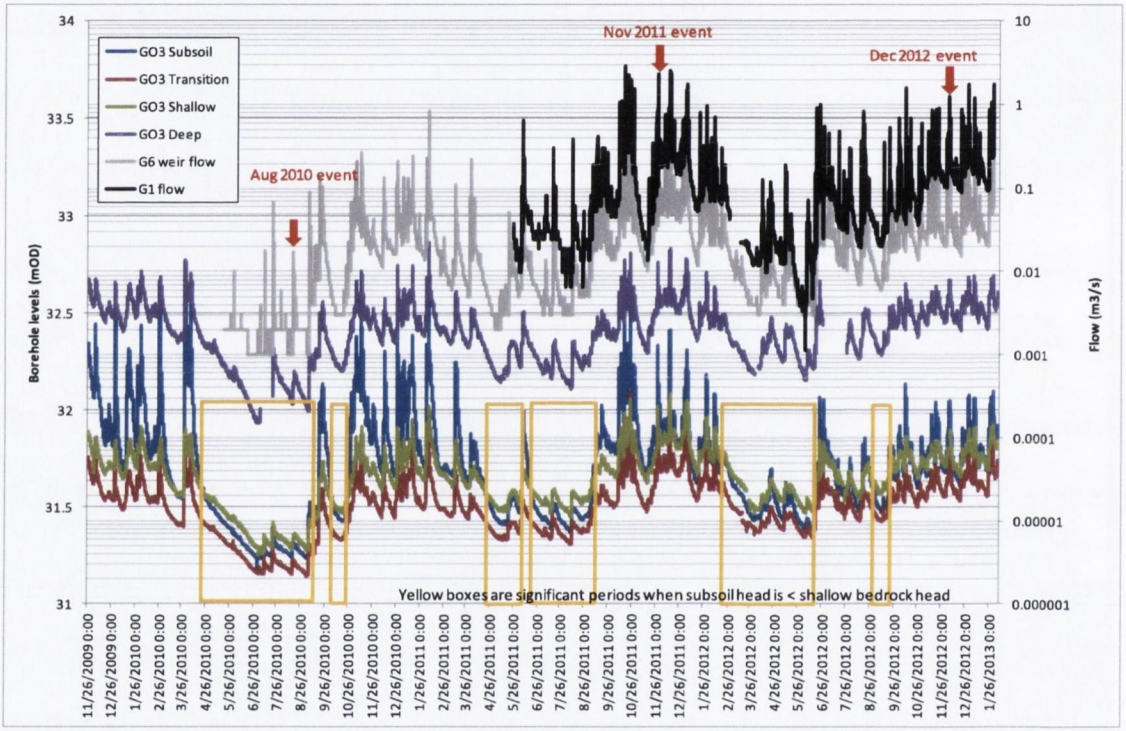

Figure 5.30. Water levels in the boreholes at GO3 close to the stream, with the available stream flow data. Yellow boxes are significant periods when the subsoil head is less than the shallow bedrock head.

These data indicate that in the river valley, the transition zone was the primary discharge zone for upwelling bedrock groundwater, which is corroborated by the higher hydraulic conductivities than the deeper bedrock horizons. Away from the river, in the upper and mid-catchment areas, the transition zone captured the recharge infiltrating downwards and delivered much of it laterally before it reached the deeper bedrock horizons. The reduction in hydraulic conductivity with depth was sufficient to support the higher fluctuations in head in the transition zone, and the buffering of the underlying bedrock groundwater from the influences of rainfall. The transition zone was therefore important at all levels in the catchment, but it operated in hydrologically different ways in groundwater recharge and discharge areas.

5.3.3.3 Electrical conductivity

Five longitudinal stream profiles of electrical conductivity were carried out in the Gortinlieve catchment between March 2012 and February 2013 (O'Neill, 2013). The profile carried out during the highest flow (0.2 m^3/s at the catchment outlet) is shown in Figure 5.31. The results show that the numerous land drains and ditches discharging into the main channel typically had higher electrical conductivity than the stream water. It is known that some of the drains and ditches were connected to point sources, but the majority were draining water from the soils, subsoils and transition zone.

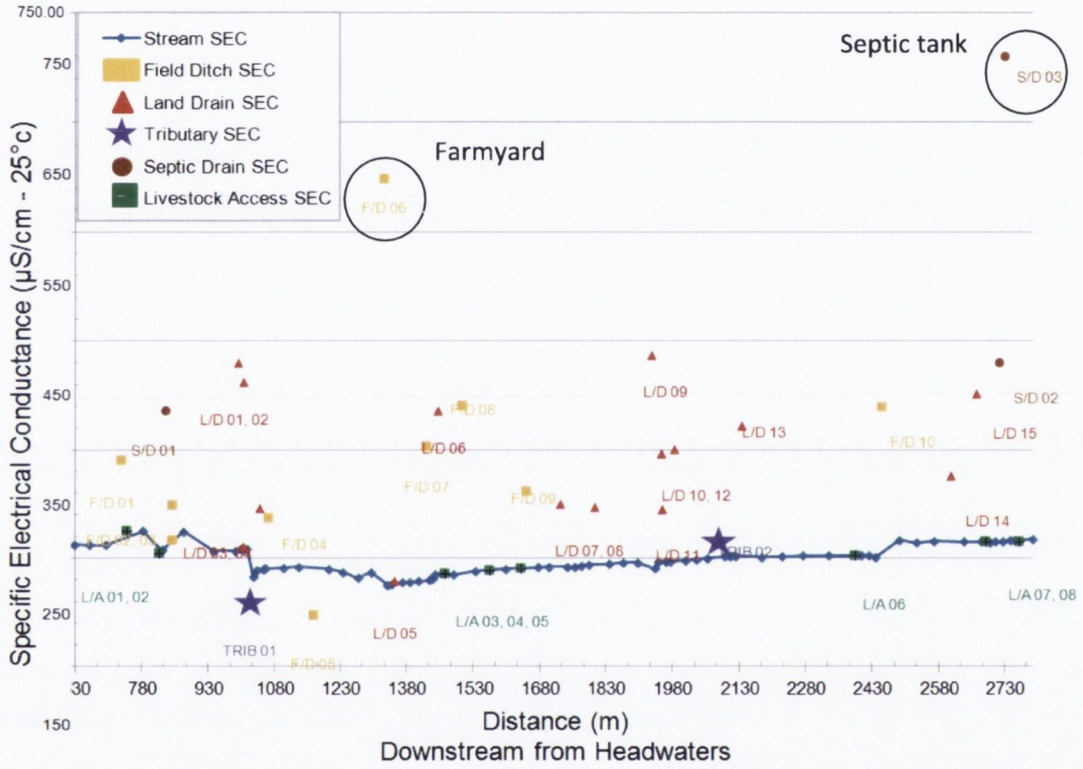

Figure 5.31. Gortinlieve stream electrical conductivity profile 10 December 2012 (O'Neill, 2013). The impacts of point sources in a land drain and ditch are highlighted in the circles.

Review of the available data for the EPA boreholes showed that in the upper and middle catchment clusters, the electrical conductivity increased with depth, reflecting the downward gradients and longer residence times in the deeper boreholes (Figure 5.32). The shallow bedrock groundwater borehole at GO2 was slightly elevated, which together with the high total coliforms, very low nitrate, increased MRP and the presence of ammonium, provided evidence of contamination. At GO3 near the stream, the electrical conductivity increased moving up the profile from the deep groundwater to the transition zone, consistent with the upward gradients. The electrical conductivity in the land drains and ditches identified through the in-stream profiling were similar to those for the shallow bedrock at GO1, the transition zone at GO2 and the alluvium

at GO3, suggesting that they drained water from increasingly shallow origins moving down into the valley, consistent with the upward gradients.

5.3.4 Nutrient transfer

5.3.4.1 Pathways sampling

At the GO1 and GO2 clusters, the depth to rock is <1 m and the vulnerability of groundwater to contamination is therefore Extreme (X-Extreme). Cattle grazing is the main pressure at GO1 and there is a farmyard close to the boreholes at GO2. The thin soils mean that contaminants infiltrate readily and rapidly with recharge. The transition zone typically had increased phosphate and nitrate concentrations (Figure 5.32), which together with the relatively high transmissivities, indicated that it was a significant pathway for nutrient transport. Concentrations of nitrate decreased with depth and there was evidence, based on the ammonium, dissolved oxygen concentrations and redox potential, that attenuation was taking place: dissimilatory reduction of nitrate to ammonium (DNRA) at GO1, and denitrification at GO2 (Orr, 2014). Concentrations of phosphate also decreased with depth. In the recharge areas therefore, the primary pathway for nutrient transport is the transition zone.

At the GO3 cluster in the groundwater discharge zone near the river however, nitrate, ammonium, MRP and coliforms were very low in all pathways, except the subsoils where total and faecal coliforms and ammonium were quite high. With the upward groundwater gradients and the low nutrient concentrations at depth, the bedrock groundwater and transition zone pathways are unlikely to be significant contributors of nutrients. The most important store of nutrients at this location was the subsoil. However, the subsoil profile was variable in the four boreholes drilled at this location, and is likely to be variable throughout the valley. It comprised a thin sequence of gravels or silts, overlain by 2.5 to 5 m of thick clays and peat. Thus, in order for the subsoils to be an effective nutrient transport pathway, the nutrients from the grazing pressures have to bypass the clays and silts to gain access to the more permeable layers at depth, and those layers then have to be connected to the river.

The available land drain, ditch and overland flow data are limited (Figure 5.33), but they suggest that overland flow and ditches are the most important transport pathways for phosphate, whereas none of these pathways could have provided sufficient nitrate to increase the stream concentrations to the levels observed. This emphasizes the importance of the deeper pathways nitrate delivery in this catchment, which based on the findings in the boreholes (Figure 5.32) is likely to be the transition zone in the groundwater recharge areas, such as at the GO2 borehole cluster.

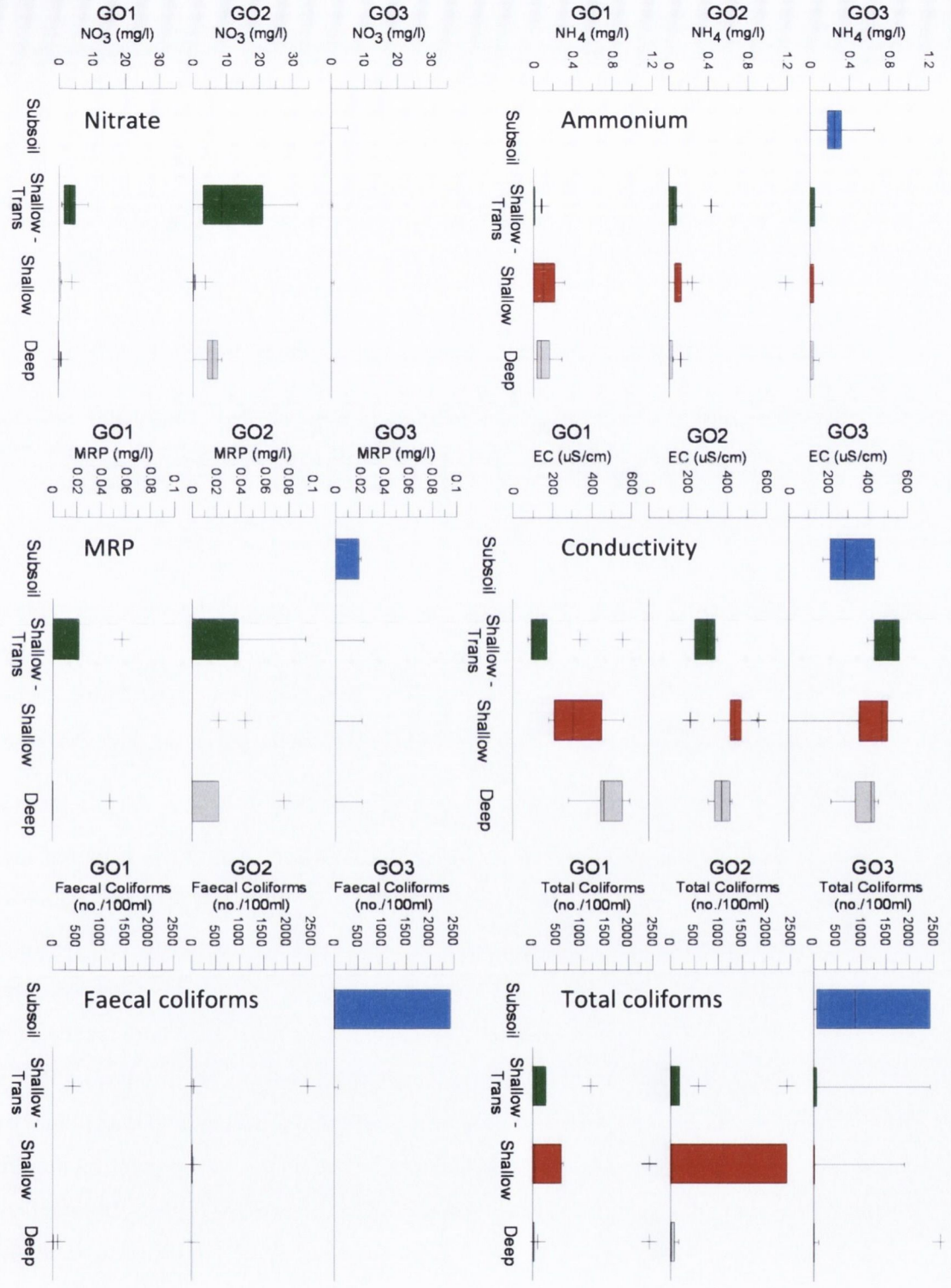

Figure 5.32. Contaminant indicators in subsoil and groundwater pathways in the Gortinlieve EPA borehole clusters. Based on quarterly sampling between June 2009 to July 2012 (n = 14) (Figure drawn by A. Orr and reported in Deakin et al. (2014)).

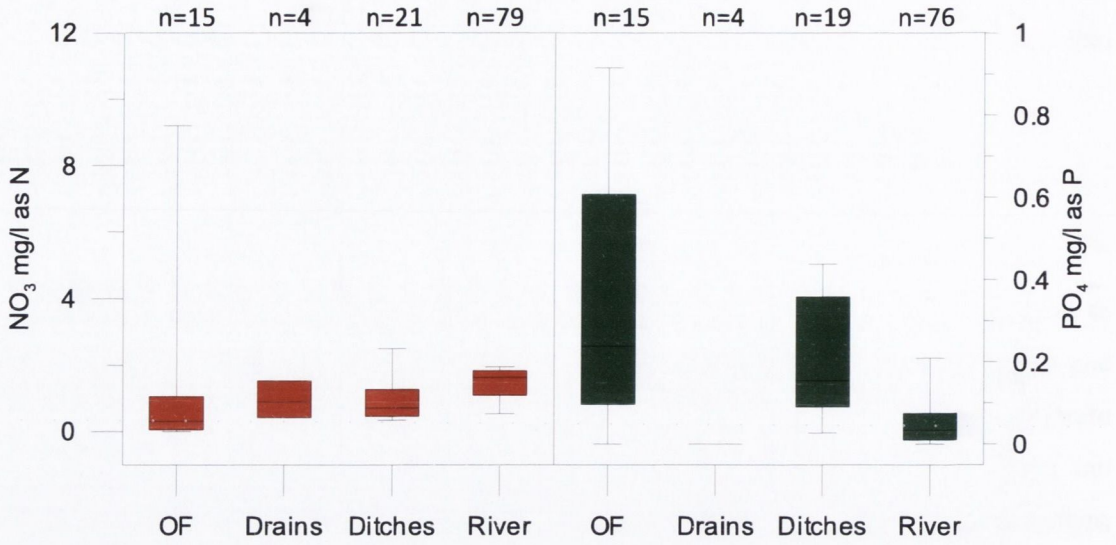

Figure 5.33. Concentrations of nitrate and phosphate in overland flow, land drains and ditches at Gortinlieve during two events in November 2011 and December 2012, in comparison to the longer-term river data. OF = overland flow; Drains = land drains.

5.3.4.2 August 2010 event

A small event with a maximum flow of 0.016 m^3/s recorded at the mid-catchment EPA weir, was captured in August 2010 (Figure 5.34). Samples for the catchment outlet were not available. The total rainfall was 18.6 mm but there was a relatively high maximum rainfall intensity of >3 mm/h for 3 h. Water levels were low prior to the event and there was an upward gradient from the shallow groundwater into the transition zone and the subsoils, indicating that the antecedent conditions were dry.

Contrary to most of the events sampled during the *Pathways Project*, most of the measured parameters in the river water samples increased in concentration and loads in response to the rain. The soluble constituents all peaked with the flow suggesting that they were delivered with the dominant flow path which, based on the groundwater level and the chemistry data, was likely to have been the transition zone. The particulate parameters peaked 1 h later, at the same time as the maximum dilution in calcium and magnesium, but receded quickly. The soluble contaminants remained elevated for some time longer and the calcium and magnesium took yet longer to recover. This is consistent with a significant, but brief fresh water contribution from the surface bringing the particulate constituents and diluting the subsurface flow. Observations from the field suggest that this may have been the sudden connection of overland flow to the river via the large ditches on both sides, at the break in slope above the sampling location (Deakin et al., 2014). The soluble contaminants in the transition zone were depleted next, followed by the bedrock groundwater component, as represented by the calcium and magnesium.

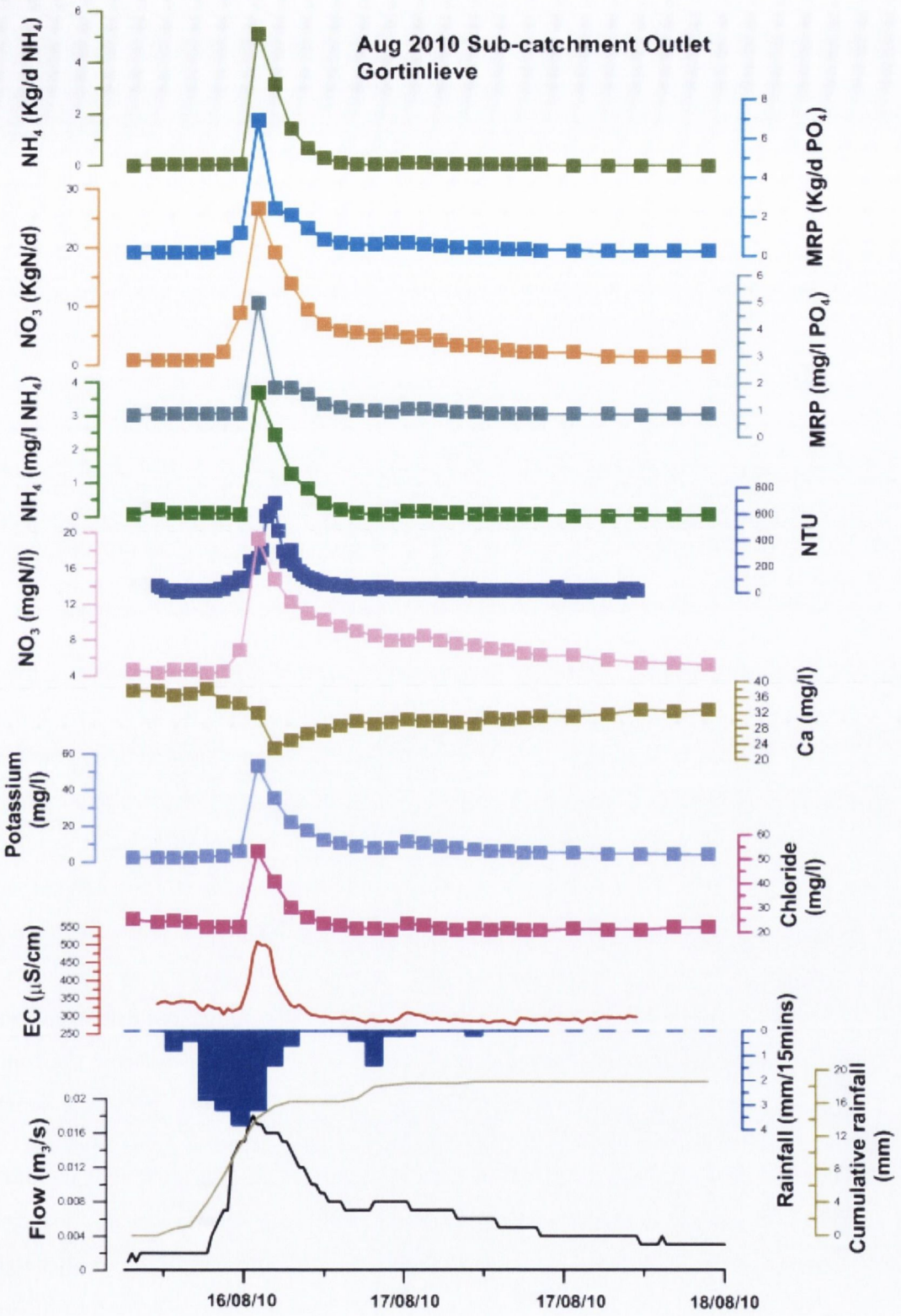

Figure 5.34. Changes in chemistry with flow at the mid-catchment monitoring point in Gortinlieve during the August 2010 event (Deakin et al., 2014).

5.3.4.3 November 2011 event

The largest event recorded during the study period was captured in November 2011. The total rainfall was 39.6 mm and the maximum rainfall intensity was very high at over 10 mm/h for over

2 h, based on 15-min data. The maximum flow was an order of magnitude greater than the August event at 1.49 m^3/s at the mid-catchment weir, or 2.36 m^3/s at the catchment outlet. The antecedent conditions were wet, as indicated by higher groundwater levels in the subsoils than in the shallow bedrock at GO3, i.e. a downward gradient from the surface, prior to the event.

At the mid-catchment monitoring point at the EPA weir, the majority of the nutrient loads responded closely with rainfall and increased with the first major flow peak (Figure 5.35). The two subsequent smaller increases in flow, however, provided some interesting insights. The first small increase delivered higher loads of potassium and total phosphorus than the second, while the second delivered higher loads of nitrate, calcium and magnesium than the first. This is consistent with potassium and total phosphorus being delivered from the land surface via the overland flow pathway and being flushed out with the high-intensity rainfall as the event progressed. The dissolved loads of nitrate, calcium and magnesium were delivered via the shallow groundwater and transition zone pathways and increased with the increases in water tables, which increased the groundwater gradients and hence the flux.

The results at the catchment outlet were similar to the mid-catchment monitoring point and are therefore not shown here. The quick flow contribution dominated the early part of the event. A number of peaks in loads, particularly total phosphorus, potassium and ammonium, which are typical of overland flow, occurred at different times throughout the event and more frequently than at the mid-catchment. These provide evidence that there are flushes of water containing nutrients and particulates to the stream, which are likely to be due to increases in the saturated area generating overland flow bringing new sources of contaminants into the stream, probably via the ditches. This delivery mechanism has been observed in the field during the events where, in the space of a few minutes, the turbidity in ditches visually increases coincident with a significant decrease in electrical conductivity. The Gortinlieve catchment is so small that the connection of even one such ditch to the stream can have a significant impact on the receiving water chemistry.

During the recession period, nitrate loads decreased at the mid-catchment monitoring point similarly to calcium and magnesium, but increased slightly and relatively uniformly at the catchment outlet. This is due to a higher proportion of bedrock groundwater discharging to the river in the lower catchment with the strong upward gradient, in comparison to the unconfined upper catchment where the loads reduce with rainfall. The data show that there was a likely contamination event in the early hours of 30th November above the subcatchment monitoring point. High dissolved organic carbon, potassium, MRP and ammonium, dilution in NO_3, and a very enriched δ^2H signal far greater than would naturally be found in the catchment, suggest that some kind of effluent collector tank or storage area may have overflowed into the stream.

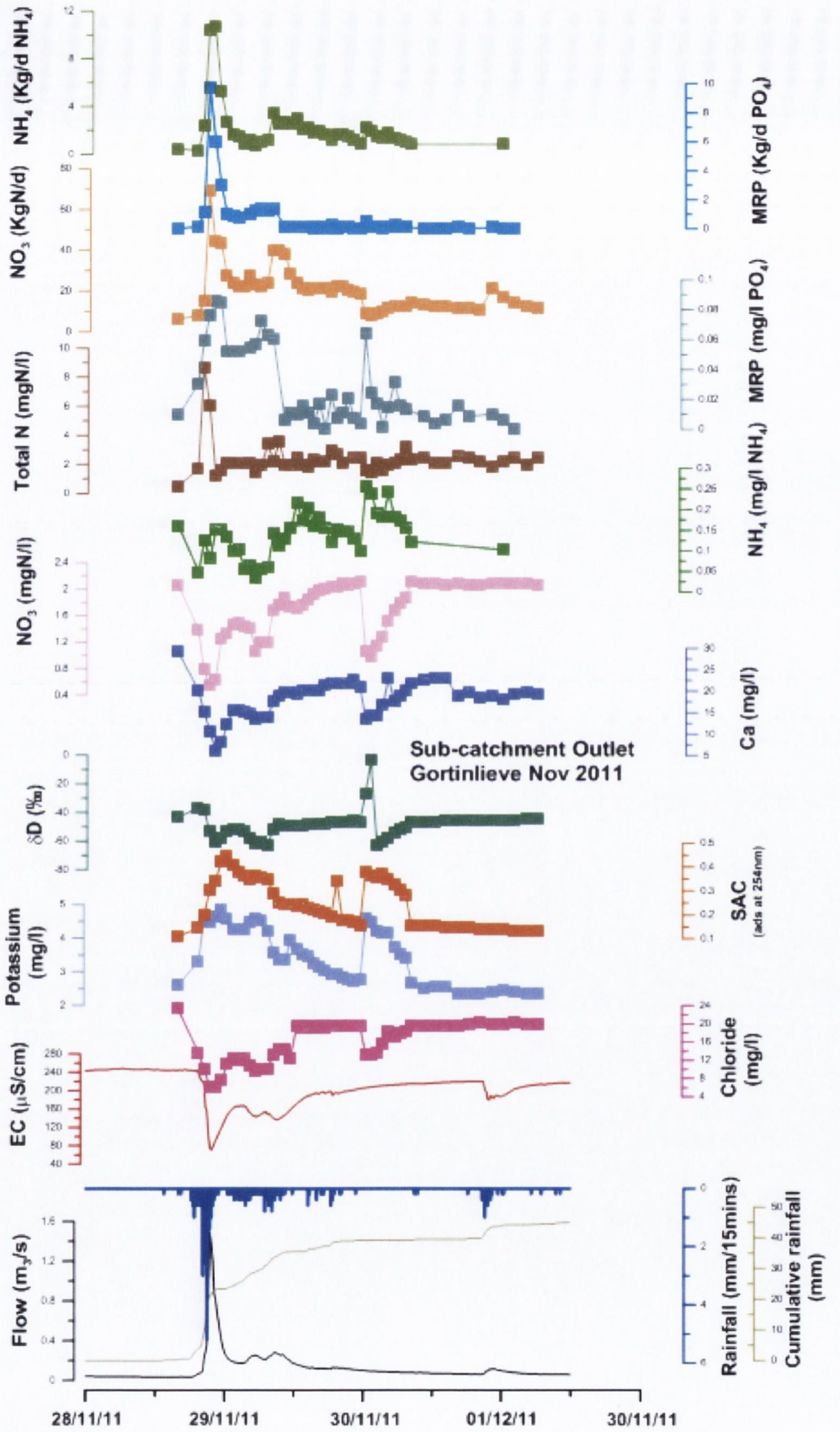

Figure 5.35. Changes in chemistry with flow at the mid-catchment monitoring point in Gortinlieve during the November 2011 event (Deakin et al., 2014).

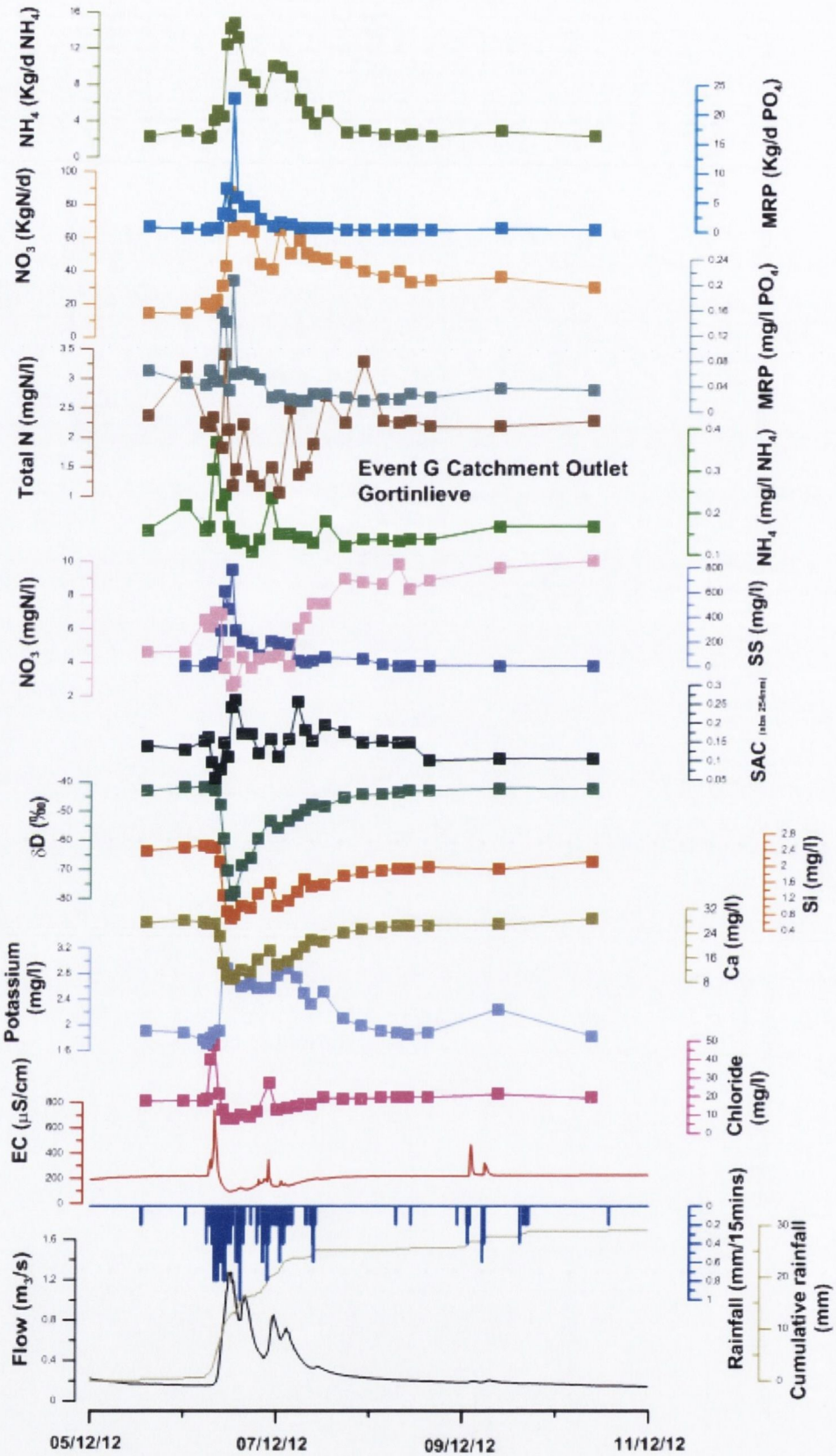

Figure 5.36. Changes in chemistry with flow at the catchment outlet monitoring point in Gortinlieve during the December 2012 event (Deakin et al., 2014).

5.3.4.4 December 2012 event

The final event was captured in December 2012 when a total of 24.6 mm of rainfall fell with a maximum intensity of 2.8 mm/h for almost 3 h. The groundwater head in the subsoil borehole was slightly less than the shallow bedrock groundwater head except during the event, but antecedent conditions were largely wet.

The responses in the river were similar to the November 2011 event, although rainfall and flow peaked twice, with the second peak smaller than the first. At the catchment outlet, the magnitude of the peaks in load during the flow peaks was different for different nutrients, consistent with the different pathways supporting their delivery (Figure 5.36). There were larger differences in loads for the overland flow pathway indicators (phosphorus, potassium and ammonium), than for the shallow groundwater and transition zone indicators (calcium, magnesium and nitrate), which were similar during both flow peaks. At the mid-catchment monitoring point (not shown), the loads of the shallow groundwater and transition zone indicators were slightly higher, or at least the same during the second flow peak, despite the reduction in flow. This reflects a reduction in the delivery of nutrients via overland flow as the event receded, and an increasing contribution of groundwater from the shallow bedrock and transition zone as groundwater levels rose.

To further investigate the nitrate transfer processes in the near-surface pathways during the December event, regular samples were taken from a large ditch ('Les's ditch') at the break of slope in the upper catchment using an autosampler, and grab samples were taken at a number of other sites around the catchment and the river (Figure 5.37). Les's ditch behaved in the same way as the river, although nitrate concentrations were slightly lower. The first flush effect seen at the mid-catchment monitoring point (SCO) was also seen in one of the other ditches, a very large ditch just upstream of the monitoring point. With the exception of the first flush, in general overland flow provided a dilution effect, both directly and via the ditches.

5.3.5 Conceptual model summary

The available evidence indicates that the stream in the Gortinlieve catchment is affected by high phosphorus and relatively low nitrate, which is consistent with the other catchments underlain by poorly productive aquifers studied. The transition zone is the key pathway for the delivery of flow to the stream in Gortinlieve, although different hydrological processes dominate in different parts of the catchment, which affects nutrient delivery. In the upper catchment, in the groundwater recharge areas, contaminants infiltrate readily through the thin soils and subsoils to the transition zone at the top of the low permeability bedrock. During rainfall events, this contaminant-rich

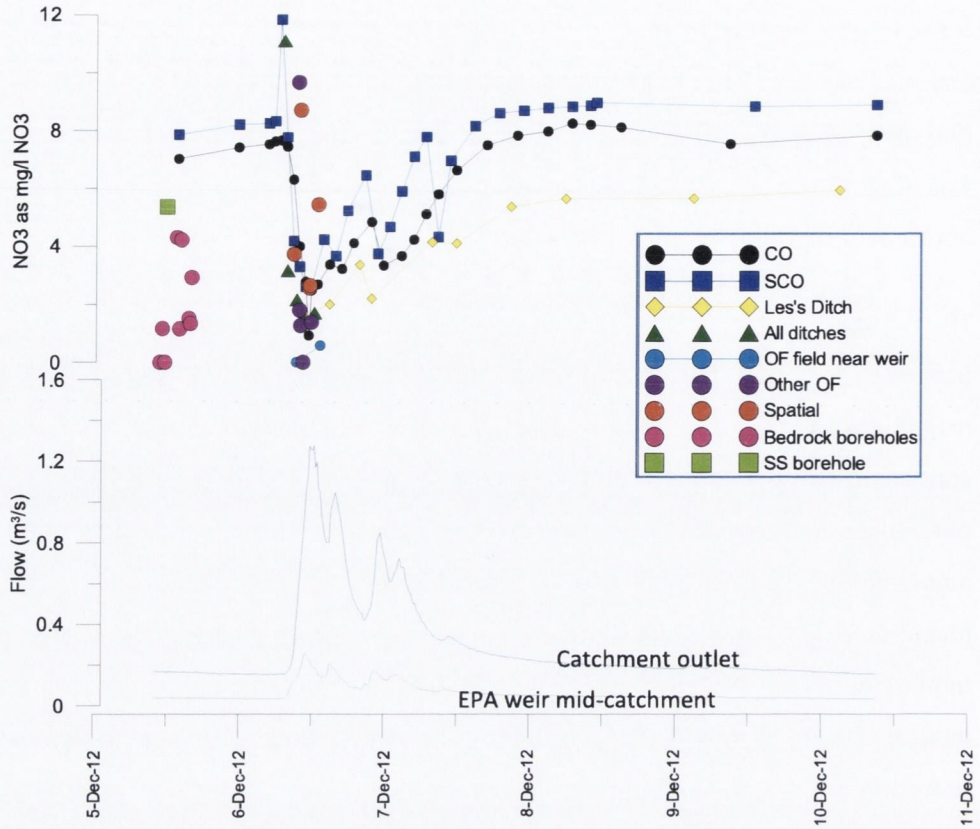

Figure 5.37. Near-surface pathway changes in nitrate concentration with flow, Gortinlieve catchment, December 2012 event. CO = catchment outlet; SCO = mid-catchment monitoring point at the EPA weir; OF = overland flow; spatial, grab samples taken from different locations within the river; SS = borehole, the borehole into the subsoil at GO3 near the river.

water is flushed out into the nearest ditch or tributary/stream channel, or as return flow,whereupon it is mixed with inputs from overland flow. In the lower catchment, the relatively flat topography and frequently saturated soils have encouraged landholders to develop artificial drainage, which helps to create a hydrological linkage between the nutrient-rich water in the permeable subsoil and the river. The upward gradient of nutrient-poor groundwater from the bedrock to the transition zone in these areas ensures that although the transition zone contributes significantly to the flow, it is not the dominant nutrient transport pathway in the groundwater discharge areas.

The transition zone is the dominant pathway for the delivery of nitrate in this catchment, whereas overland flow and ditches are important for the transport of phosphorus. Nutrient flushes with the early rainfall delivered by overland flow were observed from the steep slopes in the upper catchment, but had been diluted out by the catchment outlet. Spikes in nutrient concentrations at the catchment outlet were evident but were attributed to the impacts of point sources.

5.4 Nuenna catchment

The Nuenna catchment in Co. Kilkenny, a subcatchment of the River Nore, is the largest of the four study catchments (36 km^2). The catchment lies at an elevation of 77 m OD at the outlet, rising to a height of 340 m to the northwest and 280 m to the southeast.

5.4.1 Geological framework

The catchment is underlain by karstified limestones which are classified by the Geological Survey of Ireland as a Regionally Important karst aquifer dominated by diffuse flow (Rk_d). The limestones are interbedded with thin, low permeability clay wayboards, which can act as a barrier to flow (Daly, 1994a). In the upland areas to the north and south, poorly productive Namurian sandstone and shale rocks overly the limestones, which are classified as Poor aquifers that are Generally Unproductive except for Local Zones (Pl) (Figure 5.38). Tracer tests carried out as part of the *Pathways Project* have linked streams running off the Namurian rocks and sinking into swallow holes at the limestone/shale boundary to the southwest of the catchment, with three of the major springs in the river valley, with travel times of the order of 23–55 m/h in dry weather (Walsh, 2011). However, a water table map can also be drawn (Dillon, 2010) highlighting a combination of slower diffuse flow through the fractures and more rapid flow through conduits to the springs.

The subsoils in the catchment are predominantly shallow, moderately permeable limestone tills although there are highly permeable sands and gravels also present in places in the valley floor, and pockets of gravelly clays and clays. The soils are typically well drained, except in limited areas near the river where the water table is close to the surface giving rise to poorly drained groundwater gleys. The subsoils on the Namurian shales are low permeability due to the higher shale content, which is reflected in the poorly drained soils in those areas. Some 65% of the catchment is mapped as being of Extreme groundwater vulnerability, which means subsoils are mainly thin, recharge is quick and there is little protection from vertical infiltration of contaminants (Deakin et al., 2014). This is corroborated by the general lack of surface drainage in the catchment. The geological framework supports a relatively highly permeable catchment with the predominant flow, and therefore nutrient transfer pathways, below the surface.

5.4.2 Land use

Land use in the catchment comprised over 70% pasture with 14% arable and 8% forest. Diffuse sources of contaminants from grazing animals were therefore widespread. Organic fertilizers from a local piggery are also land spread throughout the catchment. Point sources of contamination included domestic wastewater treatment systems, farmyards and several locations where cattle directly accessed the river (McAleer, 2011).

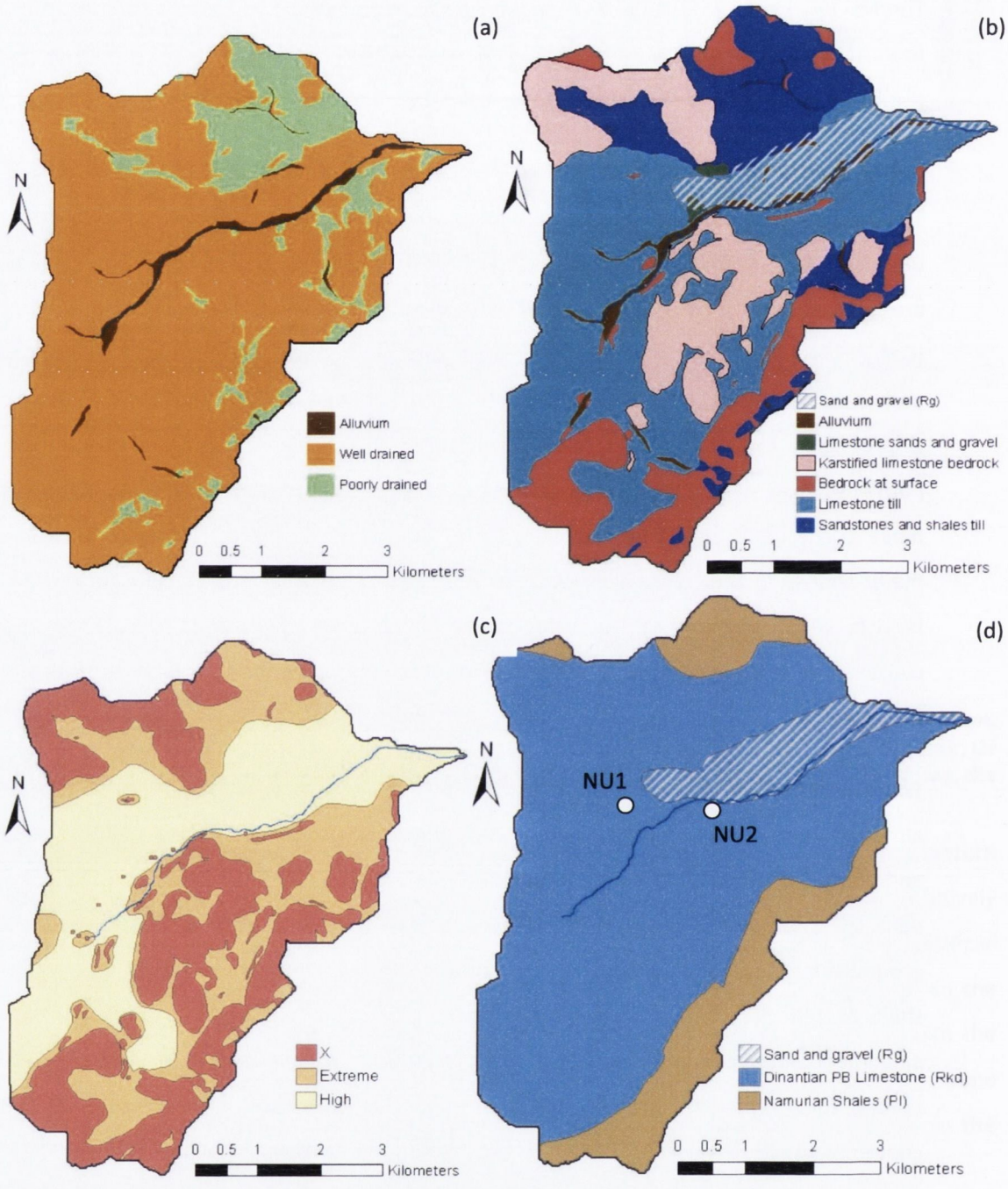

Figure 5.38. The Nuenna catchment geological framework. (a) Soils; (b) bedrock; (c) groundwater vulnerability; and (d) aquifers and the two monitoring borehole clusters NU1 and NU2 (Deakin et al., 2014).

5.4.3 Pathways

5.4.3.1 Stream flows

Longitudinal stream flow measurements showed that the river is largely fed by a number of large karst springs along the main river channel (Deakin et al., 2014); between 70 and 95% of the flow

was delivered to the river via these springs depending on the season and there was a high baseflow index of >0.87 (O'Brien, 2013). The background water quality sampling in the river, the springs and the groundwater monitoring boreholes identified that, with the exception of the streams on the Namurian rocks, all the water in the catchment had a similar calcium bicarbonate–rich hydrochemical signature, reflecting the dominance of the limestone bedrock groundwater pathways.

5.4.3.2 Groundwater levels

There are two monitoring borehole clusters in the Nuenna catchment: NU2 close to the river and NU1 in the mid-catchment (Figure 5.38). At NU2, there was an upward gradient from the bedrock through a gravel horizon to the river, which confirmed the contribution of the bedrock groundwater to the river. The groundwater level data for NU1 Deep however, show that away from the river there was a downward gradient with a significant unsaturated zone. Large water table fluctuations between 18 and 27 m below ground have been recorded in the deepest borehole.

Interestingly, the shallow borehole at NU1 Trans (adjacent to NU1 Deep), which intersects the transition zone between a 4 m thick gravel/gravelly clay unit and the underlying bedrock, also had a perched water table for much of the year. In this karst environment, the transition zone operates effectively as the epikarst, and it is hydraulically connected with the overlying gravels where they are present (Figure 5.39). Water quality sampling shows that this zone was often higher in total phosphorus during the sampling period than might be expected, at an average of 0.033 mg/l as P. Nitrate was relatively low at 13.8 mg/l as NO_3, but nitrite was often present at low levels and ammonium and faecal bacteria were present on occasion, which suggests a relatively short distance and/or rapid transit time from a contaminant source. There was similar but slightly better water quality in the deep borehole at NU1 and greater improvements in all parameters in the discharge zone at NU2, further along the groundwater flowpath.

This highlights that a type of transition zone also operates in karst settings and can be a significant flow and nutrient transport pathway. However, in contrast to the poorly productive aquifers, the extent of lateral flow in the transition zone in the karst is limited. This is because the underlying bedrock is relatively permeable and flow percolates downwards through dissolution features in the limestone to the permanent water table (Figure 5.39). Thus, the transition zone does not typically contribute directly to the river, but rather via the deeper bedrock groundwater pathway.

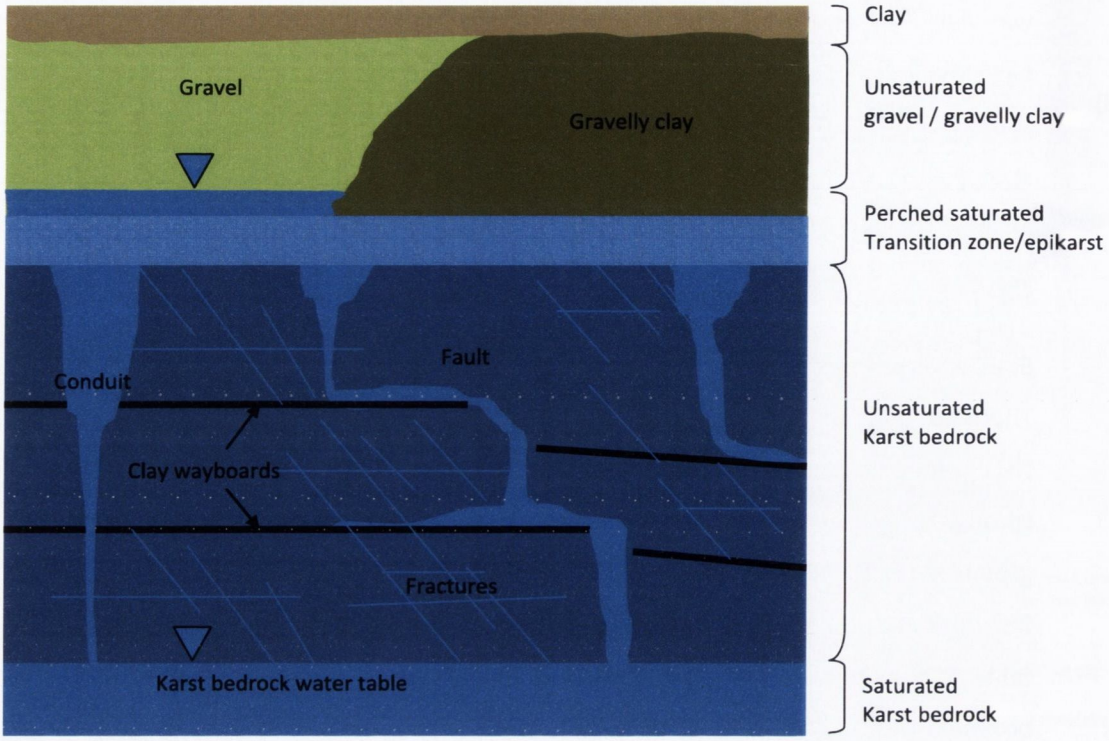

Figure 5.39. Schematic conceptual model of the interaction between water in the transition zone and in the deeper bedrock in the Nuenna karst catchment.

5.4.3.3 Electrical conductivity

The average electrical conductivity in the bedrock groundwater in the deep borehole at NU1 was 680 µS/cm; that in the transition zone borehole was slightly higher at 746 µS/cm, possibly due to the contamination and/or greater interaction time with the unconsolidated sediments. There are a limited number of land drains present in the headwaters of the catchment close to where the river rises and, although they do not flow for most of the year, two measurements with an average of 732 µS/cm suggest that they drain rising bedrock groundwater when flowing rather than downward infiltrating rainwater. Overland flow was found to measure as little as 100 µS/cm in road runoff during intense rainfall, but more commonly where present elsewhere, it was in the range 680 to 770 µS/cm. This suggests that the majority of overland flow is also derived from groundwater pathways which, depending on the location in the catchment, may be either bedrock groundwater discharging at the surface in the river valley, or shallow groundwater seeps where the saturated transition zone intersects the land surface.

5.4.4 Nutrient transfer

Nitrate concentrations in the river were the highest of all the study catchments at between 25 and 30 mg/l as NO_3, and the vast majority of the nutrient fluxes were delivered via the large springs. Total phosphorus concentrations were typically very low at an average of 0.010 mg/l as P, although values >0.1 mg/l were detected in one of the springs connected to a sinking stream on

the Namurian shales. The nitrate was transported via the bedrock groundwater pathways to the springs; the relatively low phosphorus values were consistent with high infiltration rates through the soils, which present greater opportunity for the phosphorus to be bound up in the soils than to run off. During rainfall events, nitrate was significantly diluted and phosphorus increased, suggesting that they are delivered via different hydrological transfer pathways. The increases in phosphorus are likely to be due to overland flow arising from the limited areas of saturated soils in the discharge areas of the valley floor, from incidental losses from point sources (e.g. cattle access points), and from phosphorus rich sinking streams from the Namurian shales. Further discussion on the changes in nutrient concentrations in the river with flow, in the context of all the catchments, is provided in Section 6.6.

5.4.5 Conceptual model summary

The Nuenna karst catchment is highly permeable. Recharge infiltrates easily through the thin and permeable soils and subsoils and the majority of water flows to the river via bedrock groundwater pathways. Overland and drain flows occur mainly on the saturated soils in the discharge zone near the river, or can be return flow from the deep or transition zone aquifers elsewhere, when they are fully saturated. The transition zone pathway plays an important role in recharging and delivering contaminants to the deeper limestone aquifer, but does not contribute directly to the stream. The near-surface pathways cannot be distinguished hydrochemically from the bedrock groundwater pathways and therefore this catchment was not considered further for chemical hydrograph separation work.

5.5 Summary

The conceptual models have highlighted that the key pathways in the poorly drained catchments were the near-surface pathways, whereas in the karst catchment, the deeper groundwater pathways in the highly permeable bedrock provided the majority of flow to the stream and the near-surface pathways were much less significant. Where the near-surface pathways did function in the karst catchment, their role was to deliver bedrock groundwater to the surface when the karst aquifer was fully saturated. In addition, the near-surface pathways on the Namurian shales which contributed to streams sinking at the shale/limestone boundary also played an indirect role.

In the poorly productive bedrock aquifers, which have low transmissivity, low storage and short flowpaths, and where rejected recharge and return flow to the surface are common, inter-mixing between the pathways takes place. Water may originate in the bedrock but be subsequently delivered to the stream via a surface or near-surface pathway. The conceptual models have

emphasized the importance of the transition zone and the artificial drainage networks as transport pathways in these environments.

5.5.1 Transition zone

With the exception of alluvial deposits, the transition zone has been identified as the most permeable geological horizon in the subsurface in the poorly drained catchments. It was also identified as an important pathway in the Nuenna karst catchment, but due to the permeability of the underlying karst bedrock, it contributes indirectly to the stream via deep groundwater. Although the transition zone was not formally identified as a high permeability weathered zone in drilling in the Mattock catchment, and it may not be universally present, the borehole data indicate that this boundary between the subsoils and the bedrock still presents a significant change in permeability that acts as an important barrier to vertical infiltration and a store for nutrients. Similar observations were made in the Glen Burn catchment where the geophysics has identified that the development of the transition zone is not uniform. In places where there is insufficient weathering to create the transmissivity to contribute significant flows to the stream hydrograph, return flow is likely to develop as water backs up to the surface when the subsoils are fully saturated. These are the environments that are also typically suited for the installation of artificial drainage networks.

In all four catchments, the transition zone was found to be a significant pathway for nitrate and phosphorus transport, except in the groundwater discharge zone in the valley in Gortinlieve where the upward gradients from the nutrient-poor deeper bedrock dominated the hydrochemistry. This highlights that the vertical hydraulic gradients and groundwater level dynamics play an important role in how the transition zone functions as a pathway.

There were two different subtypes of transition zone identified in the study catchments. In groundwater discharge areas the transition zone is closely aligned with the shallow groundwater pathway. It occurs in the lower parts of catchments where there are upward gradients from the lower bedrock groundwater. It is fully saturated and is often confined under low permeability clayey tills in catchments underlain by poorly productive aquifers. The hydrochemistry and nutrient content in this type can be similar to that in the underlying bedrock, or can be a mixture of the bedrock and overlying subsoils depending on the antecedent conditions. An example of this type occurs in the lower catchment in Gortinlieve, and in the Glen Burn catchment in winter.

In groundwater recharge areas, the transition zone is more closely aligned with the interflow pathway. It has a quicker response time, is not always fully saturated, and contains groundwater that is often, but not always perched. Recharge infiltrates from the overlying subsoils reaches the

lower permeability barrier in the upper bedrock and flows laterally along the upper weathered zone. These zones are especially important for the transport of nutrients because they are typically more aerated and travel times are relatively quick, which means there is little opportunity for attenuation. In catchments underlain by poorly productive rocks, the transition zone water often discharges into the nearest ditch or drain, or it may also discharge as return flow to the surface where the soils and subsoils are thin. An example of this type occurs in the upper parts of the Gortinlieve and Mattock catchments, and in the Glen Burn catchment in summer. In catchments underlain by more permeable bedrock, such as the upper cluster (NU1) in the Nuenna, the flow moves laterally until it reaches a higher permeability zone within the bedrock that can accept the recharge to the deeper bedrock groundwater.

Recent geophysics work by the *Griffiths Project* team in many of the same catchments (Comte, *pers comm.*) has identified the presence of a thin horizontal low resistivity layer sandwiched between a thin upper high resistivity layer at the top of the rock, and the rest of the high resistivity bedrock below. The change in resistivity is due to the presence of a layer of clays that have washed downwards from the upper bedrock and subsoils. These infilled clays may reduce the permeability below the upper weathered layer that is relatively clay free, and therefore may effectively isolate the top few metres of the rock from the rest of the bedrock below. This layer has been found in all the poorly productive catchments being investigated in the Griffiths programme and may prove to be the reason that the transition zone can behave differently to the rest of the bedrock. Further work is required to confirm the hydrological characteristics of the transition zone and this is referred to in the recommendations.

These new findings build on the work of (Gabrielli et al., 2012) as discussed in Chapter 2, who noted in the forested catchments of the Maimai catchment, and the HJ Andrews Long Term Ecological Research Network experimental catchment in Oregon, that the transition zone behaved differently in different hydro(geo)logical settings. They found no connection however, between the bedrock groundwater and the transition zone, and noted that the water discharged through the transition zone pathway was a mix of vertically infiltrating soil water and rainfall. Other authors (Tromp-van Meerveld and McDonnell, 2006, Liang and Uchida, 2013) attribute the delivery mechanism to a fill and spill process where micro-depressions in the topographic surface of the bedrock fill up and interconnect, resulting in significant increases in the delivery of flow and consequent rises in the stream hydrograph.

Based on the results of this study, it is considered that in glaciated, low-lying, poorly drained catchments, the dynamics of the deeper bedrock groundwater have a much greater bearing on the flow mechanisms in the transition zone than the relief of the bedrock surface. The fill and spill

process may operate in groundwater recharge areas, particularly if it transpires that the newly discovered low resistivity layer of displaced clays is a hydraulic barrier to flow. It is suggested however, that in groundwater discharge zones, it is the relationships of the vertical hydraulic gradients throughout the geological profile that dictate the contribution of flow from the transition zone. These types of groundwater discharge zones are likely to be more prevalent in Irish catchments than in the steep, non-glaciated, forested catchments of the previous studies.

This research suggests that the type of transition zone has a significant bearing on the likelihood of it being an important transfer pathway for diffuse nutrients in Irish catchments. In the groundwater recharge areas, the transition zone can be high in nitrate especially as it is not fully saturated and the source of water (and contaminants) is recharge through the soils and subsoils. In groundwater discharge areas, however, water in the transition zone has had a much longer residence time in saturated conditions and the source of the water is deeper bedrock groundwater, which means that overall there has been greater opportunity for attenuation and dilution. In these scenarios, it will be the quality of the bedrock groundwater that dictates the water quality in the transition zone. Further work is required in different catchments with different nutrient pressures to confirm this hypothesis.

5.5.2 Artificial drainage

The artificial drainage networks, particularly the ditches, deliver a mixture of waters from different geological horizons to the stream and are essentially extensions of the river network. Evidence from all three catchments underlain by poorly productive aquifers highlights that the mixture includes water from the groundwater pathway at breaks in slope, in upper catchment areas at seeps where low permeability tills begin to thicken, or where water tables are high such as in inter-drumlin areas. This means that groundwater can contribute to the stream within much shorter time frames than would otherwise be possible were the drainage networks not present. This suggests that the widely adopted assumption used in many of the physical hydrograph separation methods, that the bedrock groundwater contribution to a stream is delivered via the slowest responding pathway (Mellander et al., 2012, O'Brien et al., 2013), may not hold true in poorly drained catchments.

The land drains equally can deliver different source waters depending on the hydrogeological scenario. In the Mattock and Glen Burn catchments, where the gradients are more often downwards, the electrical conductivity in the land drains is typically less than in the stream, consistent with infiltrating rainwater with relatively short residence times and little contact with the soils. In the Gortinlieve catchment, in the discharge zone in the valley floor where most of the land drains were identified, the electrical conductivities were higher than in the stream, which is

likely attributable to the mixing between the soil/subsoil water and the groundwater being forced upward from the bedrock. Thus, it is apparent that the hydrogeological setting has a significant bearing on the behaviour of the near-surface pathways.

In the Mattock catchment, the conductivity in the land drains was lower than in the subsoil boreholes, which brings into question whether it is reasonable to assume that their chemistry truly represents the interflow pathway. The permeability of the clayey till subsoils has been shown to be very low based on pumping tests using packers, suggesting that on the scale of responses in the stream hydrograph, which is the important scale for nutrient transport, the contribution to the stream from the subsoils is likely to be limited without the land drains or other preferential flowpaths to speed up the delivery. This interpretation is consistent with the definition of interflow adopted by Beven (2006b). Although hydraulically active fractures, often infilled with a variety of grain size materials, have been shown to be present in similar glacial till in the United Kingdom, and were observed to increase the bulk hydraulic conductivity to between one and three times that of the till matrix (Cuthbert et al., 2010), they were found to decrease with depth and the resulting transmissivity was still likely to have been too low to contribute significantly to the stream at the temporal scale of stream flow events. It is considered, therefore, for the purposes of this research, that the land drains provide a suitable sampling window for the soil water that is likely to be delivered to streams at the temporal scale of the events.

The conceptual model development in each catchment has been instructive, and indeed essential, to support the understanding of each catchment's pathway functioning, providing a firm basis for the hydrograph separations detailed in Chapter 6.

6 Catchment-scale pathway separation

6.1 Introduction

Quantifying the contribution of each pathway to the stream helps to distinguish the key pathways and hence contributes to the identification of the critical source areas, i.e. the highest-risk areas for nutrient transfer. Chemical hydrograph separation methods were applied in three of the study catchments, and were integrated with the findings of the NAM modelling and physical hydrograph separation methods carried out by O'Brien (2013), and the conceptual models detailed in Chapter 5, to provide a more robust conceptualization and quantification of the pathway contributions. As described in Chapter 4, two different approaches to chemical hydrograph separation were applied that recognized the differences in data availability in the study catchments: a conceptual model–based, stream-focussed approach, which was carried out in all catchments, and a statistical approach in the data-rich Mattock catchment, which was used to assess the applicability of the conceptual model approach and determine the degree of uncertainty in the results. This chapter discusses the integrated pathways separation results for each catchment in turn, and presents a method developed to generalize them to help constrain the hydrological model used in the catchment modelling tool (Section 3.2.3). A final section discusses some of the issues arising in the use of the methods.

6.2 Chemical hydrograph separation

Chemical hydrograph separation methods were applied in the Mattock, Glen Burn and Gortinlieve catchments, but not in the Nuenna catchment. This was because the near-surface pathways were largely absent as the soils and subsoils were so permeable, and where they were present, they could not be distinguished hydrochemically from the bedrock groundwater pathways.

6.2.1 Mattock catchment

In the Mattock catchment, the conceptual model identified that overland flow, water infiltrating through the soils and subsoils and discharging via land drains (interflow), and shallow bedrock groundwater were the key sources of water for the stream (Section 5.1.5).

6.2.1.1 Tracer selection

Silica was initially selected as a suitable tracer to represent the subsurface pathways, as in the majority of studies in the literature (Section. 3.3.2). Silica concentrations increase with increasing contact time with geological materials. The use of chloride was also considered as it is

conservative, but as contaminants such as fertilisers and domestic wastewater treatment systems can also be a source, it was concluded that this would give rise to an unacceptable level of uncertainty in the results.

As there are no peat deposits in the Mattock catchment, it was possible to use the spectral absorption coefficient at 254 nm (SAC_{254}), a proxy for organic content, as a suitable tracer to identify overland flow (Kane, 2009, Tipping et al., 2009). The benefits of using SAC_{254} are that it is very cheap and simple to analyse. The method does not differentiate the type of organic matter being analysed and it therefore represents an approximation, but the background monitoring data showed there is a strong positive relationship between SAC_{254} and DOC (R^2 = 0.83) in the Mattock catchment, which suggested that it was appropriate for use.

6.2.1.2 Event data

Silica and SAC_{254} data were available for the river for six events, including both winter and summer events, events at all three catchment scales, i.e. upper (Diversion), middle (Collon) and lower (Berrrils), and one event of extended duration over 6 days that comprised six smaller events. The rainfall events ranged in size from 27 mm to 67 mm, with a range in maximum rainfall intensity from 2.2 to 7.19 mm/h (Table 6.1). In general, the maximum intensities were only sustained for short periods, and rainfall intensities over the remainder of the events were <1.5 mm/h, which is typical of Irish catchments (Logue, 1971, Rohan, 1986). A full suite of chemical analyses was available for four of the events, and a reduced suite including Si, SAC_{254}, NO_3 and electrical conductivity (and alkalinity on one occasion) for the other two.

Table 6.1. Characteristics of the six events captured.

Event no.	Location	Event start	Event duration (days)	Total rainfall (mm)	Max intensity (mm/h)	Chemistry suite sampled
1	Mid-catchment, Collon	2 Feb 2011	6.0	67.0	5.97	Reduced suite
2	Upper catchment, Diversion	28 Jan 2012	3.6	27.7	2.20	Full suite
3	Lower catchment, Berrils	28 Jan 2012	3.6	27.7	2.20	Full suite
4	Upper catchment, Diversion	6 Jun 2012	3.8	59.0	7.19	Reduced suite
5	Upper catchment, Diversion	14 Jun 2012	5.7	40.6	4.23	Full suite
6	Lower catchment, Berrils	14 Jun 2012	5.7	40.6	4.23	Full suite

6.2.1.3 End member sampling

The near-surface pathway end members were sampled during 27 rounds of background sampling; data from 14 sampling rounds were available for the EPA boreholes. The number of SAC_{254} samples available for the EPA boreholes was unfortunately limited to 19 in total, as the EPA laboratory does not have the capacity to analyse for this parameter. Samples were obtained during the team events, and by opportunistically coordinating with the EPA subcontractors to subsample from the national sampling rounds. However, the values obtained were considered to

be reasonably representative because they were all typically very low, consistent with the conceptual model, and the standard error was small at 0.006. To increase the available dataset for the purposes of the mixing model (Section 6.2.1.5), the median of the available SAC_{254} data for each borehole was paired with the additional silica values. In all, there were some 670 samples of the end members available for the analysis.

6.2.1.4 Principal components analysis

Once sufficient event data had been collected, principal components analysis (PCA) was carried out to assess the relationships between the different tracers and how they behaved in the stream during events. This was to provide insights into the number of statistical components, and hence potentially the pathways, in the dataset. Results were also used to cross check that the use of silica and SAC_{254} was appropriate in this catchment. PCA was not carried out for events with reduced suites of tracers because it is less effective with limited datasets. In the four events analysed, PCA demonstrated that there was one major statistical component that dictated the majority (>62%) of the variance in the stream flow samples (Table 6.2). The tracers aligned with this statistical component included those associated with the subsurface (e.g. Si, Mg and alkalinity), and those indicative of overland flow (e.g. SAC, total organic carbon (TOC) and δ^2H), with which they were negatively correlated. This is consistent with the process of dilution of subsurface water with overland flow.

The second statistical component in the Mattock datasets typically identified a contamination signal. In the winter event in the upper catchment, this was dictated by a source of nitrate, chloride and sulphate, which were highly positively correlated, but which were weakly negatively correlated with total phosphorus, i.e. when nitrate, chloride and sulphate increased, total phosphorus decreased. This may suggest that the source was located in the near-surface soils because of the positive relationship with sulphate and the negative correlation with total phosphorus, which is typically a surface contaminant. In the lower catchment, the contaminant signal was dominated by potassium, ammonium and phosphate, which were positively correlated, and were strongly negatively correlated with sodium. The ammonium, which was relatively high during the event, is indicative of a relatively fresh source of contamination, and as it is correlated with potassium and phosphorus, it may suggest a farmyard source given that this was a winter event and the animals were housed indoors. Alternatively, as the closed period for slurry spreading had just finished the previous week, it could also have been the result of a flush of organic fertilisers that had been freshly applied. The negative correlation with sodium, which is associated with both the subsurface and rainfall, may reflect dilution of the contaminant source. In the summer event, the

Table 6.2. Pattern matrix PCA outputs for stream flow samples, for the upper and lower Mattock catchments, during the winter and summer events. The numbers in the cells represent how strongly the tracers are correlated with the patterns of each component. Greyed cells highlight the component each tracer is best aligned with. % variance is the variance in stream flow that can be explained by each component.

28 Jan event, upper and lower catchments						
Upper catchment	Component			Catchment outlet	Component		
	1	2			1	2	3
% variance	80.8	7		% variance	62.3	18.8	5.9
Cond	1.102	-.172		SO4	.989	.086	-.047
Alk	1.095	-.218		Mg	.986	.250	-.007
Mg	.994	-.008		Ca	.985	.207	-.030
d2H	.944	.063		Cond	.983	.109	-.001
d18O	.922	-.006		SAC	-.979	.031	.011
Ca	.884	.135		d2H	.970	-.076	.130
K	-.876	-.101		Si	.963	-.149	-.070
SAC	-.812	-.223		Alk	.942	.287	-.009
Na	.790	.256		DOC	-.924	.136	-.024
PO4	-.778	-.243		NO3	.887	-.337	-.086
DOC	-.754	-.254		d18O	.737	-.126	.527
NH4	-.730	.007		TP	-.545	.495	-.185
Si	.681	.390		TN	.512	-.045	-.389
NO3	.060	.930		Na	-.283	-.903	-.137
Cl	-.061	.917		NH4	.564	.817	.140
SO4	.199	.831		K	-.457	.699	.114
TN	.065	.743		PO4	-.460	.552	.167
TP	-.380	-.500		Cl	-.038	.136	.902

14 June event, upper and lower catchments							
Upper catchment	Component			Catchment outlet	Component		
	1	2	3		1	2	3
% variance	66.6	13.9	6	% variance	66.5	11.8	7.3
Cl	1.019	.513	-.010	Si	.982	-.107	.052
Na	1.013	.129	.026	SO4	.968	-.048	.026
Cond	.988	.043	-.058	NO3	.955	-.051	.101
Mg	.971	-.010	-.085	TOC	-.951	-.087	-.026
TN	.927	-.078	.316	Cond	.945	.087	.056
d2H	.888	-.016	-.022	Mg	.941	.093	.063
SO4	.876	-.215	-.081	SAC	-.935	-.089	-.070
Alk	.875	.188	-.233	Alk	.911	.125	-.023
Si	.871	-.226	-.073	Na	.908	.186	.060
SAC	-.866	.238	.075	Cl	.854	.280	.040
TOC	-.862	.233	.060	TP	-.848	.587	.145
NO3	.850	-.270	-.103	d2H	.646	.053	.418
Ca	.597	-.295	.105	TN	.449	.429	.399
d18O	.372	-.210	.176	K	.060	.906	-.059
K	-.119	.908	.157	NH4	.388	.778	-.267
Phosphate	-.037	.897	-.032	Ca	-.002	-.204	.773
NH4	-.093	.874	-.036	d18O	.111	-.108	.770
TP	-.113	.109	.950	Phosphate	-.120	-.276	-.495

contamination signals comprised potassium and ammonium at both catchment scales, with the addition of phosphate in the upper catchment, which is likely to be a signal from manures.

Of the tracers identified as being associated with the most significant statistical component, silica, magnesium, alkalinity and electrical conductivity best represented the subsurface contribution, and SAC and TOC/DOC performed best as overland flow indicators. Silica and SAC were therefore confirmed as appropriate tracers. Further discussion on the usefulness of the PCA approach is presented in Section 6.8.3.

6.2.1.5 Mixing models

A pathways mixing model shows that at the commencement of all events, the baseflow from the subsurface was high in silica and low in SAC_{254}, as would be expected, but that as the events progressed, the silica was diluted and the organic content increased as the overland flow pathways became dominant (Figure 6.1). There is a linear progression in the stream chemistry during the events that could potentially be interpreted as representing just two significant pathways: the subsurface water and overland flow. This would be supported by the PCA, which suggests that the majority of the variance in the stream samples can be explained by just one process: the dilution of subsurface water with overland flow (Section 6.2.1.4).

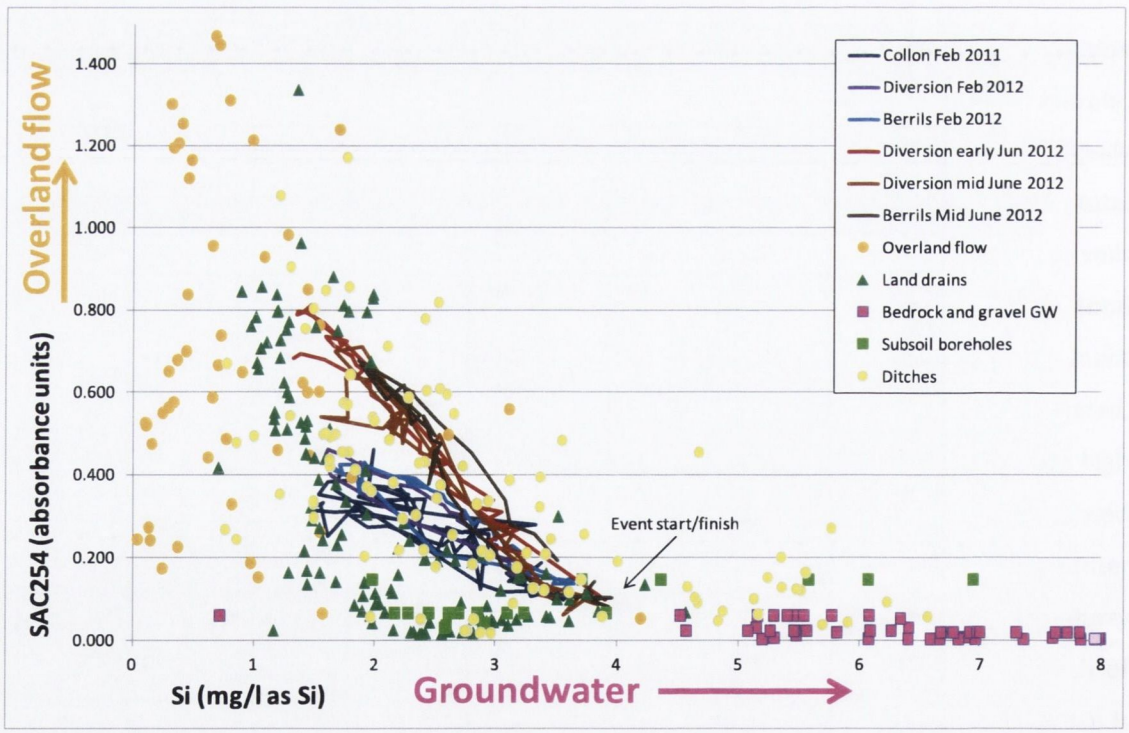

Figure 6.1. Mattock pathways mixing model. Background pathway samples and stream flow data for all six events. Note how the samples for each pathway cluster within a distinct region on the graph, with the exception of the ditches which largely overlap with the stream (and bedrock groundwater) highlighting they are derived from the same sources. Note also the different summer/winter event trends in the river.

However, it is clear from the background sampling in the catchment and the conceptual model described in Chapter 5 that the subsurface component comprises a mixture of water from the shallow bedrock, transition zone, subsoils and soils, and that its transport to the stream is greatly enhanced by the presence of the land drains and ditches. In the interests of trying to determine the role of the interflow pathway, and because, based on the findings in Chapter 5, the interflow pathway is important for the transport of nitrate — which is an important water quality issue in Ireland — the three pathways were retained in the analysis.

6.2.1.6 End member signatures

It is evident from the Mattock end member sampling data that overland flow is high in SAC_{254} and low in silica, while bedrock and gravel groundwater is low in SAC_{254} and high in silica, and land drains and ditches are in between (Figure 6.2). As discussed in Chapter 5, MK3 Shallow and Deep do not contribute to the stream. The tracers selected can therefore adequately distinguish the pathways under consideration, which satisfies one of the major assumptions of the method.

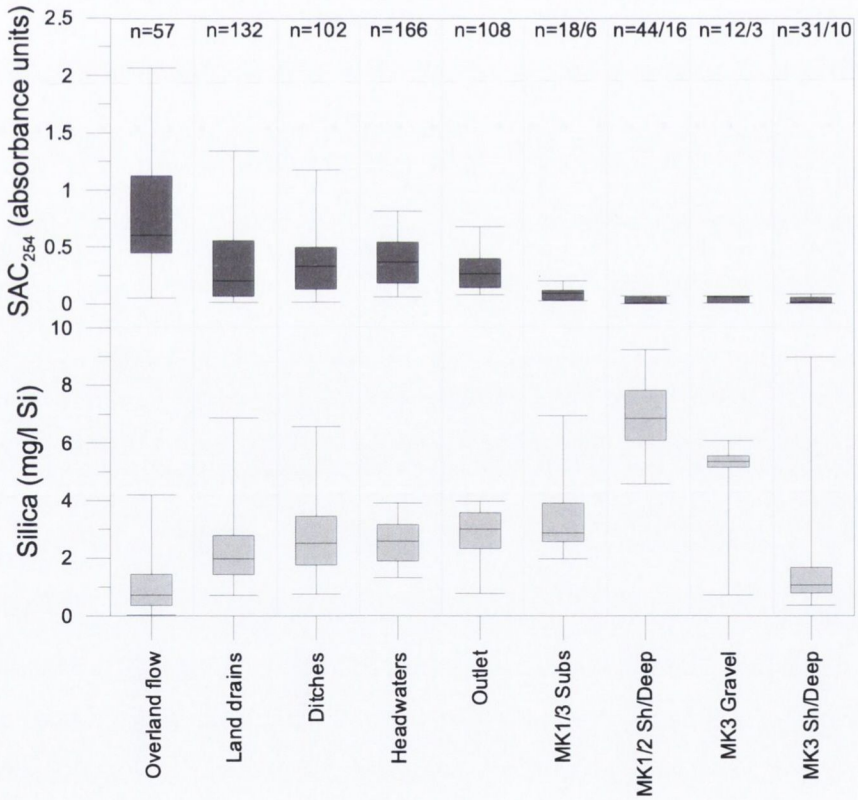

Figure 6.2. Signatures of the end members, Mattock catchment. n = the number of samples. Where two numbers are given, the first is the number of silica samples and the second is the number of SAC_{254} samples.

The signature of water in the ditches is, in general, very similar to the river water, which supports the findings of the conceptual model (Section 5.3.3.3) that they can be considered as extensions of the river system and that they deliver mixed water. Measured silica concentrations in all

ditches for example, ranged from <1 to >6 mg/l as Si (electrical conductivity varied from <100 µS/cm to >400 µS/cm), reflecting changes in the dominant contributions from overland flow to shallow groundwater, respectively.

There is also a wide distribution in the land drain data, highlighting that some drain water more closely resembles the organic-rich overland flow at the surface, whereas other drain water from deeper soils has had a slightly longer residence time and has had the organic matter filtered out. On the whole, however, it is the land drains, rather than the ditches, that most closely reflect the signature of the water in subsoil boreholes. The end of pipe sampling location is also closer to the soil water source, in comparison to sampling in ditches where mixing of pathways is much more prevalent. The land drains therefore best represent the interflow component. It must be noted that the four subsoil borehole samples that have silica contents approaching that of bedrock and gravel groundwater were taken from the alluvium borehole at MK3 near the river during dry periods, when the upward gradient from the underlying gravels influenced the water chemistry.

The three pathway end members are thus overland flow, interflow via land drains, and groundwater from the shallow bedrock and the gravels. The median values of the available silica and SAC_{254} data for each end member were selected for use in the calculations (Table 6.3). Data for one land drain located in organic peaty soils in the upper catchment were omitted from the dataset, because they presented too large a bias in SAC_{254} that was not considered to be representative of the wider catchment conditions.

Table 6.3. Selected values for end member signatures used in the mixing calculations.

Summer	Si mg/l Si	SAC absorbance units
Overland flow	0.89	1.143
Interflow	1.95	0.141
Groundwater	6.67	0.008

Winter	Si mg/l Si	SAC absorbance units
Overland flow	0.45	0.550
Interflow	1.95	0.141
Groundwater	6.67	0.008

The selected tracer values generally bound the stream flow data (Figure 6.3) with one or two minor exceptions, which typically occur during conditions of high flow when SAC values are higher than expected or silica values are lower than expected. This may be due to the influences of surface runoff from hard stand areas. Sample analytical error is also a possibility. For the most part, however, the results suggest that another of the assumptions of the method is met in this catchment, i.e. that the end members represent the extremes in the catchment and the stream samples are bounded by those extremes. The standard error of the end member signatures is relatively small, as the number of samples was large.

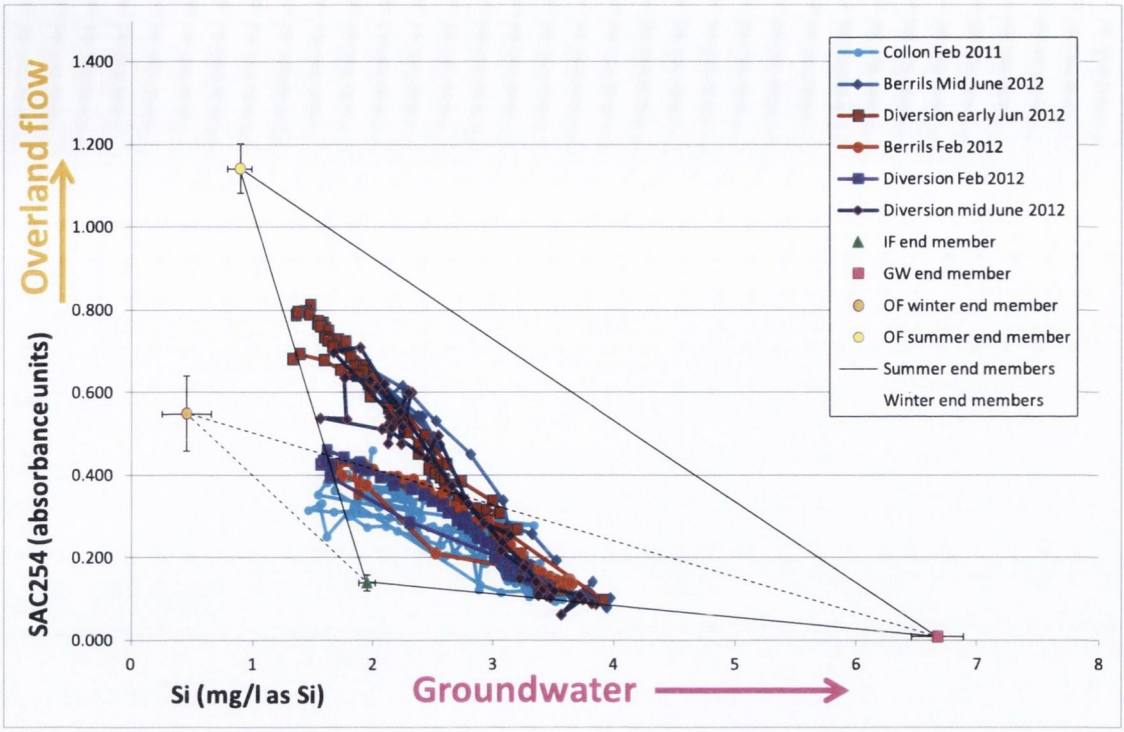

Figure 6.3. End member signatures in relation to the river event data. Error bars show the standard error.

Plotting the data highlighted that there are consistently two different peaks in SAC_{254} in the river data that coincide with the seasons; there is less organic matter washed in with overland flow in the winter months than during the summer. This is likely to be due to a combination of less organic matter in the fields in the winter when the animals are housed indoors, and more dilution in the wetter winter antecedent conditions. Similar seasonal changes in organic matter concentrations were identified by Hooper et al. (1990) in one of the earliest papers using this method. This needed to be taken into consideration in the hydrograph separation calculations, because it could otherwise have been interpreted as a lower contribution of overland flow. This emphasizes that, in practice, and contrary to the second assumption of the method, the end members do vary temporally in the field. This has been accounted for in this study by selecting different overland flow end members for the summer and winter events.

6.2.1.7 Pathway contributions

The predicted flows through each of the pathways for the three winter events are presented in Figure 6.4, and for the three summer events in Figure 6.5, together with the total observed flow. A summary table of the percentage pathway contributions to the river at low flows, peak flows and in total over the sampled event, is included. For the first event, an additional table showing the pathway contributions at peak flow in each of the six sub-events is also presented. Gaps in the datasets are due to autosampler failures when samples were not collected.

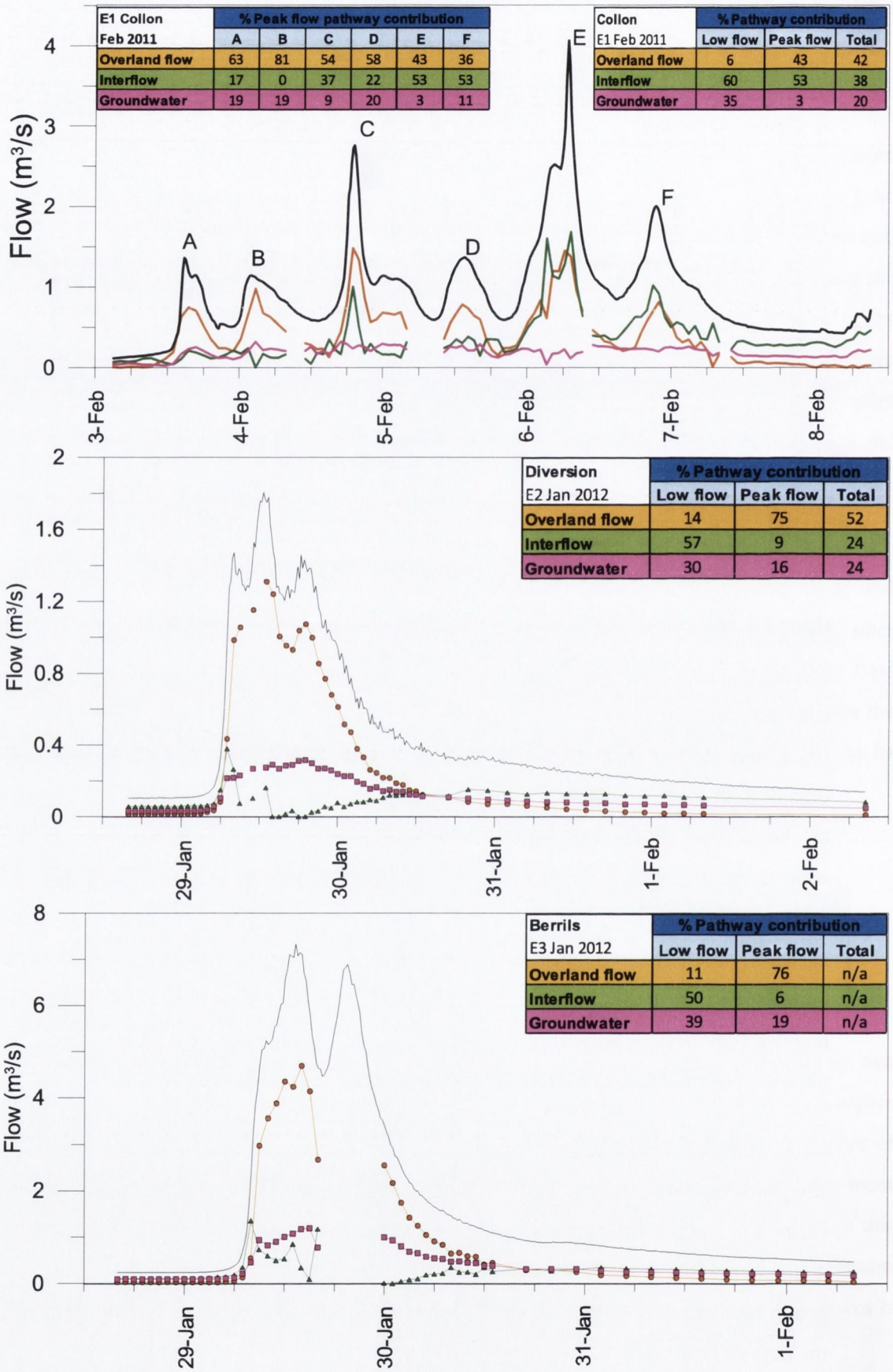

Figure 6.4. Pathway contributions for winter events 1–3. Black lines, total observed flow.

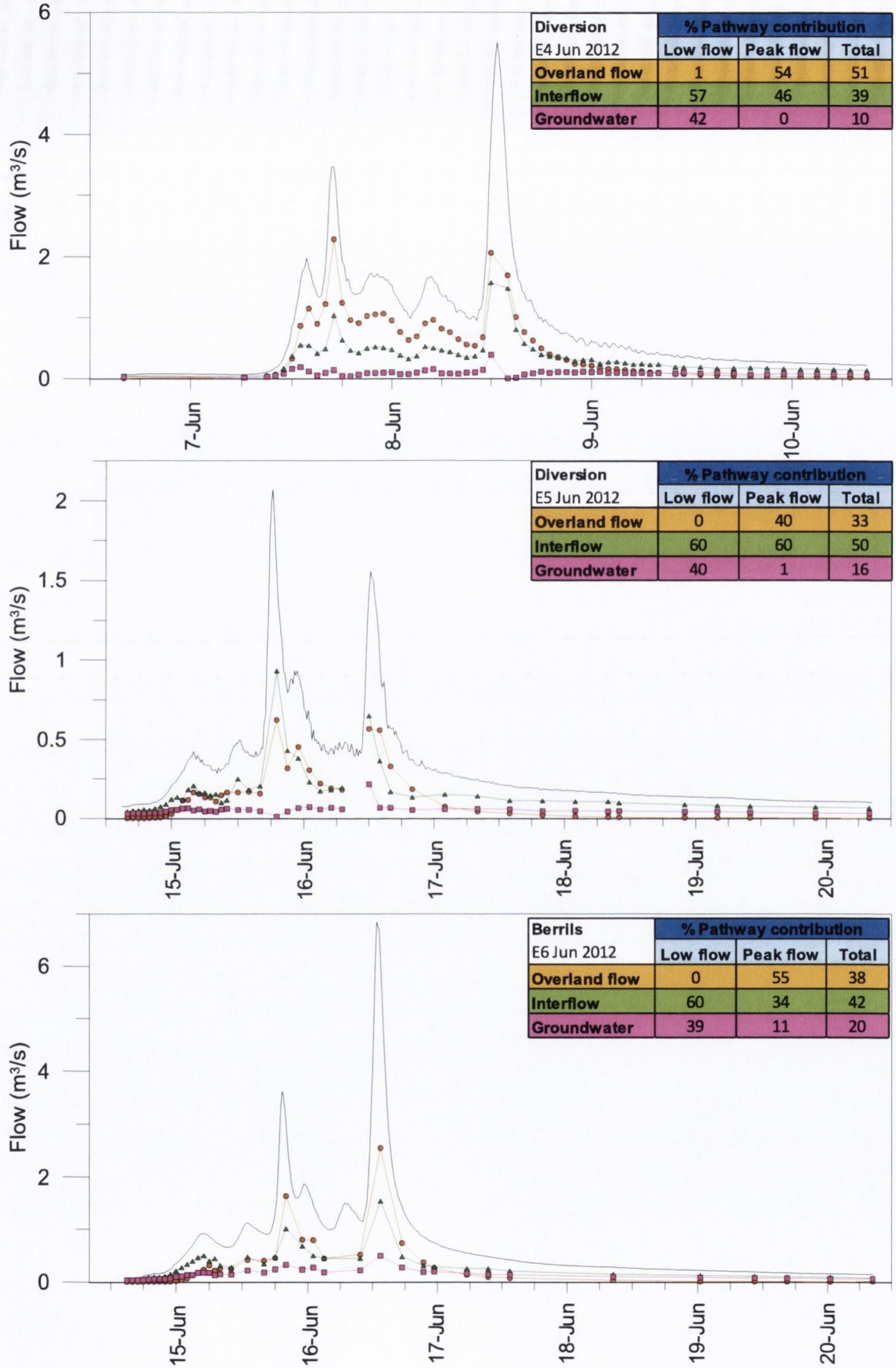

Figure 6.5. Pathway contributions for summer events 4–6. Black lines, total observed flow.

The results show that during the winter periods, over the total duration of each event, overland flow was the dominant pathway (42–52%), followed by interflow (24–38%), while the groundwater pathway contributed least (20–24%). At low flows prior to the events, the interflow pathway contributed more flow (50–60%) than bedrock groundwater. At peak flows, the data from the 6-day event indicate that the proportion of overland flow in the stream varied greatly, from 36 to 81%, and that the percentage decreased as the catchment became wetter in favour of the interflow pathway. Note that the zero value obtained for the interflow pathway during the second peak of the first event was because that particular sampling point was not bounded by the end members. This may have been due to a flush of fresh water from a hard stand area in Collon, which is adjacent to the sampling location.

During the summer months, groundwater (10–20%) and overland flow (33–51%) contributed proportionally less overall to the river than during the winter months, whereas the interflow pathway was slightly higher overall at 39–50%. At low flows, similar to prior to the winter events, the interflow pathway remained dominant at approximately 50–60% of river flow. At peak flows, evidence from Events 3 and 4 in the upper catchment, which were only a few days apart, show that there was a similar pattern of increasing interflow and decreasing overland flow with wetter antecedent conditions, despite the drier conditions overall.

Although it may initially appear counter-intuitive that the proportion of overland flow in a stream decreases as the catchment becomes progressively wetter, it occurs because, as the chemistry data indicate, the stream flow gradually increases proportionally in water with a subsurface origin as the events progress. This is consistent with the findings of the early researchers who observed that subsurface water was able to contribute to streams at the scale of events (Sklash and Farvolden, 1979).

The predominance of water with an interflow signature prior to the events in all seasons suggests that in the Mattock catchment, the baseflow is derived predominantly from the soils and subsoils rather than bedrock. This is consistent with the conceptual model finding that there is a palaeochannel isolating the bedrock groundwater from the river in the valley.

Comparison of Events 5 and 6 highlight that there was an apparent scale-related change in the dominant pathway at peak flow, from interflow dominating both peaks in the upper catchment, to overland flow being more important at the catchment outlet. This is likely to be due to quick runoff from the hard surfaces in the built-up area in Collon, which is located between the sampling locations.

Further insight into the pathway contributions was provided by combining the results with those from the physical hydrograph separation methods as detailed in Section 6.5.

6.2.2 Glen Burn catchment

The conceptual model for the Glen Burn determined that the near-surface pathways were dominant in the catchment, particularly the upper weathered bedrock/transition zone in the inter-drumlin areas, which are drained by the artificial drainage network. The overland flow component was expected to be large because there is little storage in the transition zone in these areas, they saturate quickly, and they receive rapid additional runoff from the drumlins giving rise to favourable conditions for overland flow.

6.2.2.1 Tracer selection

The stable hydrogen isotope deuterium (δ^2H) and silica were selected as having good explanatory power based on PCA (Section 6.2.2.4), the available event data and the catchment conceptual model. Deuterium distinguishes pre-event and event water in the stream: pre-event water that has been subjected to some degree of evaporation has a higher proportion of the heavier δ^2H in its molecular structure and is said to be more enriched, i.e. less strongly negative, whereas fresh rainfall is more depleted in δ^2H, i.e. more strongly negative, notwithstanding that there are variations in δ^2H in rainfall during and between events. Incorporating a solute and an isotope tracer is advantageous because it combines insights from two different hydro(geo)logical processes: dissolution of minerals, a source-origin approach, and the time-based approach of the isotopes (Buttle, 2006). The peat deposits in the upper part of the Glen Burn catchment meant that the use of SAC_{254} was not appropriate as a catchment-wide pathway tracer. It was, however, useful in identifying the importance of the upper catchment flow to the overall catchment water balance.

6.2.2.2 Event data

There were two rainfall events captured in the Glen Burn at the catchment outlet, in May 2012 and November 2012 (Table 6.4). The events were similar in magnitude and maximum rainfall intensity, but the May event was much more drawn out lasting twice as long as the November event, which meant that the average rainfall intensity was much lower. The peak flow level of the May event was also approximately the same as the baseflow level before the November event. Consequently, the winter antecedent conditions were much wetter and the response in the river was therefore much greater.

Table 6.4. Event characteristics, catchment outlet (MS2), Glen Burn.

Event no.	Event start	Event duration (days)	Rain duration (hours)	Total rainfall (mm)	Max intensity (mm/h)	Ave intensity (mm/h)
1	9 May 2012	4.7	36	19.3	3	0.56
2	18 Nov 2012	3.7	13	22.4	3.4	1.2

One additional chemistry dataset was available for the mid-catchment location for the May event, but as there are no comparable flow data available, they are not used in the hydrograph separations. However, the data contributed useful additional information for the conceptual model.

6.2.2.3 End member sampling

Near-surface pathway end member sampling was restricted to the two campaigns during the team events, which meant that the background data were very limited in comparison to the Mattock catchment. A slightly different approach to the selection of the end member signatures was therefore required, which is described further in Section 6.2.2.6. In all, there were less than 10 samples available for each of the near-surface pathway types.

In contrast, there was an intensive bedrock sampling programme carried out in the Glen Burn catchment boreholes as part of a sister *Pathways Project* research project (Orr, 2014), so there were 88 silica samples available for the bedrock groundwater from the borehole monitoring suite. Unfortunately however, there was no capacity to analyse for δ^2H during the background sampling campaigns, so data for the groundwater end member were limited to the analysis carried out by a commercial laboratory as part of the two team events.

6.2.2.4 Principal components analysis

The PCA carried out on the stream event data highlighted that there were four main components contributing to the variance in stream chemistry at the catchment outlet in both seasons, although there was far greater uniformity among the tracers during the winter event when the antecedent conditions were much wetter (Table 6.5). The principal component was dictated by the major ions associated with the rock minerals, such as sodium, magnesium and silica, and included the isotopes, which suggests the signal may be attributed to the dilution of subsurface water with overland flow. The much weaker signal in the May event (39% of the variance) is consistent with the overland flow pathway being less influential at lower flow levels.

The second component in the May event, which still represents quite a high percentage of the variance at 25%, includes TOC and SAC, with ammonium and potassium. This may represent the

Table 6.5. PCA outputs for stream flow samples at the catchment outlet in the Glen Burn during the summer and winter events. The numbers in the cells represent how strongly the tracers are correlated with the patterns of each component. Greyed cells highlight the component each tracer is best aligned with. % variance is the variance in stream flow that can be explained by each component.

May 2012 event, catchment outlet				
Catchment outlet	Component			
	1	2	3	4
% Variance	39	25	12	9
Sodium	.987	.032	-.045	.002
Magnesium	.985	-.092	-.099	.370
Chloride	.957	.289	-.193	.025
Alkalinity	.809	.028	.302	-.074
d2H	.699	-.384	.228	-.167
Silica	-.697	-.178	.165	.399
d18O	.649	-.242	.150	-.309
TOC	.091	.940	.515	-.001
Potassium	.231	.782	-.386	-.012
NH4	-.051	.731	-.343	-.044
SAC	-.358	.506	-.070	.110
PO4	.130	-.156	-.928	-.092
NO3	-.123	.209	-.817	.087
Calcium	-.093	.256	-.206	.819
Sulfate	.167	-.310	.401	.790

Nov 2012 event, catchment outlet				
Catchment outlet	Component			
	1	2	3	4
% Variance	63	14	7	6
Conductivity	.987	.071	-.019	-.044
Calcium	.983	.041	-.014	-.055
Magnesium	.981	.065	-.053	-.063
Sulfate	.980	.016	-.002	-.064
Sodium	.976	-.006	.114	.028
Silica	.966	.065	-.060	-.090
Bromide	.954	.170	-.080	-.050
Chloride	.917	-.108	.250	.160
Alkalinity	.916	-.016	-.261	-.050
d2H	.881	-.218	.211	.250
Nitrate	.870	.037	-.389	-.079
Phosphate	-.810	.178	-.314	.067
d18O	.652	-.351	.388	.268
Potassium	-.632	.147	-.198	.292
Fluoride	-.124	.843	.168	.319
Ammonium	.064	.772	.003	-.310
Nitrite	.197	.291	.887	-.143
TOC	-.319	-.391	.649	.044
SAC	-.058	.075	-.146	.921

contributions from the upper catchment where the soils are peaty and organic and there are known to be significant small point sources of contamination, or alternatively incidental losses of organic fertilisers near water courses. The equivalent signal in the November event is much weaker, which reflects the higher flows across the catchment, the dilution of the upper catchment contributions and the housing of the animals indoors. The remaining components represent much smaller percentages of the overall variance and are typically contamination signals. It is not clear why component 4 in the May event includes calcium and sulphate, which would normally be associated with the dilution of subsurface water, but it may represent the transfer of excess calcium ammonium nitrate (CAN) fertilisers to the stream from the upper catchment peaty soils.

The PCA confirmed that the use of silica and δ^2H was appropriate as they are both represented in the principal component in both seasons. Sodium and magnesium would have also been suitable alternatives for the subsurface component. Further discussion on the usefulness of the PCA approach is presented in Section 6.8.3.

6.2.2.5 Mixing models

Pathways mixing models show that there were different progressions in the stream event chemistry at the catchment outlet during the summer and winter events, a trend that was not found in the other catchments (Figure 6.6). Prior to the May event, the chemistry of the stream water was dominated by waters enriched in δ^2H and low in silica, consistent with shallow subsurface water in the peat in the upper catchment. This was confirmed by the chemistry of spot samples taken from the stream in the upper catchment. As the event progressed, the slightly fresher influx of more δ^2H depleted water is evident, whereas towards the end of the event, there is a gradual increase of groundwater higher in silica. Prior to the November event, the baseflow is more strongly influenced by subsurface water much higher in silica, which, based on the spot samples, was similar to the bedrock groundwater. The δ^2H content was higher than in typical bedrock groundwater however, which may reflect slight mixing with nearer-surface pathways.

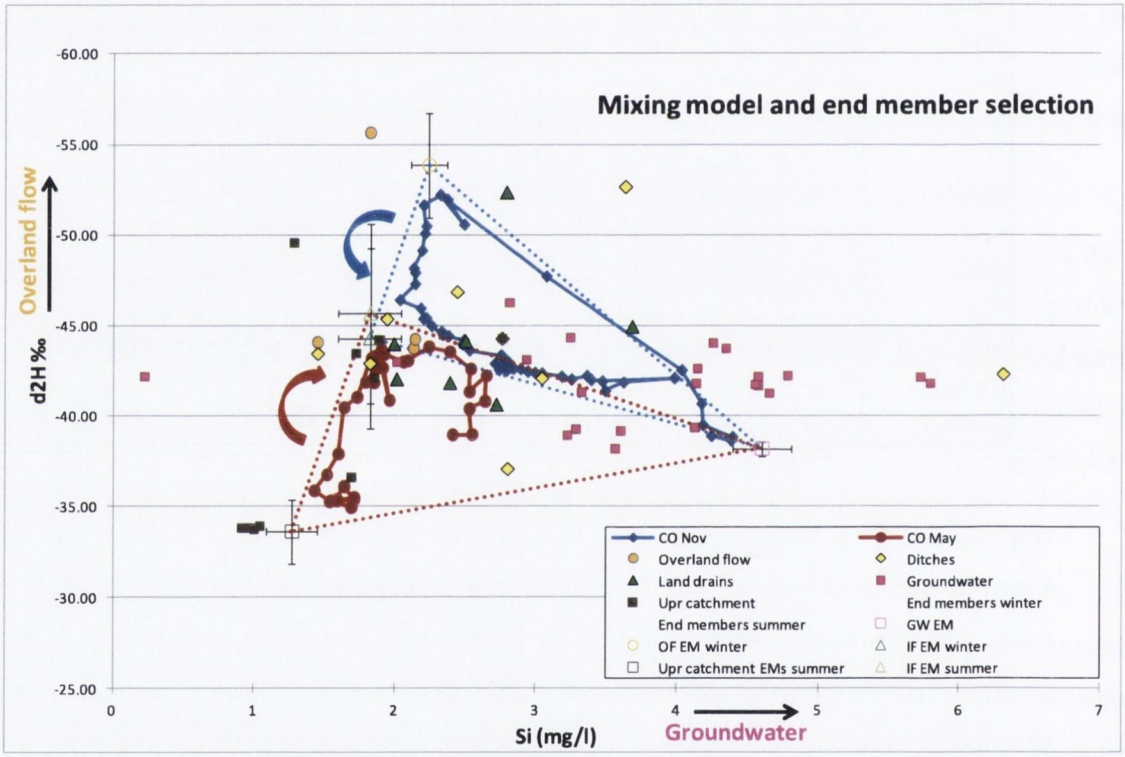

Figure 6.6. Mixing model for the Glen Burn catchment. Error bars show the standard error.

6.2.2.6 End member signatures

Given the limited number of end member samples in the Glen Burn catchment, a different approach to selecting appropriate end members was required. The end member signatures were selected based on the evidence provided by the stream chemistry, supported by the data collected from the end member pathways and the conceptual model. In simple terms, the approach took the stream chemistry as the starting point and used the end member samples in the context of the conceptual model to try to explain what was contributing to it at different points in the hydrograph, rather than initially determining the end members independently based

on spot samples from the catchment, as is the more traditional approach. The selected end member signatures and the justification for them are presented in Table 6.6.

Table 6.6. End member signatures and their basis, Glen Burn. The average electrical conductivities of each pathway are given for comparison to support the findings.

Pathway	Si mg/l	δ^2H ‰	Description and basis
November event only			
OF	2.24	−53.84	Quick response overland flow. Si, average measured event values; δ^2H, average measured event rain. Measured OF δ^2H values not used as evaporation influences evident in the data, which may suggest some return flow contributions. Average EC 176 µS/cm
IF	1.82	−44.29	Soil water discharging via the drainage network with minimal residence time and little evaporation. Si, average measured IF values; δ^2H, average measured IF values. Average EC 227 µS/cm
GW	4.60	−38.17	GW as represented in the 12 catchment boreholes. Si, average measured borehole background and event groundwater data; δ^2H, lowest measured value in event. No background data available. Alluvium, shallow and deep holes included as almost all holes are influenced by shallow GW due to poor construction. Average EC during the event 458 µS/cm
May event only			
Upper catchment	1.27	−33.61	Peaty water from the upper catchment. Si, average measured values at S11 and baseflow in mid-catchment; δ^2H, most enriched value mid-catchment away from the influence of another ditch. Average EC during the event 465 µS/cm although contamination is an issue
IF	1.82	−45.66	Soil water discharging via the drainage network with minimal residence time and little evaporation. Si, lowest IF value taken to incorporate the minor OF component; δ^2H, average IF values. Average EC during the event 311 µS/cm
GW	4.60	−38.17	As for November event

OF, overland flow; IF, interflow; GW, groundwater; EC, electrical conductivity.

Based on the stream chemistry and the conceptual model, it was determined that different end member signatures were required for the near-surface pathways for each event. For the most part, the average of the measured tracer concentrations for the sampled end members were used, but with three notable exceptions. In the November event, the δ^2H values for the overland flow samples collected did not bound the stream samples as they were too enriched. This is likely to be because the winter overland flow incorporated some return flow that had previously been subjected to some degree of evaporation, yet the water was clearly sufficiently dilute such that the silica values were still low. This was consistent with observations of the electrical conductivity of overland flow values of >200 µS/cm in some places in the field, which is much higher than fresh rainfall. In the May event, the stream was more enriched in δ^2H than the waters sampled from the upper catchment, so the most enriched value was adopted as the end member concentration. This is an example of the near-surface pathways sampling not adequately capturing the full extent of variability in the stream. The lowest of the silica values measured for the interflow end member was required to adequately bound the stream samples. The resulting mixing triangles bound the

stream data; they do not bound all the end member samples because they represent the average, (or best estimate) of the end member characteristics which in this catchment are very variable due to considerable intermixing of the pathways.

Review of the end member mixing triangles with the stream tracer concentration data shows that, for this catchment, very clear differentiation is achieved between the pathway contributions using these tracers, i.e. the stream chemistries plot in a distinct triangular pattern showing clear progression from the dominance of one pathway to another. For a three-pathway component catchment, this is the ideal scenario as it means that, in effect, the stream data force the selection of the appropriate end members and there is less reliance on the data from the limited end member sampling with all its associated errors.[7] This can only be achieved, however, if there is a sound conceptual model of the catchment dynamics that leads to correct selection of appropriate tracers in the first instance. Several combinations of tracers were reviewed in this analysis before an acceptable differentiation that could be hydrogeologically and defensibly explained was achieved. This process also added to the development of the conceptual model. Although this approach may not lead to precise percentages of end member contributions due to slight inaccuracies in the appropriate end member tracer concentrations selected, it nevertheless provides defensible relative pathway contributions for each time step in the stream. Further discussion on uncertainty and end member signature selection is provided in Sections 6.4 and 6.8.

6.2.2.7 Pathway contributions

The predicted flows through each of the pathways for the two events are presented in Figure 6.7 and Figure 6.8, together with the summary statistics. The results from the May event show that the pre-event baseflow signature was dominated by seepage water discharging from the peaty soils in the upper catchment (72%). This is confirmed by the background catchment sampling data, which shows that more than 50% of the flow at the catchment outlet is contributed from the uppermost catchment area when the flows at are 10 l/s or less at the outlet. During the first peak in stream flow, the increase in stream flow was predominantly due to the increase in interflow as the groundwater contribution was still at a minimum (5%). As the event progressed, shallow groundwater from the lower-lying areas began to contribute, reaching a maximum of 28% at peak stream flow. Overland flow was not observed except on made ground.

[7] Although the standard errors for the end members are larger for this catchment than for the Mattock, they still allow proper differentiation of the different components. However, this may not always be the case in data-poor catchment studies.

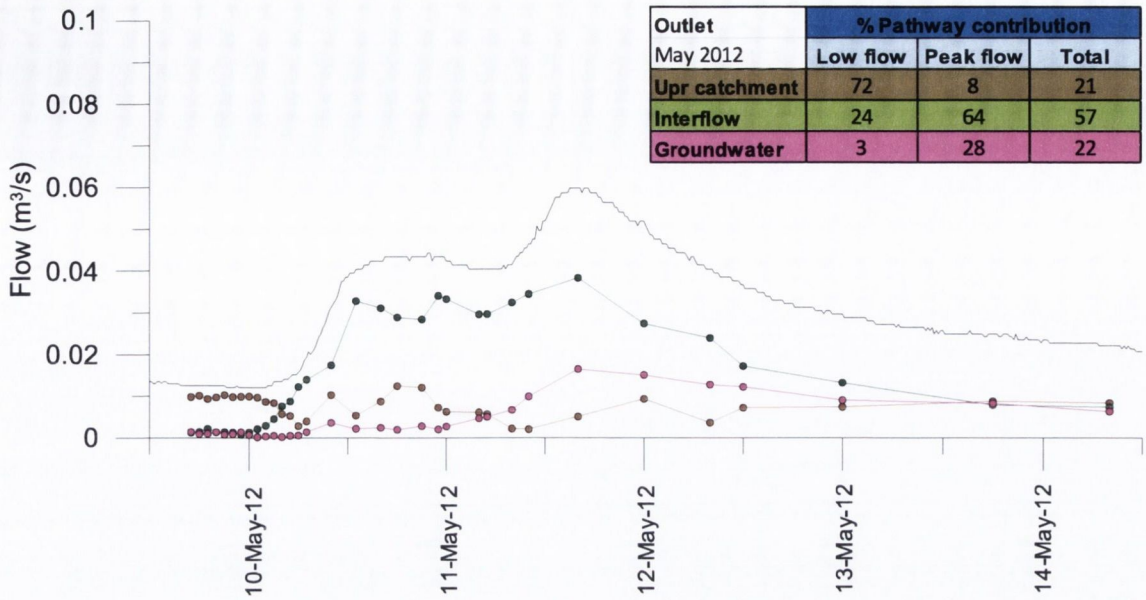

Figure 6.7. Pathway separations for the May event, Glen Burn.

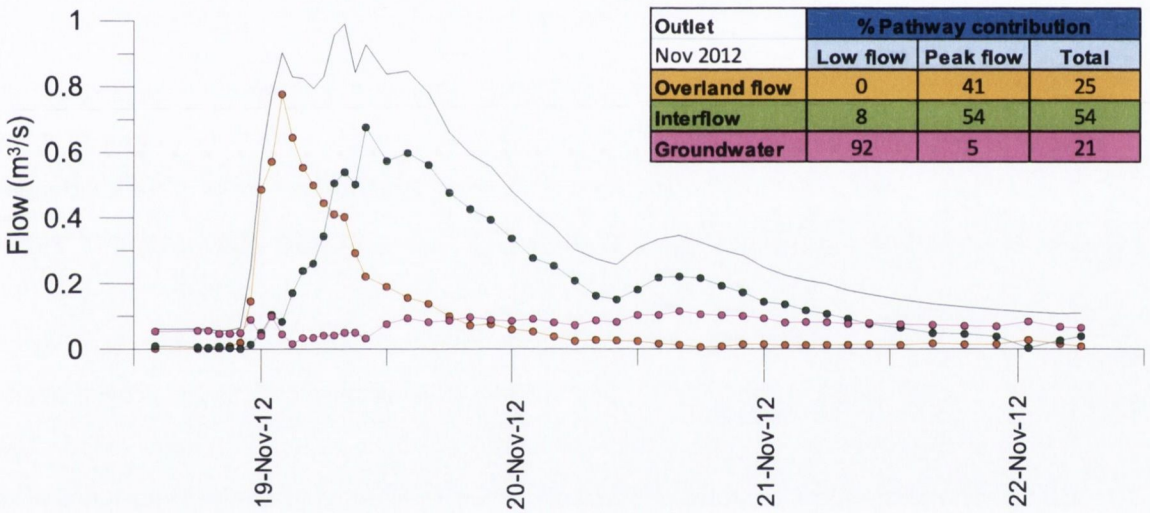

Figure 6.8. Pathway separations for the November event, Glen Burn.

In November, the river flow was dominated by groundwater (92%) prior to the rainfall event. A large surge of overland flow (maximum 86%) occurred shortly after the onset of rain but it was substituted by a large component of interflow (maximum 72%) as the event progressed. At the time of peak stream flow, there was 41% overland flow and 54% interflow. The groundwater contribution remained low throughout the event, increasing again during the recession.

The interflow pathway was the dominant pathway overall (54–57%) in the Glen Burn catchment during both seasons. This is because in this catchment, a permeable transition zone in the upper bedrock is not present everywhere, and the competent bedrock acts as a barrier to vertical flow for the soil/subsoil water. The delivery of this soil and subsoil water to the stream is enhanced very effectively by the artificial drainage network. The overland flow component dominated, as

expected, in the November event, but only during the early part of the event when the fresher water gained quick access to the stream. As the event progressed, there was more mixing in the near-surface pathways and the interflow pathway became more important.

6.2.3 Gortinlieve

The conceptual model suggested that the transition zone is the key subsurface pathway for the delivery of flow to the stream in Gortinlieve, although different hydrogeological processes dominate in different parts of the catchment, which affects nutrient delivery. In the groundwater recharge areas in the upper catchment, during events, water is flushed out into the nearest ditch or tributary/stream channel, or as return flow whereupon it is mixed with inputs from overland flow. In the groundwater discharge areas, upwelling groundwater is nutrient poor but the artificial drainage network that has been developed to alleviate the high water table, as well as overland flow, is important for the delivery of phosphorus.

6.2.3.1 Tracer selection

Analysis of the event data, the PCA, the EPA borehole data and the conceptual model, suggested that the most suitable tracers for the mixing analysis were δ^2H representing the overland flow component, and calcium to reflect the contribution from the subsurface. Although use of silica would have been preferable due to the nature of the Precambrian rocks in the catchment, there were unfortunately quality control issues with the silica data for the November event, which meant they could not be used. Electrical conductivity was also found to be generally useful, but as there were known point sources of contamination in the river during the events, it was decided against using electrical conductivity for the hydrograph separations. SAC_{254} proved not to be an appropriate tracer in Gortinlieve because of the presence of peaty organic soils in the upper catchment areas in the headwaters (see Section 5.3.1). This highlights the importance of selecting catchment-specific tracers.

6.2.3.2 Event data

Two major team-based event sampling campaigns were conducted in November 2011 and December 2012 (Table 6.7). A significant summer event unfortunately proved elusive in the Gortinlieve catchment, but nevertheless the characteristics of the winter events were sufficiently different to provide complementary information; the November 2011 event produced one of the largest stream flow responses recorded during the 2-year sampling period. A smaller event was also captured in August 2010 but as there were a restricted number of analytes included in the monitoring suite, the scope of possible analyses was limited.

Table 6.7. Event characteristics, Gortinlieve.

Event no.	Location	Event start	Event duration (days)	Total rainfall (mm)	Max intensity (mm/h)
1	EPA weir	16 Aug 2010	2	18.6	3
2	EPA weir	28 Nov 2011	2.56	44.3	12.4
3	Catchment outlet				
4	EPA weir	5 Dec 2012	4.8	28.4	2.8
5	Catchment outlet				

6.2.3.3 End member sampling

Near-surface pathway end member sampling was again restricted to the two campaigns during the team events, although the number of samples collected was slightly higher than in the Glen Burn. In addition, an autosampler was used to continuously sample ditch water during the December event. Fourteen rounds of calcium analyses from the EPA boreholes were available, but there were unfortunately no matching δ^2H data available. This meant that groundwater monitoring data incorporating both selected tracers was also restricted to the team events.

6.2.3.4 Principal components analysis

The PCA showed that in the four event datasets, more than half of the variance in the stream samples was accounted for by the first component, which, based on the tracers and similar to the other catchments, represents the dilution of subsurface water with overland flow (Table 6.8). The minor constituents typically comprised the contaminant indicators and DOC/SAC, which may represent the contribution from the organic-rich upper catchment.

Interestingly, the δ^2H and $\delta^{18}O$ tracers comprised their own component in the November event, which was different to that found in the other catchments. This is because there was a large spike in the isotope data in two samples taken over the space of 2 h that indicated that they were significantly more enriched (i.e. more evaporation) than any of the other samples found in any of the study catchments. The results were cross checked with the laboratory and were confirmed as correct. Closer inspection of the full dataset revealed that the spikes were correlated with sharp increases in potassium, ammonium, phosphate and SAC, which may suggest a relationship with some kind of contamination spill from a storage source, or perhaps a slug or minor landslip of some of the peaty organic matter from the upper catchment. Further discussion on the usefulness of the PCA approach is presented in Section 6.8.3.

6.2.3.5 Mixing models

The mixing model (Figure 6.9) shows that there was a similar progression in stream chemistry in respect of the selected tracers for both events and at both sampling locations within the catchment. The contaminant spike in the November event at the mid-catchment sampling point

Table 6.8. Principal components analyses, Gortinlieve events. The numbers in the cells represent how strongly the tracers are correlated with the patterns of each component. Greyed cells highlight the component each tracer is best aligned with. % variance is the variance in stream flow that can be explained by each component.

Gortinlieve Nov 2011 event			
Catchment outlet	Component		
	1	2	3
%Variance	63	14	7
SO4	.992	.035	-.108
Ca	.983	.012	-.048
Mg	.983	.000	-.042
Na	.981	-.006	-.108
Cl	.958	-.078	-.076
Cond	.953	-.013	-.032
NO3	.912	-.109	-.147
d18O	.876	.158	.283
D2H	.873	.027	.232
K	-.846	.089	.140
Alk	.833	-.233	-.183
SAC	-.770	-.083	-.419
DOC	-.451	-.958	.045
NH3	-.288	.763	-.012
NO2	-.398	.686	.231
PO4	-.347	.482	-.213
TP	-.499	.022	.690
TN	.415	-.306	.494

Gortinlieve Nov 2011 event					
Mid catchment	Component				
	1	2	3	4	5
%Variance	50	11	9	7	5
Cl	.942	-.029	-.099	.012	.015
SO4	.926	-.068	-.109	.046	.088
Ca	.924	-.129	.011	.242	.111
TDP	-.919	-.020	.045	.147	-.033
PO4	-.918	-.019	.046	.148	-.031
NH3	-.900	-.079	-.240	.164	.001
K	-.889	.015	.016	-.025	.372
Mg	.871	-.112	-.146	.295	.034
SAC	-.853	-.065	-.243	-.175	.353
Na	.847	-.137	-.248	.171	-.016
NO3	.843	-.135	-.229	-.029	-.282
Cond	.771	.228	-.033	.127	.150
NO2	-.752	-.151	.082	.382	-.129
Temp	-.632	-.120	.062	.423	-.303
Br	.565	-.121	-.043	.297	.546
Flow	-.515	-.140	.449	-.004	-.030
d18O	-.101	.947	-.167	.068	.221
d2H	.263	.918	-.015	.165	.038
TDN	.084	-.207	-.067	.014	.083
TN	.143	-.043	.996	-.049	.040
TP	-.135	.032	.926	.151	.097
DOC	-.205	-.222	-.069	-.813	.147
Alk	.448	.057	.008	-.562	-.491
F	-.046	.215	.069	-.236	.881

Gortinlieve Dec 2012		
Catchment outlet	Component	
	1	2
%Variance	70	12
d18O	1.054	-.228
NO3	.995	-.046
Ca	.982	.024
Mg	.975	.034
SO4	.968	.038
Alkalinity	.956	.033
d2H	.948	.033
Flow	-.938	-.067
K	-.895	-.040
TSS	-.883	.194
F	-.835	.012
Si	.833	.229
Cond	.750	.385
PO4	-.682	-.237
TN	.451	.092
NH4	-.208	1.017
Cl	.278	.766
Na	.279	.765
DOC	.001	-.764
SAC	-.180	-.672

Gortinlieve Dec 2012		
Mid catchment	Component	
	1	2
%Variance	78	10
Na	.989	.039
SO4	.981	-.020
Cl	.980	.084
d2H	.970	.056
Ca	.965	-.093
Mg	.964	-.097
Si	.955	-.102
d18O	.941	.010
K	-.937	.054
NO3	.937	-.072
Cond	.936	-.129
Flow	-.926	.078
PO4	-.915	.002
NH4	-.853	-.271
Alkalinity	.778	-.277
F	-.671	-.122
DOC	.070	.972
SAC	-.203	.924

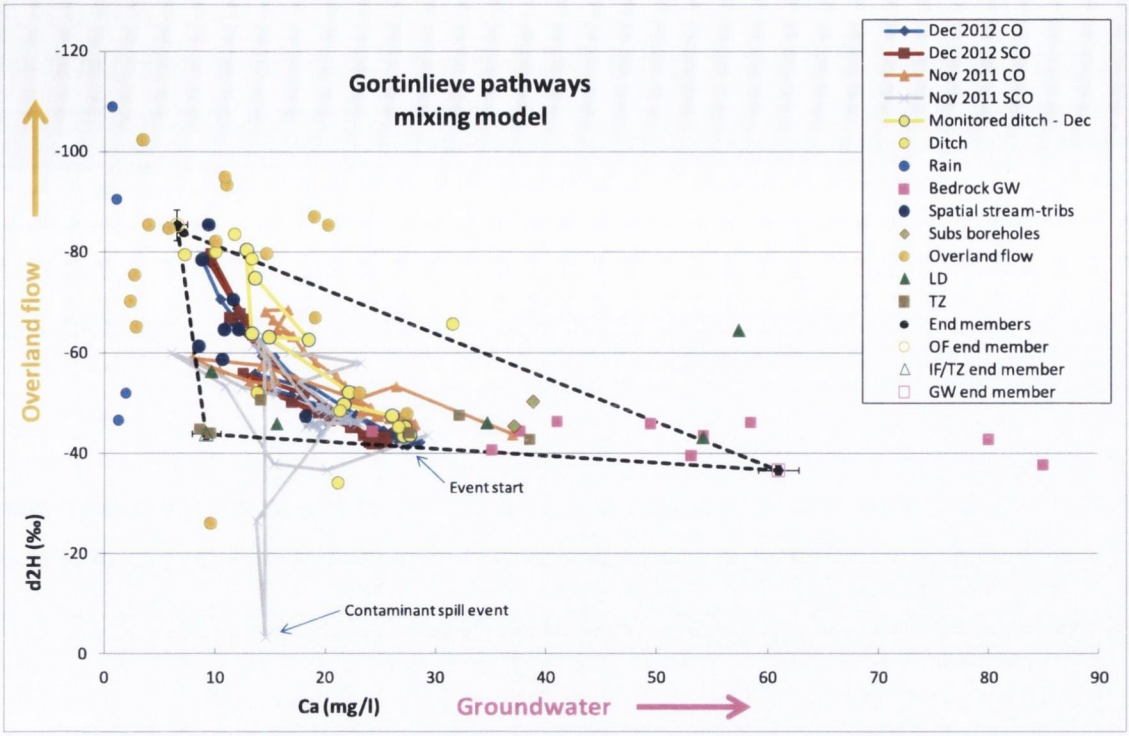

Figure 6.9. Mixing model for the Gortinlieve events. Error bars show the standard error of the end member tracer concentrations. CO, catchment outlet; SCO, subcatchment outlet/mid-catchment.

was clearly evident. The data suggest that there were three main components contributing to the stream during the rainfall events: groundwater (high in Ca and enriched in δ^2H), which was dominant in the stream prior to the event; overland flow (low in Ca and depleted in δ^2H); and a third pathway that was lower in Ca but still enriched in δ^2H. Review of the borehole data and the near-surface pathway samples collected during the events revealed that this was the signature of the transition zone water in the GO1 and GO2 boreholes in the upper catchment. Similar chemistry was also evident in some of the land drains and ditches, and even in an overland flow sample. This indicates that the transition zone water in the upper catchment has relatively short residence times, is closer in chemistry to a soil water component and can readily return to the surface via the return flow.

Hourly sampling from one of the major ditches just downstream of the mid-catchment sampling point during the December 2012 event shows that there is a strong correlation and overlap between the chemistries of the ditch and the stream ($R^2 = 0.85$), suggesting that they are derived from similar sources.

In comparison to the Glen Burn and Mattock catchments, the mixing model was less definitive in the Gortinlieve, particularly with respect to the interflow/transition zone pathway. There was a large spread and more overlaps in the tracer concentrations from overland flow, land drains, the transition zone and the subsoil boreholes. This is because there is a great deal of intermixing

taking place in the near-surface pathways throughout the catchment. There are also different residence times and hydrological processes in the near-surface pathways in the groundwater recharge areas than in the groundwater discharge areas, depending on the vertical gradients. Additional sampling of this pathway, and segregation of the data into groundwater recharge zone water versus groundwater discharge zone water, would have been beneficial. However, the total catchment area is already very small at 4.3 km^2 and if the findings were to be of benefit in informing the catchment modelling tools, the data required a degree of generalization at the catchment scale.

6.2.3.6 End member signatures

The end member signatures are shown in Figure 6.9. For the groundwater end member, the calcium tracer concentration was well constrained with the large number of samples available, but none of the sampled δ^2H values were enriched enough to bound the stream samples so the lowest value measured in the stream at baseflow was selected.

The overland flow end member was influenced by the changing isotopic signature of the rain in the catchment as the events progressed. In both events, the δ^2H values in the rainfall samples halved between the start and end of the event, but it was the more depleted values that dominated the overland flow and this was therefore the signature that was used in the analysis. The concentration of calcium in overland flow samples varied considerably. Fourteen samples had concentrations <11 mg/l and there were six samples with concentrations of 15–35 mg/l. The group with the higher concentrations was considered to be representative of return flow, i.e. interflow that is discharged at the surface because the soils are too saturated, and was therefore not included in the calculation of the mean concentration. This was consistent with the calcium concentrations in overland flow in the Mattock catchment (<7 mg/l) where there was less return flow.

As discussed earlier, the data representing the transition zone in the upper catchment in the GO1 and GO2 boreholes were used to characterize a transition zone end member. This was considered conceptually reasonable in view of the relatively high hydraulic conductivity, the piezometric head profile and the electrical conductivity data, in the context of the conceptual model outlined in Section 5.3.3.

6.2.3.7 Pathway contributions

The pathway separations predicted for the four main events are presented in Figure 6.10. It must be noted prior to this discussion that the flow measured at the catchment outlet at the peak of

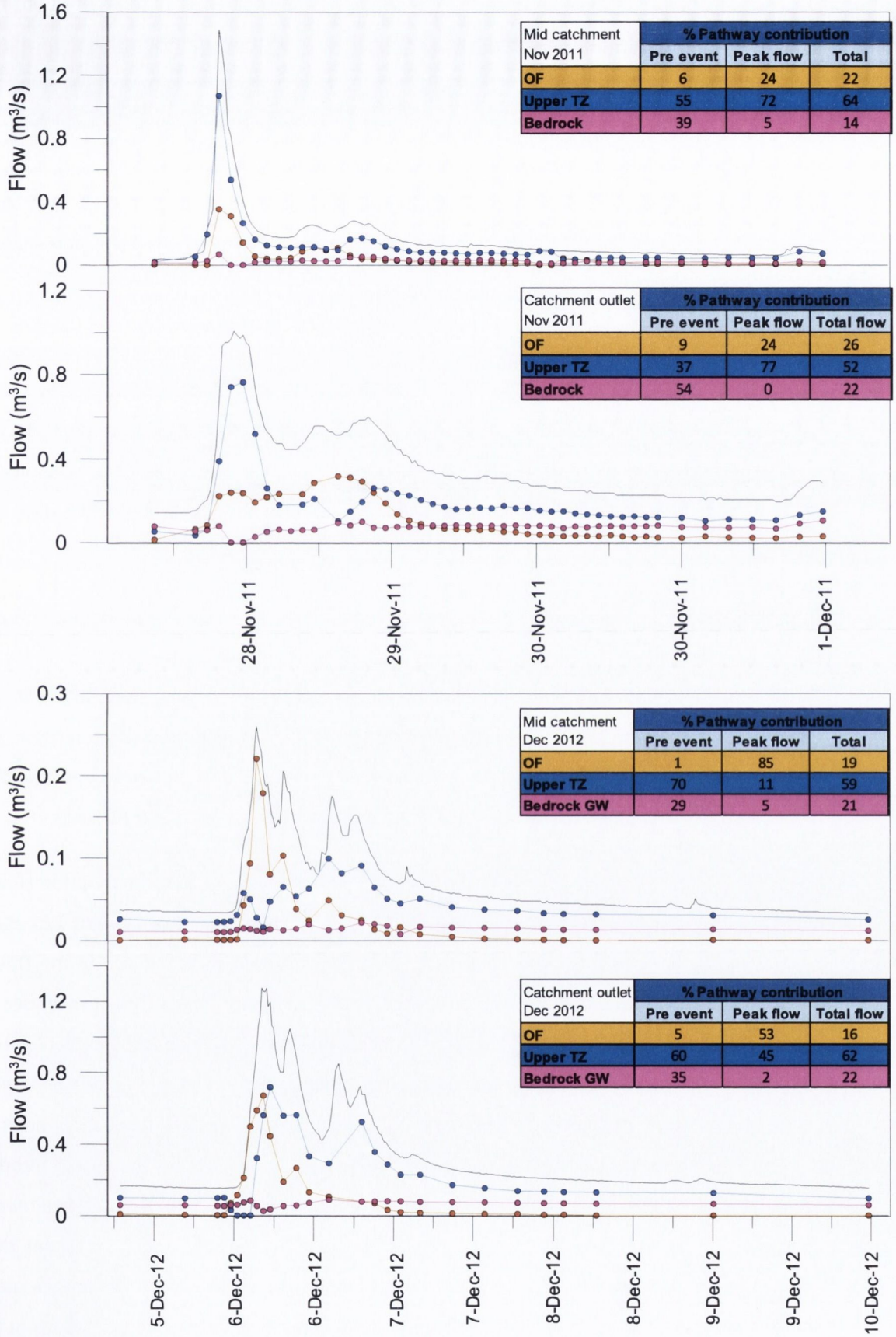

Figure 6.10. Pathway separations for Gortinlieve events. Black lines, total observed flow.

the November 2011 event is smaller than that measured at the mid-catchment location, which is unrealistic. This is because this event was one of the largest seen in the catchment during the course of the project and the rating curve for the site does not cover flows at that high a stage level. In contrast, the mid-catchment gauging station is an EPA monitoring site and fortuitously, on the day of the event, a high flow measurement was taken by the EPA hydrometrics officer at that location. The erroneous peak flow data at the catchment outlet do not affect the relative or percentage pathway contributions, but are apparent on the graph when the percentages are converted to flows.

Prior to the November event, the groundwater contribution was higher in the lower catchment than at the mid-catchment scale. This is consistent with the upward gradient in the lower catchment delivering higher proportions of groundwater flow to the stream. At low flows prior to the December event, the groundwater contributions were lower overall, which was likely as a result of drier antecedent conditions and lower shallow groundwater levels in the days prior to the event.

At peak flows during the December event, the overland flow pathway was dominant in the upper catchment and marginally higher than the transition zone component at the catchment outlet. This is consistent with the steeper slopes in the upper catchment. At peak flows in the November event however, the largest component of water in the stream was from the transition zone at both catchment scales. As it is counter-intuitive that there would be less overland flow during a higher intensity rainfall event, further investigation of the available data was carried out.

The average electrical conductivity of the overland flow samples collected during the November event was quite high at 161 µS/cm and three of the samples were higher than 225 µS/cm, in comparison to values of less than half that (73 µS/cm) in overland flow during the December event. This would support a subsurface origin for the overland flow in the November event. Comparison of the water levels in the GO3 boreholes near the river during events (Figure 6.11) highlights that, in November, there was a larger and more rapid increase in the water level in the transition zone than during the December event, which would have increased the gradients and therefore increased the discharge close to the stream and drainage channels. Similar trends were seen in the boreholes in the two other clusters further up the catchment. In the remainder of the catchment, away from the drainage channels, the wet antecedent conditions meant that the subsurface was already full, which forced much of the extra water out to the surface as return flow or apparent overland flow. This was supported by field observations during the event (Figure 6.12).

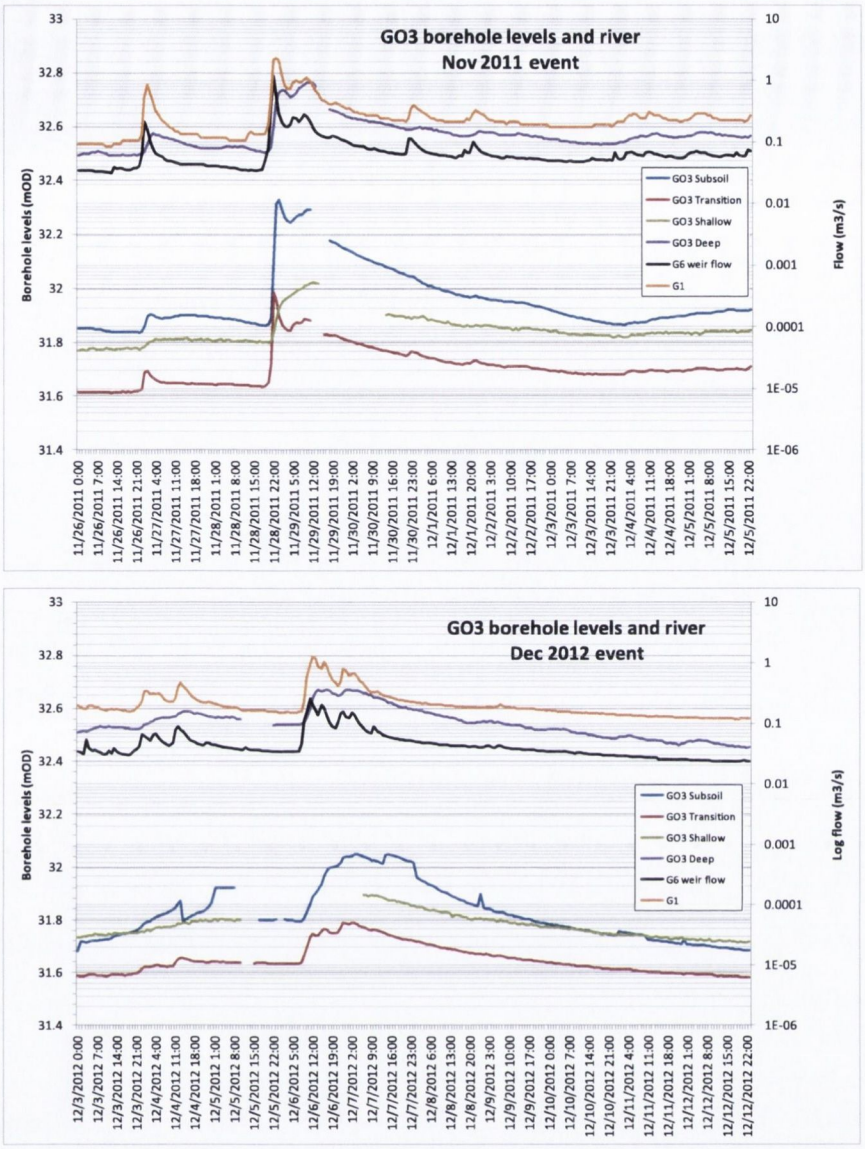

Figure 6.11. Comparison of the water levels in the boreholes in GO3 and stream flows in the upper (G6) and lower (G1) catchments during the November and December events.

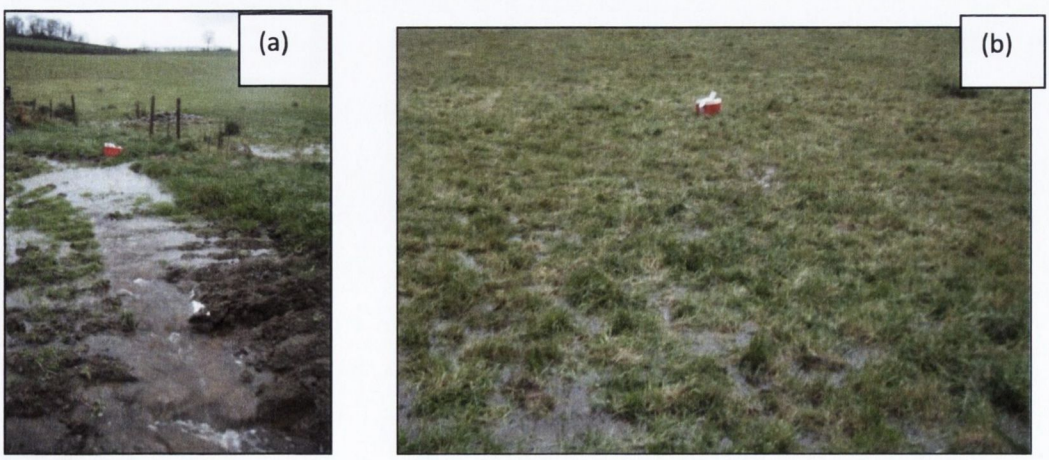

Figure 6.12. (a) Overland flow at the base of the steep slope in the upper catchment concentrated into a channel; (b) ponded surface water upgradient of photo (a).

This hypothesis is further supported by the pattern of transport of NO_3 loads at the catchment outlet. During the November event, the maximum exported load was 845 mg/s as N, and the load remained high during the recession at approximately 670 mg/s as N. During the December event, however, the maximum exported load was 724 mg/s as N, but it was gradually reduced towards pre-event levels (271 mg/s as N) with the stream recession. It is known from the borehole water quality sampling that the transition zone pathway is the dominant pathway for the transport of nitrate, and the increase in nitrogen export loads is consistent with an increase in the contribution from the transition zone. The average concentrations of NO_3 in overland flow samples taken during the November event was 1.9 mg/l as N, whereas it was much lower in December at 0.4 mg/l. Samples that were significantly higher in NO_3 in November were also high in electrical conductivity and minerals (e.g. Na, SO_4 and Ca), but not in K, NH_4 or total phosphorus, reflecting a subsurface origin.

At both scales in both events, the transition zone pathway dominated the overall contribution to the stream. Further discussion on the pathway contributions is provided in Section 6.5.

6.3 Cross checks with other methods

The results of the chemical hydrograph separations were cross checked with calculations from a range of other pathway estimation methods to improve the degree of confidence in the results. This was considered especially important in the Gortinlieve and Glen Burn catchments as the end member datasets were limited.

6.3.1 Recharge coefficients approach

For each of the study catchments, the total interflow and overland flow pathway contributions from each event using the chemical hydrograph separation methods were combined to give a quickflow component (Table 6.9). This was then compared against the quickflow estimate from the recharge coefficient approach as applied by O'Brien (2013). The equivalent NAM pathway modelling results, which are further discussed in Section 6.5, are also provided for convenience. In general, the results for the chemistry pathway separations compare very favourably to those from the recharge coefficient approach. The Gortinlieve catchment was estimated to have a slightly higher groundwater component using the chemistry, which was nevertheless lower than that from the NAM. This may be an artefact of the recharge coefficient approach being an annual calculation in contrast to the chemical methods which estimate contributions from single events. It may also indicate that the recharge cap of 100 mm applied in the recharge coefficient approach (refer to Section 3.2.2) in this catchment to account for the poorly productive aquifer characteristics may lead to an under-estimation of recharge.

Table 6.9. Comparison of the chemical hydrograph separation results with those from the recharge coefficient approach and the NAM pathways separation carried out by O'Brien (2013).

	Chemical hydrograph separation %		Recharge coefficient approach %		NAM %	
Catchment	GW	IF+OF	GW	Quickflow	GW	Quickflow
Mattock	18	82	23	77	17	83
Glen Burn	21	79	19	81	16	85
Gortinlieve	20	80	11	89	27	73

6.3.2 Groundwater flow calculations

Estimates of the likely bedrock groundwater flow to the stream in Gortinlieve and Glen Burn were calculated by applying Darcy's Law (Section 2.3.2) with catchment-specific borehole data derived for aquifer thickness, hydraulic conductivity and groundwater gradients through the *Griffith's Project* (Comte et al., 2012). In the Glen Burn catchment, a bedrock groundwater contribution of 2.5 to 4.8 l/s was estimated, which is small in comparison to the mean annual stream flow of 70 l/s (3.5–6.9%), and is consistent with the small percentage of groundwater predicted by the chemical hydrograph separation method during the low flow period prior to the May event. The groundwater contribution was higher during the winter event because when the aquifer is fully saturated, the saturated thickness and hydraulic gradients are higher. The extensive ephemeral drainage ditch network, which is estimated to be almost double the length of the main channel, also significantly increases the cross-sectional area through which shallow groundwater can be delivered. In the Gortinlieve catchment, the flow through the transition zone was estimated to be between 1.5 and 3 l/s in the upper catchment, a significant proportion of the 95th percentile flow of 3 l/s, which is consistent with the transition zone being the dominant transport pathway.

6.3.3 Two-component mixing model

A two-component mixing model was applied to stream flow data in Gortinlieve to distinguish the proportion of transition zone water versus bedrock groundwater in the stream at low flow. The average electrical conductivity of the upper catchment transition zone water from the EPA monitoring borehole suite (211 µS/cm), i.e. the transition zone end member used in the three-component hydrograph separations, was selected as one end member; and the average of that from the bedrock groundwater (469 µS/cm) was taken as the second. This returned an estimate of 58% of flow from the transition zone at low flow prior to the December event, which was consistent with the three-component model result (60%). The baseflow prior to the November event, however, was much lower in electrical conductivity, which gave a smaller estimated groundwater contribution of 18% in comparison to the 54% derived from the three-way separation. The mid-catchment groundwater contribution provided a closer estimate of 39%. These results may indicate that the wetter antecedent conditions in November had diluted the

upper soil water component in the lower catchment, which would have been included artificially with the transition contribution in the two-component model.

6.3.4 Land drain flow contributions

In the Mattock catchment, a water balance calculation was used to calculate whether the volume of flow estimated to be delivered to the stream via the interflow pathway using the chemical method was realistic based on field measurements of land drain flow. The average of all measured land drain flows was 0.07 l/s. Taking an average interflow contribution to the stream based on all six events of 40%, there would need to be an average of 0.6 functioning land drains per hectare to deliver the interflow component to the stream, which is not considered to be unrealistic. During the summer months, when many of the land drains dry up, the interflow contribution is likely to be provided by the alluvial deposits near the stream.

6.4 Uncertainty

It is widely known that there is considerable uncertainty inherent in carrying out chemical hydrograph separation methods. Uncertainties are typically considered to include (a) sampling and laboratory analytical errors, and (b) spatial and temporal variability in end member concentrations (Bazemore et al., 1994). Some researchers rely on sensitivity analyses to assess the degree of uncertainty where end member concentrations are somewhat arbitrarily varied by a percentage defined based on the available data and results of multiple separations are compared (Neal et al., 1990, Soulsby et al., 2003b). Bazemore et al. (1994) developed a Monte Carlo approach that incorporated both sorts of uncertainty, where end member concentrations were randomly selected from a predefined range of concentrations and used in the mixing calculations. Genereux (1998) used an uncertainty propagation technique where the uncertainty in each of the components in the mixing model is squared and summed, and the overall uncertainty is given by the square root of the total. This technique was reported to provide similar results to that of Bazemore et al. (1994) but was considered to be preferable because it was computationally more simple.

Model uncertainty, which cannot be quantified statistically, was also considered by Joerin et al. (2002) who considered four different hypotheses of temporal and spatial variability in end member concentrations based on field data. For example, they identified that the hydrochemistry of the groundwater was not the same in all subbasins and they adapted the groundwater end member concentrations accordingly. They found that the precision and coherence of hydrograph separations was greatly improved by incorporating information from the field about the temporal and spatial variability of the end members.

In order to assess the degree of uncertainty in the chemical hydrograph separation methods in this study, the mixing calculations for two of the Mattock catchment events were carried out in a Monte Carlo framework, based on the method of Bazemore et al. (1994). Using the concepts outlined by Joerin et al. (2002), model uncertainty was also reduced by using different tracer concentrations for the summer and winter overland flow end members, based on the field data. The tracer concentration data for each end member were distributed in a non-uniform way, so the data were first transformed to a normal distribution using a Matlab routine[8]. End member signatures were then randomly selected from the data and were transformed back again before being inputted into the mass balance mixing equations described in Chapter 3. Just over 5000 iterations of the model were run so that the outputs could be analysed in Excel within its file size constraints. Of the iterations, only 471 (9.4%) presented feasible separations in which the resulting end members bound the stream samples. The median values from the feasible separations were selected to represent the contributions from each end member. The 5th and 95th percentile values were then identified to highlight the degree of certainty in the results (Figure 6.13).

The results highlighted that at this high confidence interval level, there were overlaps between the 5th and 95th percentile uncertainty bands among all pathway components. Using the method outlined in Hugenschmidt et al. (2014), the uncertainty was taken to be the mean of the differences between the $5^{th}/95^{th}$ percentiles and the medians, expressed as percentages of the medians, at each timestep, for each pathway. The calculated uncertainty surrounding the component contributions therefore ranged from 33 to 59% for the two selected events (Table 6.10). There was greatest uncertainty in the groundwater end member and least uncertainty in overland flow. This was not surprising given the smaller number of SAC samples for groundwater ($n = 16$) than overland flow ($n = 57$). Nevertheless, the median values of the pathway contributions were readily distinguishable.

Similar uncertainty has been found by other authors using chemical hydrograph separation methods to separate the same three pathways. Hugenschmidt et al. (2014) for example, found that errors due to uncertainty across their end members varied from 3.6% to 35.2%. Bazemore et al. (1994) and Genereux (1998) found that the uncertainty for the end members from one event both studies analysed ranged from 18% to 46%. In another event, Bazemore et al (1994) found the soil water contribution ranged from 48–88% at peak flow. However, all three of these research papers used a lower confidence interval of 68%, which would give the appearance of

[8] Assistance with writing the Matlab script was generously provided by Ronan O'Brien, a *Pathways Project* colleague.

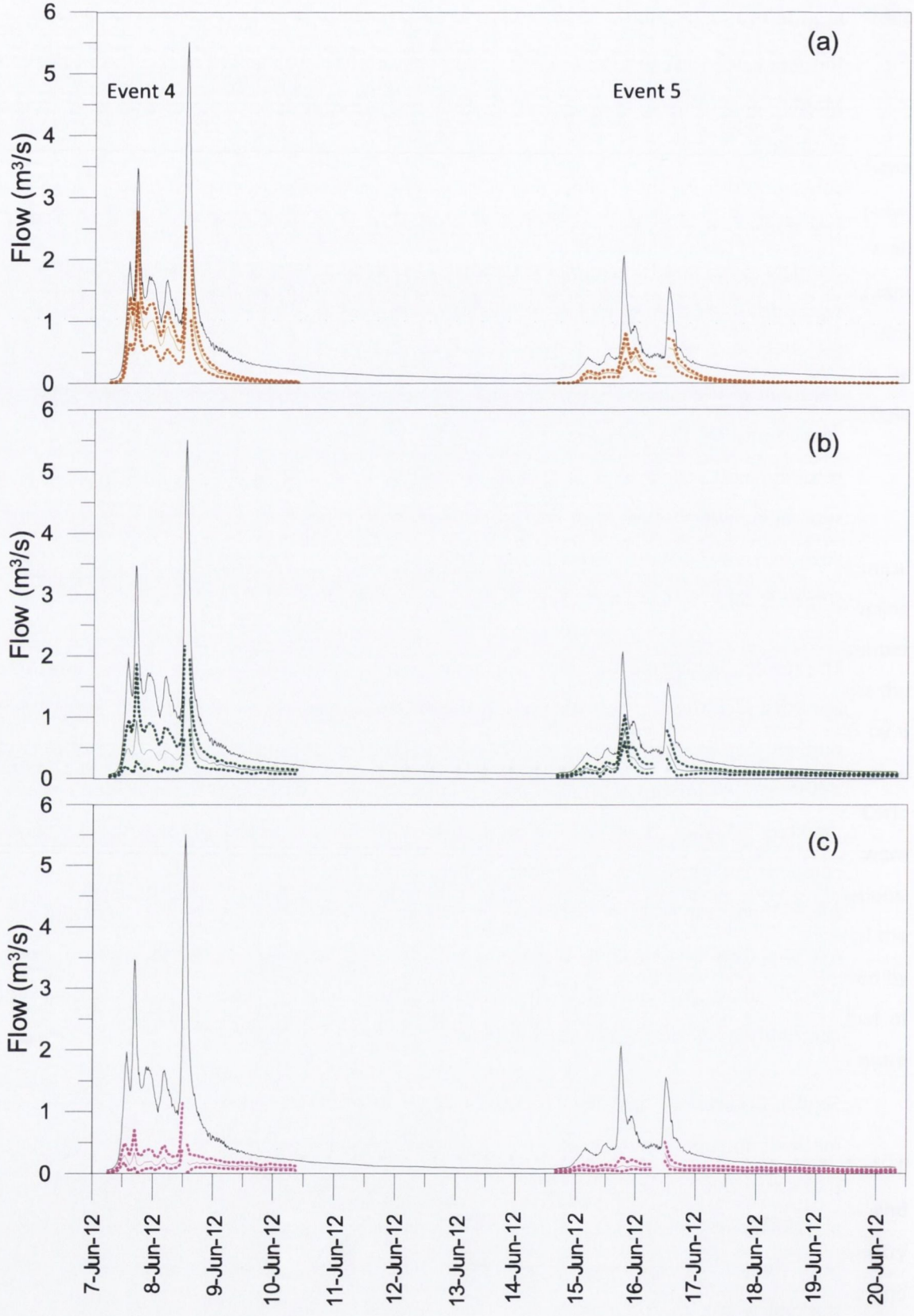

Figure 6.13. Pathway contributions for Events 4 and 5 based on the Monte Carlo results. (a) Overland flow; (b) interflow; (c) groundwater. Black lines = total flow; solid coloured lines = median values; broken coloured lines = 5th and 95th percentiles taken from the Monte Carlo simulations.

Table 6.10. Mean and standard deviation of the relative uncertainty, at the 5th and 95th percentile confidence limits, of the separated components of two of the events in the Mattock.

	Overland flow		Interflow		Groundwater	
	Mean %	Standard Deviation %	Mean %	Standard Deviation %	Mean %	Standard Deviation %
Event 4	33.4	5.9	53.7	20.7	59.2	25.2
Event 5	36.4	11.2	43.1	13.6	48.0	13.5

better results. Soulsby et al. (2003b) found, using a sensitivity approach that varied just one end member by one standard deviation, that the uncertainty was much lower at typically <10%. In a contemporaneous study by the same research group, much greater uncertainty of up to 75% was obtained for a comparative study based in a catchment in a similar setting but using a more rigorous uncertainty estimation method. The method incorporated a Monte Carlo framework using the 5% and 95% confidence intervals (Soulsby et al., 2003a) and was similar to the one used in this research although considerably more complex. Thus, it appears that uncertainty estimates can vary, often greatly, depending on the method of assessment and the confidence intervals applied.

It is considered that the uncertainty estimates in this study compare favourably with those from other studies due to a combination of a number of factors. First, strong sampling and laboratory analysis procedures kept sampling and analysis errors to a minimum. For example, the accuracy for the silica analyses carried out in this research was estimated at 6.9% (Table 4.2), which is much better than the 10% reported by Hugenschmidt et al. (2014). Second, a relatively large number of end member samples were collected in the Mattock, which kept the standard errors very small. For example, 132 samples of interflow were collected in the Mattock catchment, in comparison to 20 reported by Hugenschmidt et al. (2014) and 52 by Soulsby et al. (2003a). In addition, a significant effort was made to incorporate spatial variability by sampling around the catchment rather than restricting the sampling locations to a limited study site.

Comparison of the results from the Monte Carlo approach with the results from the conceptual model approach presented in Section 6.2.3.7 shows that the methods return similar findings in relation to the relative pathway contributions and the pathway trends throughout both events (Figure 6.14). For example, both approaches concurred in identifying that the overland flow pathway was dominant in the first event peak, but was superseded in the second by the interflow pathway. However, the Monte Carlo approach estimated slightly higher proportions of groundwater and less interflow than the conceptual model approach. This may be less realistic in this instance given the presence of the palaeochannel and the known disconnect between the majority of groundwater within the catchment and the river. As only feasible pathway separations were selected as part of the Monte Carlo approach, the results were less influenced by individual samples not being bounded by the end members, and therefore there were no instances of

pathways contributing zero flow, which is an issue with the conceptual model approach. Although the absolute percentages of the pathways may not be accurate based on the uncertainty analysis, the results suggest that there is reasonable confidence based on the conceptual model that the relative pathway contributions presented by both methods are realistic.

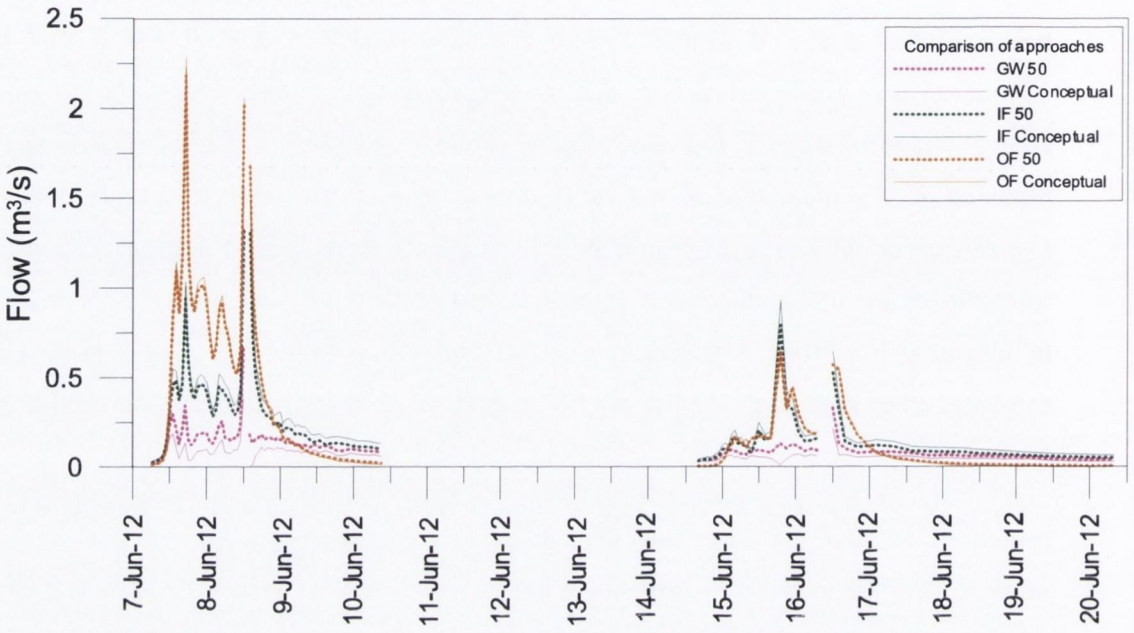

Figure 6.14. Comparison of the pathway contributions derived from the median values from the Monte Carlo approach (GW50, IF50, OF50) with the results from the conceptual model approach (GW conceptual, IF conceptual, OF conceptual).

Monte Carlo simulations were not carried out for the Glen Burn and Gortinlieve catchment events because the end member datasets were limited, the catchment dynamics were complex with intermixing in the near-surface pathways, and there was threshold behaviour in the stream chemistry driven by changes in groundwater levels in the Glen Burn. Selection of the end members and the pathways separations were considered best achieved by relying on the conceptual model. In general, it was found that the limited number of near-surface end members sampled did adequately bound the stream samples, but in the very worst case where they did not, such as for the upper catchment δ^2H value in the Glen Burn and the groundwater δ^2H in Gortinlieve, the extremes from the stream chemistry were used to represent the end member chemistry. This approach has been adopted as routine by some authors, particularly for the groundwater component, which it is often assumed is represented by the stream baseflow signature (Soulsby et al., 2003b). The standard errors for the end members in the Glen Burn and Gortinlieve catchments were relatively small, which suggested that the end members have been adequately distinguished, but it is acknowledged that the level of uncertainty in the percentage pathway contributions in both catchments is nevertheless high. In order to reduce this

uncertainty, the results from the chemical separations were compared with results from other methods in Sections 6.3 and 6.5.

Although the uncertainties inherent in using chemical hydrograph separation methods could be conceived as being relatively high, they are not considered to detract from the usefulness of the approach, so long as it is used within its limitations. At a well-respected catchment science summer school in Aberdeen in 2012, discussions with Rick Hooper, a presenter on the course who initially devised the end member mixing analysis approach, revealed that he does not consider it appropriate to depend on the precise calculated percentage pathway contributions using EMMA, but rather that the strength of the method lies in determining the relative pathway contributions (Hooper, *pers comm.*). This research would support that assertion but would also contend that additional confidence in the assessment can be achieved by carrying out the analysis within the context of a well-founded, four-dimensional conceptual understanding of how the pathways operate in the field, and by combining the results from a number of different methods such as physical hydrograph separation techniques and water balance calculations (refer to Sections 6.3 and 6.5). Further discussion on the uncertainty issues are provided in Section 6.8.4.

6.5 Physical hydrograph separation

Physical flow pathways separation methods were applied to the available data for all four study catchments by a *Pathways Project* colleague, Ronan O'Brien. O'Brien used the NAM model, which was informed using a combination of master recession curves, digital filter algorithms and recharge coefficients (O'Brien, 2013, O'Brien et al., 2013, O'Brien et al., 2014) and his results were used in this research to compare and contrast against the results of the chemical hydrograph separations. A brief summary of the relevant results from O'Brien's research are first provided, followed by a discussion on their implications for this research.

6.5.1 NAM pathway separation results

The contributions from the four flow pathways identified at the outset of the *Pathways Project* were quantified in each catchment in the same locations as the chemical analyses (Table 6.11), with the exception of the catchment outlet in Gortinlieve where there had been issues with the rating curve at the time the work was carried out. In the Mattock catchment, only one combined groundwater pathway could be derived in the upper catchment at the Diversion as the available dataset was relatively short. The pathways were separated based on their response times with the assumption that the deeper the pathway, the slower the response time. Deep groundwater therefore had the slowest response time, whereas overland flow was the quickest.

In general, the modelled outputs performed well when compared against the observed total discharges, with R^2 values of 0.84–0.97. The modelled data for the Mattock catchment had the lowest R^2 value of all study catchments, which is attributed to a number of complexities in the

Table 6.11. Contributions of the pathways to the streams in the four study catchments, based on the results of the NAM modelling (O'Brien, 2013).

Catchment	Area (km^2)	Deep Groundwater	Shallow Groundwater	Interflow	Overland	R^2	$\sqrt{R^2}$	Bias
		%	%	%	%			
Gortinlieve	0.9	12.9	14.5	50.8	21.8	0.9	0.89	0.0011
Glen Burn (Sub)	4.8	12.2	6.1	39.9	41.8	0.91	0.94	-0.0022
Glen Burn (Outlet)	5	4.9	7.8	43.6	43.7	0.95	0.93	0.0036
Mattock (Div Weir)	7	16.1		51.2	32.7	0.84	0.96	-0.0028
Mattock (Collon)	11.6	6.2	11.8	48.3	33.7	0.88	0.86	-0.0153
Mattock (Berril's)	16.9	9.9	6.8	45.7	37.6	0.89	0.86	-0.0139
Nuenna (Castle)	10.2	30.6	44.6	15.4	9.4	0.97	0.95	-0.0003
Nuenna (Rocky)	19.9	31.9	47.8	13.2	12.1	0.96	0.9	-0.0077
Nuenna (Mon)	35	31.7	45.3	13.4	9.7	0.97	0.98	0.0046

water balance including a river offtake in the upper catchment and groundwater pumping at Collon for public water supply, and the influence of the palaeochannels causing a disconnect between the river and groundwater (see Section 5.1.3.2). Nevertheless, the R^2 values obtained for the Mattock of 0.84 to 0.89 are still considered reasonable (O'Brien, 2013).

To reduce issues of equifinality, the individual pathway contributions were constrained using the autocalibration routine in the model, together with other methods such as the master recession curve, digital filtering routines and hydrograph separations using temperature (O'Brien, 2013). The average level of uncertainty in pathway contributions across all catchments, expressed as the percentage difference between the NAM result and the average across all methods, ranged from 9 to 30%. These uncertainties are lower than those achieved through the chemical hydrograph separation techniques, although they pathways modelled by each method are not directly comparable. Refer to Section 6.8.2. for further discussion.

The results suggest that on an annual basis, the interflow pathway was dominant in the Mattock and Gortinlieve catchments (46–51%), and that it was comparable with overland flow in the Glen Burn (40–44%). This is towards the upper end of the interflow range identified in Table 3.2 in previous Irish studies across all aquifer types (18–55%) but is consistent with the poorly productive aquifer classification.

6.5.2 Integration with the results of the chemical methods

The NAM pathways separations are compared on an event by event basis in each catchment with those from the chemistry results presented earlier. Modelled event data were not available for the 2011 event (E1) in the Mattock catchment.

In the Mattock catchment at low flows in winter at both catchment scales, the NAM model predicted that the majority of the flow had an 'interflow' response signal (82–89%), which is much higher than the interflow contribution estimated using the chemistry (Figure 6.15). The NAM model also predicted just half of the actual groundwater contribution based on the chemistry. This highlights that water with a groundwater chemical signature reached the stream more quickly than anticipated by the model. This is likely to be because in the field, the drainage network facilitates the delivery of groundwater to the streams from the upper parts of the catchment more rapidly than would otherwise be possible in their absence.

NAM Diversion E2 Jan 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	90	54
Interflow	89	8	34
Groundwater	11	2	12

Diversion E2 Jan 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	14	75	52
Interflow	57	9	24
Groundwater	30	16	24

NAM Berrils E3 Jan 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	92	62
Interflow	82	6	31
Sh GW	5	0	3
Deep GW	13	1	5

Berrils E3 Jan 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	11	76	n/a
Interflow	50	6	n/a
Groundwater	39	19	n/a

NAM Diversion E4 Jun 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	3	94	76
Interflow	82	4	14
Groundwater	15	2	11

Diversion E4 Jun 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	1	54	51
Interflow	57	46	39
Groundwater	42	0	10

NAM Diversion E5 Jun 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	88	55
Interflow	4	7	23
Groundwater	96	5	22

Diversion E5 Jun 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	40	33
Interflow	60	60	50
Groundwater	40	1	16

NAM Berrils E6 Jun 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	91	57
Interflow	22	6	25
Sh GW	33	1	8
Deep GW	45	2	10

Berrils E6 Jun 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	55	38
Interflow	60	34	42
Groundwater	39	11	20

Figure 6.15. Comparison of pathways separation from NAM (left) and chemical methods (right), Mattock catchment.

During the summer months, with the exception of E4, the NAM predicted that the slowest 'groundwater' response pathway was the largest contributor to flow (78-96%), but based on the chemistry this slow flow component was actually made up of a combination of groundwater and interflow in the ratio of 2:3. This is because the land drains also continued to drain the soils and subsoils during the baseflow period, which represents the apparent modelled groundwater contribution. It is not clear why the NAM predicted a low groundwater contribution during E4 at the end of a long dry recession period that was more similar to the winter event at that location.

In high flows, the NAM predicted the vast majority of flow in the river to be derived from the quickest response pathway, nominally 'overland flow', with typically <10% coming from interflow and groundwater combined. Comparing these results with the chemistry highlights that the land drains, and a small component of groundwater, can respond very quickly in places during events such that this water is being accounted for with the overland flow pathway in the model. This is due to the drainage network hastening the delivery of water from these pathways to the stream.

Both the NAM model and the chemistry indicate that during the sequential events in June 2012, the overland flow component was higher at peak flows during the first event than the second. This may have been due to the drier antecedent conditions before the first event and the higher rainfall intensities, which favoured higher overland flow and little flow from the land drains, in comparison to when the soils were more saturated during the second event and the land drain proportion increased. This was corroborated by observations in the field during the events. More overland flow (as sheet flow) was observed than usual at the start of the event while the land drains were still dry. It could be argued that the organic matter on the land surface might be expected to be higher than usual following a long dry period due to wash-off from grazed pastures, which would give the appearance of an artificially increased estimate of overland flow in the chemical mixing model because the SAC_{254} is used to represent overland flow. However, the fact that the NAM model also predicted an increase, notwithstanding that it was slightly lower than that from the chemistry, suggests that this was not a significant factor.

In the Glen Burn catchment at low flows prior to the May event, the NAM model predicted that 95% of the flow in the river responded with an interflow response signature and that the deep groundwater component made up the remaining 5% (Figure 6.16). The chemistry was also consistent but could further subdivide the interflow into water from the upper peaty catchment and soil water from elsewhere. At peak flow, the NAM results showed that 70% of the flow responded as overland flow; however, the chemistry indicates that this 'quick flow' was actually largely interflow. The chemistry also shows that the groundwater responded more quickly than

estimated by the NAM. Delivery of both the interflow and the shallow groundwater was expedited by the extensive ditch and drain network.

NAM Outlet May 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	70	48
Interflow	95	29	50
Sh GW	0	0	0
Deep GW	5	1	1

Outlet May 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Upr catchment	72	8	21
Interflow	24	64	57
Groundwater	3	28	22

NAM Outlet Nov 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	86	67
Interflow	88	10	25
Sh GW	4	3	5
Deep GW	8	1	2

Outlet Nov 2012	% Pathway contribution		
	Low flow	Peak flow	Total
Overland flow	0	41	25
Interflow	8	54	54
Groundwater	92	5	21

Figure 6.16. Comparison of pathways separation from NAM (left) and chemical (right) methods, Glen Burn catchment.

The data from the November event show that the NAM model apparently underestimated the true groundwater contribution to an even greater extent than during the May event. At peak flows, the methods were consistent for the groundwater contribution, but the NAM model was unable to differentiate adequately between overland flow and interflow.

In the Gortinlieve catchment, the NAM modelled pathways are consistent between the two events and across scales and suggest that at low flows the dominant pathway is interflow (67–78%) with the remainder derived from the groundwater pathway (Figure 6.17). This is similar to the transition zone contribution highlighted by the chemistry (37–70%). As noted in Sections 6.2.3.5 and 5.5.1, the transition zone end member in the Gortinlieve catchment represents water at the soil/bedrock interface in the upper catchment groundwater recharge zone where it is influenced by water infiltrating from the surface through the soils (Type (b) transition zone). It is considered therefore that the NAM has identified the transition response time as the 'interflow' response. The chemistry suggested the transition zone contribution was slightly less at the catchment outlet in favour of the groundwater pathway, which can be explained by the upward groundwater gradients.

At high flows, the NAM predicted that the vast majority of the flow (84–95%) responded very quickly as 'overland flow'. However, the chemistry indicated that this quickflow response was actually derived from a combination of the overland and transition zone pathways. This highlights that the return flow and artificial drainage ditches play a significant role in rapidly transporting subsurface water to the stream.

G6 Nov 2011	% Pathway contribution (NAM)		
	Low flow	Peak flow	Total flow
OF	0	95	58
IF	70	3	27
Sh GW	15	1	9
D GW	15	1	6

Mid catchment Nov 2011	% Pathway contribution		
	Pre event	Peak flow	Total
OF	6	24	22
Upper TZ	55	72	64
Bedrock	39	5	14

G1 Nov 2011	% Pathway contribution (NAM)		
	Low flow	Peak flow	Total flow
OF	0	93	61
IF	67	4	25
Sh GW	18	1	9
D GW	14	1	5

Catchment outlet Nov 2011	% Pathway contribution		
	Pre event	Peak flow	Total flow
OF	9	24	26
Upper TZ	37	77	52
Bedrock	54	0	22

G6 Dec 2012	% Pathway contribution (NAM)		
	Low flow	Peak flow	Total flow
OF	0	84	34
IF	78	13	48
Sh GW	11	2	10
D GW	11	2	8

Mid catchment Dec 2012	% Pathway contribution		
	Pre event	Peak flow	Total
OF	1	85	19
Upper TZ	70	11	59
Bedrock GW	29	5	21

G1 Dec 2012	% Pathway contribution (NAM)		
	Low flow	Peak flow	Total flow
OF	0	87	42
IF	76	10	41
Sh GW	13	2	10
D GW	11	1	7

Catchment outlet Dec 2012	% Pathway contribution		
	Pre event	Peak flow	Total flow
OF	5	53	16
Upper TZ	60	45	62
Bedrock GW	35	2	22

Figure 6.17. Comparison of NAM (left) and chemical (right) pathways separations, Gortinlieve catchment.

The very high 'overland flow' predictions in the NAM model during peak flows in the November event, in contrast to the dominance of the transition zone pathway highlighted by the chemistry, supports the hypothesis suggested in Section 6.2.3.7 that subsurface water gained more rapid access to the stream due to the high-intensity rainfall than was the case in the December event.

6.5.3 Discussion

The integration of the NAM modelled pathway response times with the results from the chemical hydrograph separation methods has provided additional information to support the conceptual understanding of the near-surface pathway processes that would not have been achievable using one or other method on its own. In all three poorly drained catchments, it was identified that there was intermixing in the near-surface pathways between the overland flow, interflow and transition zone pathways. This intermixing was at its most dominant in the Gortinlieve and Glen Burn catchments where the low permeability subsoils were shallow. The artificial drainage networks significantly enhance the delivery of water from the near-surface pathways and provide a means for subsurface water to gain access to the stream with response times similar to that of overland flow. Moreover, in wetter antecedent conditions, the proportion of subsurface water

forming the hydrograph peak increases relative to the fresher overland flow component. This has implications for the delivery of nitrate, which are discussed in Section 6.6.

6.6 Implications for nutrient transport

The conceptual model has identified that in the catchments underlain by poorly productive aquifers, nitrate accumulates in the subsoils and transition zone and that the near-surface pathways, including artificial drainage are important for its delivery. The chemical hydrograph separation methods have established that the near-surface pathways are important for the delivery of flow, and potentially therefore nitrate, to the stream at both low and high flow levels. The relationships between nitrate and flow at the catchment outlet of all three poorly drained catchments were reviewed to consider this hypothesis (Figure 6.18). The equivalent data for the contrasting Nuenna karst catchment were also included for comparison.

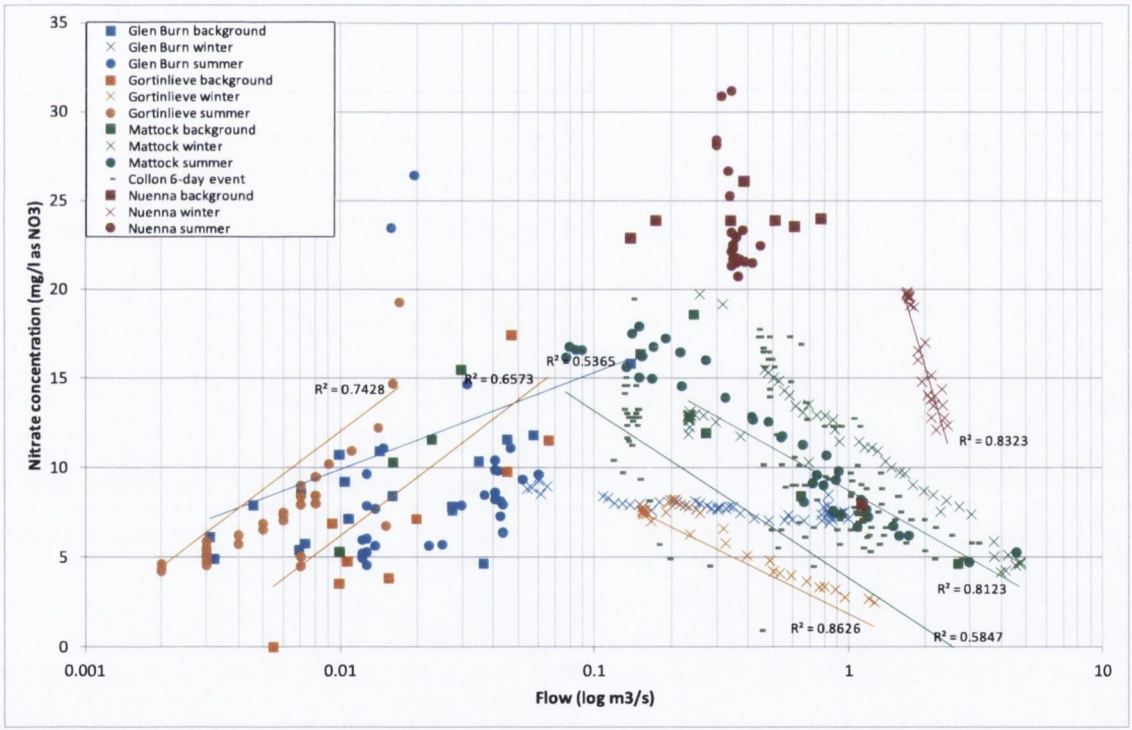

Figure 6.18. Relationship between flow and nitrate at the catchment outlet in all four catchments. Sample points are taken from background sampling and during the winter and summer events. Gortinlieve data are plotted in orange, Glen Burn in blue, Mattock in green and Nuenna in dark red. Linear regression trend lines for datasets where the coefficients of determination were >0.5 have been included as an aid for visual identification of the trends.

The data indicate that in the poorly drained catchments, at the lower flow levels, nitrate increases with flow until a point is reached when the concentration begins to consistently decrease. This was also demonstrated in Figure 5.10 in the nitrate/flow hysteresis plot for the 6-day event at

Collon where nitrate typically increased in the baseflow between each successive event, but during the events the concentrations were readily diluted in the higher flows. As demonstrated in Figure 5.24, the point at which dilution becomes important in the Glen Burn catchment is at around 0.055 m^3/s when the overland flow pathway begins to become dominant. In the Mattock catchment, which is larger, it appears to be at a higher flow level of around 0.12 at Collon or 0.15 m^3/s at Berrils. Additional nitrate samples from the streams in the three poorly drained catchments in the flow range 0.07 to 0.15 m^3/s would be advantageous in the future to more accurately determine the change point.

These findings support the hypothesis that in these poorly drained catchments, nitrate is delivered to the stream mainly via the near-surface and transition zone pathways. Minor contributions from the shallow groundwater may also possible where it can gain access to the stream. Mobilization is increased with higher water tables and wetter antecedent conditions but as these are 'flashy' catchments, dilution takes place quickly when soils become saturated and overland flow increases. It is suggested that the switch to saturated flow conditions occurs at the threshold points noted above.

This increase in dilution capacity in saturated conditions may be one of the reasons why the concentration of nitrate in the streams in these three poorly drained catchments is rarely more than 20 mg/l as NO_3, unless there are point sources present at low flows as in the case of the Glen Burn. It must also be considered however, that there is also likely to be a natural control on the extent of the nitrate pressures in these low permeability soil settings, that is related to poor land suitability for agricultural practices. A brief review of the available stream chemistry data for three of the other EPA poorly productive aquifer monitoring sites, for 10 sampling rounds over 2 years between 2010 and 2012, confirmed that the concentrations of nitrate were also low in these catchments (Glencastle, 2 mg/l as NO_3, New Village <0.6 mg/l as NO_3, Ryewater, 5.3 mg/l as NO_3 and Dripsey, 14.09 mg/l as NO_3).

In contrast, the pathways in the Nuenna karst catchment are dominated by groundwater (refer to Section 5.4.5) and the mean nitrate concentration from the project background sampling was higher at 25.5 mg/l as NO_3. It was estimated as part of the *Pathways Project* however, that at peak flows during the events, approximately one-third of the water discharging at the major springs originated as surface runoff from the Namurian shales (Orr, 2014). This water, together with overland flow from hard surfaces and saturated soils in the groundwater discharge areas near the stream, had an important temporary dilution effect on the nitrate concentrations in the river. This is represented in Figure 6.18 by the Nuenna event data plotting with a much steeper slope than in the poorly drained catchments. It is hypothesized that the greater dilution occurred

in the Nuenna catchment because the source of nitrate was the deep bedrock groundwater and it was diluted by newer event water that was lower in nitrate. This is the more traditionally understood nitrate response (Tesoriero et al., 2009). In the poorly drained catchments however, the source of nitrate was the near-surface pathways and this source/pathway increased and became dominant during the events. Thus while there was a degree of dilution, it is apparent that it did not have the dilution capacity of that in the Nuenna.

The results for a similar assessment of phosphate transport are less definitive (Figure 6.19), which is likely to be because there are multiple sources and pathways for soluble phosphorus in these catchments. The relationships may reflect the dilution of point sources at low flows, and the increased delivery of phosphate via the overland pathway, with increasing flows. This is consistent with the findings in other studies (Jordan et al., 2012, Mellander et al., 2012).

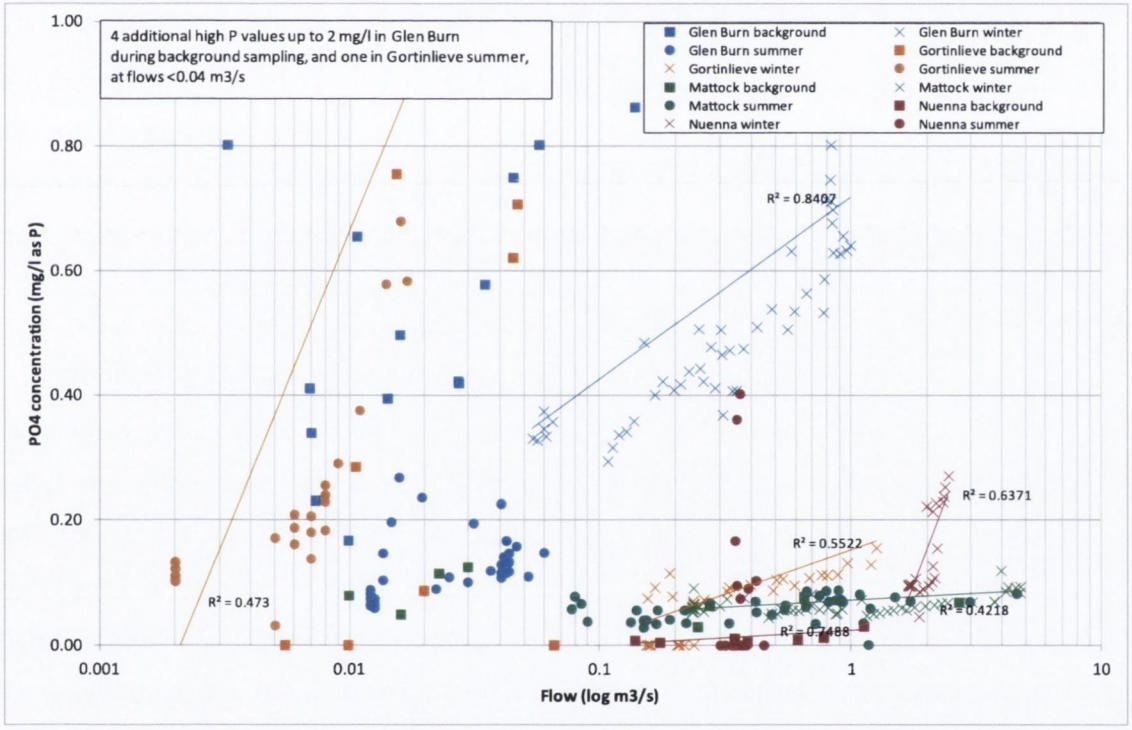

Figure 6.19. Relationship between flow and phosphate at the catchment outlet in all three catchments. Sample points are taken from background sampling and during the winter and summer events. Gortinlieve data are plotted in orange, Glen Burn in blue, Mattock in green and Nuenna in dark red. Linear regression trend lines for datasets where the coefficients of determination were >0.4 have been included as an aid for visual identification of the trends.

It is well known in the literature that nitrate is delivered via subsurface pathways (Schulte et al., 2006, Kröger et al., 2007, Tesoriero et al., 2009) and there is evidence that losses can be high in catchments where the soils are naturally free draining (Ryan et al., 2005) or artificially drained (Royer et al., 2006). Melland et al. (2012b) found that, contrary to expectations in a poorly drained Irish arable catchment, the concentrations of total oxidizable nitrogen (TON, i.e. NO_2 +

NO_3) increased with discharge during the winter, in contrast to a comparable well-drained site. This was attributed to nitrate leaching from the root zone into perched subsurface water overlying a clayey subsoil layer between 0.5 and 3 m below ground level, and discharging via ephemeral ditches. It is interesting to note that the mean nitrate concentration at the catchment outlet in that poorly drained catchment was 22 mg/l as NO_3, which was not too dissimilar to that found in the three catchments in this study, despite the arable land use that would likely have had higher nitrogen fertilizer application rates.

The findings in this research are in broad agreement with Melland et al. (2012b) but also show that a sufficiently low permeability layer, i.e. the poorly productive bedrock, that acts as a barrier to vertical flow and encourages lateral nitrate delivery, is more widely present around the three catchments in this study. It has also been ascertained that the change in nitrate delivery dynamics can be related to a change in the dominant flowpath contributing to the stream hydrograph. This is consistent with a recent study by Tedd et al. (2014) who assessed the factors influencing the presence of nitrate in groundwater in the southeast region of Ireland. They concluded that it is the pathway factors, not the pressure factors, that have the largest bearing on the delivery of nitrate to groundwater. Preliminary findings from this study suggest that the same may be true for nitrate in surface waters. Future collaborative work using the national river water quality dataset in a manner similar to the groundwater study would be beneficial.

6.7 Annual pathway separation estimates for use in SMART modelling

The disadvantage of applying chemical hydrograph separation methods using tracers that cannot be measured continuously is that it is not possible to generate an extended time series of the pathway separations and therefore to calculate the annual average contribution from each flowpath. Such estimates were required by the modellers for use for cross checking the pathway separations generated for each catchment, using the hydrological model (SMART) as part of the development of the catchment management tool (see Section 3.2.3). An approach using the flow duration curve was therefore devised with the aim of estimating the average annual groundwater, interflow and overland flow contribution to surface water in each catchment based on limited observed data.

The concept involved the following for each catchment:

(a) The hydrograph was divided into high, medium and low flow bands using the flow duration curve. The conceptual model was used to guide the selection of the flow bands so that each flow band was dominated by one pathway where possible.

(b) The available event data were assigned to the relevant flow band and their chemical hydrograph separation data were used to characterize that flow band. In some instances,

the data were applicable to more than one flow band where they spanned a large range; for example, the pre-event low flow separations for the May event data in the Glen Burn were used to characterize the low flow band, whereas the high flows from the same event were appropriate for the medium flow band. Where there were no event chemistry data available for a flow band, the percentage flow contributions were extrapolated on the basis of the conceptual model.

(c) The proportions of each pathway in each flow band were multiplied by the duration of that flow band to provide an estimate of the average annual flow.

The approach applied to the Glen Burn catchment is provided in Table 6.12 as an example. Six pathway segments were identified on the flow duration curve in Figure 5.17. For the purposes of this exercise, bands 2/3, and 4/5 are grouped to simplify the analysis.

Table 6.12. Annual estimates for pathway contributions, Glen Burn catchment.

Flow regime		*Very low flow*	*Low flow*	*Med flow*	*High flow*	*Annual estimate*
Flow band (from Fig. 5.17)		1	2/3	4/5	6	
Conceptualisation		Upper catchment and bedrock groundwater	Aquifers unsaturated, interflow dominant	Aquifers saturated, pathways well mixed	High overland flow	
Flow range m^3/s		<0.0045	0.0045–0.027	0.027–0.2	>0.2	Full
Duration %		24	29	40	7	100
Pathway %	**Overland flow**	0	0	10	40	7
	Interflow	96	77	33	55	62
	Groundwater	4	23	57	5	31

The relatively high groundwater contribution in the medium flow band is attributed to the hydrogeology in the drumlin catchment (see Section 5.2.5). At these flows when the bedrock is fully saturated, the water table rises in the inter-drumlin areas, and as there is very little soil and subsoil, the ground readily becomes saturated. These inter-drumlin areas are natural collector basins for runoff from the surrounding drumlins, which mixes with the shallow groundwater. High pressure heads under the low permeability drumlin tills maintain steep groundwater gradients, and although the contribution of groundwater is limited by the low transmissivity, there is significant mixing in these areas giving rise to a higher groundwater contribution than expected.

The approach needed to be basic as the chemical data were limited to typically two events per catchment over a 2-year period, and there were considerable uncertainties inherent in the pathway estimates. The data were, however, supported by a strong conceptual understanding of the catchment functioning and nevertheless provided an independent field-based comparison for the modelled hydrograph separation techniques and optimized simulations of the SMART model.

The method was devised in an iterative process by this author and the modeller, a *Pathways Project* colleague Eva Mockler, and so should be considered as a combined effort. Testing and validation of the results in the context of the SMART model were carried out by Mockler and are reported on in the *Pathways Project* Final report Vol. 4.

6.8 Discussion

6.8.1 Importance of the conceptual model

In small, low-lying, poorly drained catchments, where rock is close to the surface and artificial drainage is common, such as in the Glen Burn and Gortinlieve catchments, the near-surface pathways dominate stream flow generation and nutrient transport. The permeability and storage in the soil and rock is low, and they saturate quickly, which results in significant rejected potential recharge and return flow. These conditions are also favourable for the development of overland flow which mixes with the water from the saturated soils and shallow groundwater. Water from the subsurface pathways can also be delivered to the river more quickly than anticipated via the artificial drainage network. Thus, there is considerable intermixing in the near-surface pathways.

In these types of hydrogeological environments, selecting appropriate end members for the mixing analysis is challenging. The method of assigning end member signatures that was developed for the Glen Burn and Gortinlieve catchments relied more heavily on the conceptual model and the understanding of the catchment dynamics, which was achieved through all the other techniques applied, rather than the data-rich, statistically based, traditional approach taken in the Mattock. Although the latter approach is certainly more statistically robust, it has the disadvantage that potential end members need to be indentified at the commencement of a study for regular sampling, in the hope that they will bound the stream chemistry during the later events. In practice, some samples typically get dismissed in the analyses at the end of the study because they are considered to be mixtures that are non-representative of the extremes and do not adequately bound the stream chemistry (Garrett et al., 2012).

If chemical hydrograph separation is used within its limitations as a means to determine relative pathway contributions rather than absolute contributions, it is argued in this research that the approach to selecting end members adopted in the Glen Burn and Gortinlieve catchments is valid. It does depend, however, on having a robust, four-dimensional, catchment-based understanding of stream dynamics that has been rigorously assembled using a range of techniques. Such conceptual models have been typically lacking in the literature (McGlynn et al., 2002).

The traditional approach to chemical hydrograph separation of extensively sampling end members and applying a Monte Carlo approach worked well in the Mattock catchment. However, the subsoils in the Mattock catchment are thicker, the catchment is larger, and there is less intermixing between pathways. It is suggested therefore, that the statistical approach is perhaps better suited to larger catchments, while the conceptual model approach is more appropriate in small catchments where the pathways are intermixed. Future studies could usefully carry out further end member sampling in the Gortinlieve and Glen Burn catchments with a view to applying the statistical methods to determine if adequate pathways separation could be achieved without the conceptual understanding in those hydrogeological regimes.

6.8.2 Origin versus delivery

There is a tendency in the literature to use the terms overland flow, interflow and groundwater to describe both the origin of water contributing to a stream and the pathway that delivers it. However, in these types of catchments, the origin of the water and the delivery pathway are not always one and the same, and water may start out in one pathway but transfer to another before it reaches the stream. Chemical hydrograph separation methods using solutes provide information on the origin of the water, rather than its delivery pathway per se. Physical hydrograph separation methods provide better information on the delivery pathways based on their response times, but are less useful in distinguishing the origin of the water. From a hydrological modelling perspective, the pathway response times are of greater interest for calibration purposes. From a nutrient transport perspective, however, the origin is more important, as nitrate and phosphate tend to accumulate in different geological layers; nitrate typically migrates to deeper levels, whereas phosphate often remains at the surface.

By way of an example, overland flow that has originated from a deeper horizon and has reached the surface as a groundwater seep or return flow is less likely to be high in phosphorus over the duration of an event than overland flow generated at the surface in variable source areas as saturation excess overland flow. This is because, after perhaps an initial flush, phosphorus concentrations in the upper soils in the return flow pathway are quickly diluted. In contrast, variable source areas keep expanding with additional rainfall, hence mobilizing new sources of phosphorus.

It is suggested on the basis of this research, that integration of the results of the physical and chemical hydrograph separation methods provided a stronger interpretation of catchment functioning and that it should be considered as a useful methodology in future studies. For example, mean event phosphate levels for the winter events in Gortinlieve were found to increase with increasing overland flow pathway contributions estimated using the chemical

hydrograph separation method (Table 6.13). In contrast, lower mean phosphate levels were associated with the highest overland flow predictions from the NAM model. The chemical methods may have identified the fresher overland flow water that originated on the surface and delivered soil phosphorus to the stream. The NAM quickflow response times, however, may

Table 6.13. Relationships between mean event phosphate and percentage overland flow contributions determined using the NAM model and the chemical hydrograph separation methods. Winter events from one catchment only were included in this assessment to avoid potential biases due to differences in land use between catchments and between seasons.

Event	Location	Mean event PO4 mg/l as P	NAM peak flow %	Chemistry peak flow %
Nov 2011	Catchment outlet	0.037	93	24
Nov 2011	Mid catchment	0.027	95	24
Dec 2012	Catchment outlet	0.102	87	53
Dec 2012	Mid catchment	0.143	84	85

better describe the quickflow responses from the drainage channels where there is greater dilution occurring during a winter event. Combining the NAM modelled outputs with the chemical analysis therefore provided improved understanding in these catchments on both the origins of the water and the response times for the delivery pathways.

6.8.3 Principal components analysis

The PCA method was less useful than anticipated for segregating the different subsurface contributions. For example, in all catchments, the PCA identified that the principal component of variance in the stream chemistry was the process of dilution of subsurface water with overland flow. The percentage variance in the first component was the highest of all the events in the upper catchment in winter in the Mattock (81%), which is likely to be due to the wet antecedent conditions and limited sources of contamination, which meant that a straightforward dilution process with rainfall was dominant. There was less scope for distinguishing the other flowpaths which is likely to be because they are glaciated terrains, in which the bedrock is the parent material for the subsoils. Where has been little glacial carry-over and the subsoils have been derived from the same bedrock as that which underlies them, there is little to differentiate them hydrochemically, and therefore they are not identifiable in the PCA.

Perhaps the greatest advantage of applying the PCA was in gaining insight into the contaminant transfer processes within the minor constituents. PCA was used in a similar way by Gvozdić et al. (2012) on 24 years of water quality data for 15 variables sampled at three monitoring stations on the River Drada in Croatia. The results were used to distinguish different pollution sources in each of the three reaches. In all three study catchments in this research, it was apparent, for instance,

that nitrate behaves very differently to phosphate, which supports the hypothesis that they are largely delivered to streams via different pathways during events. In this research, the smallest percentage variance in the first component was in the Glen Burn catchment in the driest conditions in May (39%), and in that event there were four main components. The results highlighted that stream flow generation processes under those conditions in the Glen Burn are more complex, with less simple dilution and more mixing of the near-surface pathways, and greater influences from point sources of contamination.

6.8.4 Temporal variability in end members

In considering the implications of the uncertainty assessment, closer inspection of what the uncertainty measured using the Monte Carlo approach actually is, is warranted. The method randomly selects end member concentrations from a given range that is assumed to be normally distributed, and uses them to quantify the proportion of a contributing component to the stream at each time step. However, it is known from observations in the field, and in this case the conceptual model, that the end member concentrations at each timestep are not random, but that they can change with antecedent conditions, river stage and rainfall conditions. For example, it is known that in the Mattock catchment, the overland flow component increases in solute concentrations as sequential events progress. The concentration of organic matter in the summer months is also higher than during the winter.

There are also other examples from the literature. Van der Hoven et al. (2002) found that the $\delta^{18}O$ content in their subsurface pathway end member varied significantly between events because subsurface flow was predominantly via preferential flowpaths, and the $\delta^{18}O$ content of previous events had a significant bearing on the end member signature. Temporal variability was also identified by Ogunkoya and Jenkins (1993) in one of the earliest applications of the three-component mixing model. They attempted to account for this variability by fitting running means to end member tracer concentrations to extrapolate concentrations at any time period. However, they concluded that although the results were in theory more appropriate, the efficacy of the method could not be confirmed because of difficulties in describing the timing of mixing and entry into the stream channel. Tetzlaff et al. (2010) tried to account for the influences of long-term temporal variability in acidification on the end member chemistries in a small upland catchment in Scotland. Non-linear relationships between alkalinity and flow, based on long-term datasets, were used to identify complex statistical distribution functions that described the end member signatures, which could then be used in the end member mixing analysis. The authors suggested that although their methodology was not a panacea, it did go some way towards improving previous methods, and not least, provided better conceptualization of the catchments studied.

The Monte Carlo statistical method, although currently widely used, incorporates the natural temporal variability in the end members into the uncertainty analysis which, it is argued by Genereux (1998), is inappropriate because the temporal variability is part of the hydrological signal that should be assessed. This was one of the reasons why Joerin et al. (2002) introduced the model uncertainty element. Ideally, if, as was recognized by Ogunkoya and Jenkins (1993), the variability in concentrations of end members could be adequately measured in the field at each time step, and the lag times in delivery of those end members to the stream could be adequately predicted based on transmissivities, velocities and/or mean residence times, then the actual contributions of each end member at each time step could be better determined. To the best of the author's knowledge, there is no published research that has achieved this aim. Preliminary work into assessing the temporal variability of the end members in the study catchments has been carried out as part of this research. However, further field research and collaboration with other authors with stronger expertise in statistical methods is required to progress the concept.

7 Soil water dynamics – evidence for interflow?

7.1 Introduction

An investigation into the soil water dynamics at a small subcatchment of the upper Mattock (Figure 7.1) was carried out to review the evidence for interflow occurring at the site/plot scale to support the catchment-scale studies. Soil moisture and matric potential were measured at different depths at four locations in a transect from the catchment divide to the river (Figure 7.2), at 15-minute intervals between November 2011 and September 2013. Site 1 was closest to the stream but was located outside the riparian zone as the study was focussed on hillslope processes rather than the hyporheic zone. Site 4 was located close to the top of the subcatchment near the catchment divide.

Significant data collection and quality control issues with the matric potential data (Appendix 1), meant that the available dataset was, unfortunately, limited. Nevertheless, there are sufficient data to make some initial observations on the dynamics of soil water in the different

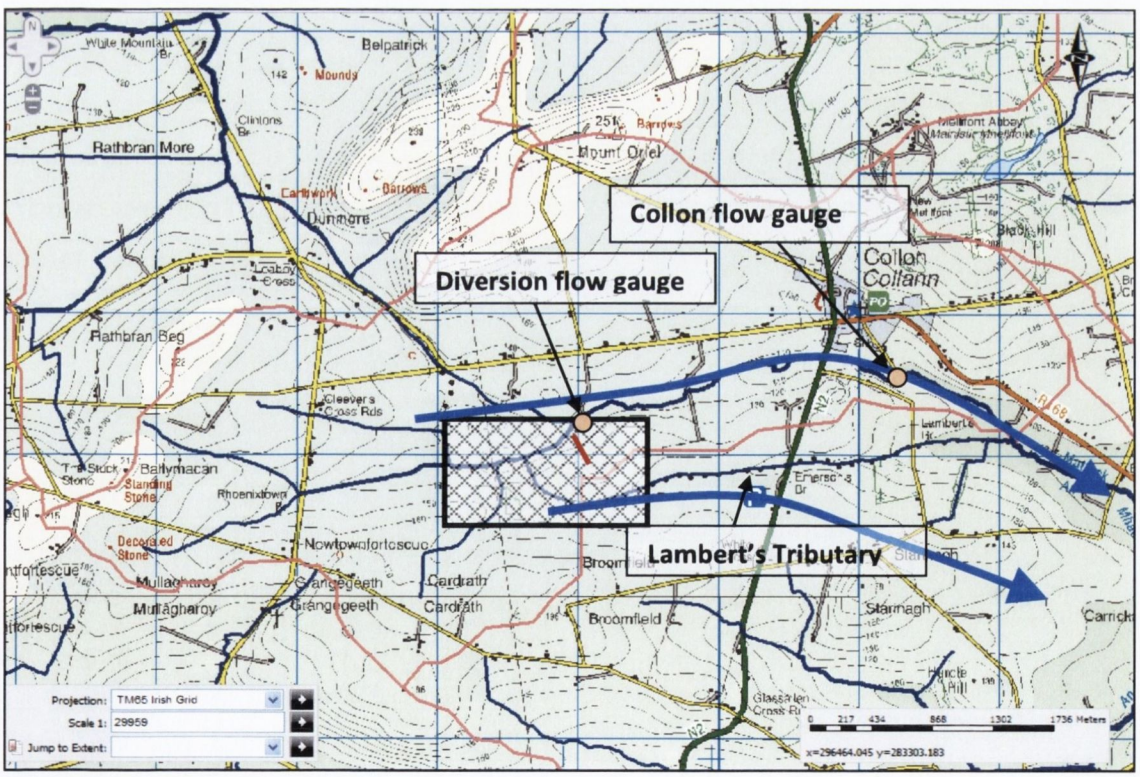

Figure 7.1. Location of the soil monitoring site (red line within the black rectangle) in the Mattock catchment and the palaeochannels (blue arrows, refer to Section 5.1.1). The catchment boundary is outlined in pink. The area within the hatched black rectangle is enlarged in Figure 7.2.

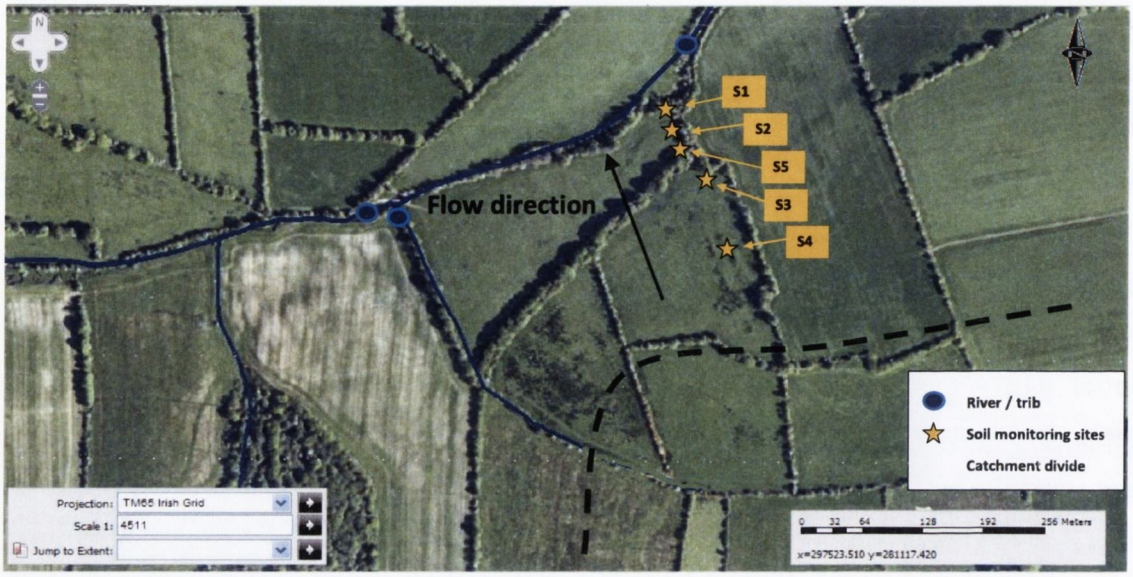

Figure 7.2. Locations of the soil water monitoring sites, Site 1 to Site 4 (S1–S4). See Figure 7.1 for location within the catchment.

hydrogeological settings along the transect in different antecedent conditions, and to test the predictions from the chemical hydrograph separation methods outlined in Chapter 6, that interflow contributes to the stream in baseflow conditions and during rainfall events.

7.2 Site characteristics

7.2.1 Geological profiles

The geophysics, trial pits, drilling and field observation data corroborated that the soil and subsoil profile across the site has four distinct horizons (Table 7.1, Figure 7.3). Thin, clay-rich topsoils overly a stiff SILT/CLAY, and a very stiff CLAY (or SILT/CLAY at Site 4) with stones. The SILT/CLAY

Table 7.1. Site characteristics, soil monitoring site, Mattock catchment.

Site characteristics	Site no.				
Site no.	1	2	3	4	5
Distance from river (m)	9	38	87	167	56
Elevation (m OD)	121.43	124.28	131.47	138.97	125.72
Profile (cm bgl)					
(a) Topsoil	0–35	0–30	0–35	0–40	0–20
(b) SILT/CLAY, stiff, no stones	35–70	30–65	35–40	40–60	20–40
(c) CLAY or SILT/CLAY, very stiff, with stones	70–365	65–180	40–130	60–230	40–310
(d) Sandy SILT†, sand/gravel‡, bedrock*	>365‡	>180†	>130*	>230‡	>310‡
Depth of soil monitoring instruments (cm bgl)					
1. Shallow (topsoil)	20	20	20	30	n/a
2. Mid (SILT/CLAY)	50	60	n/a	75	
3. Deep (CLAY)	80	120	n/a	157	
Depth of piezometers (m bgl)	3.80	4.1	1.93	3.96	3.51

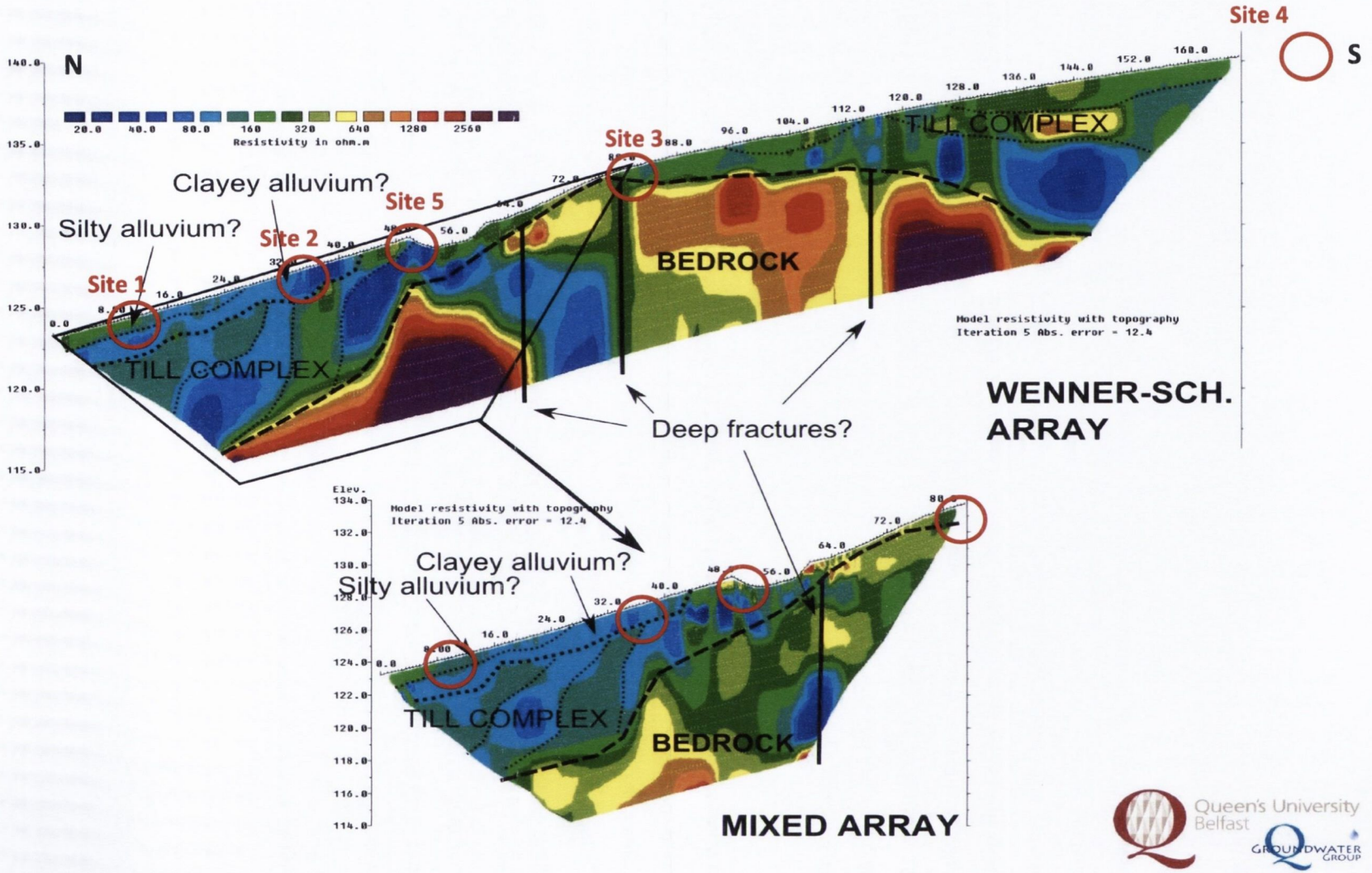

Figure 7.3. Resistivity profile through the soil moisture dynamics transect perpendicular to the river which is 5 m to the north of the start of the profile. Red circles = monitoring sites. The silty alluvium mapped here was identified as SILT/CLAY using the GSI methodology and the clayey alluvium was CLAY.

horizon was generally free of stones, contained rootlets in the upper part and was mottled, indicating that it was saturated on occasion. This horizon was interpreted as a meltout till (Dr. R. Meehan, *pers. comm.*). The CLAY layer[9] was between 90 and 295 m thick, was typically dry on drilling, over-consolidated, and contained manganese and sometimes iron staining around the fractures suggesting reducing conditions typical of low permeability subsoils. This horizon was interpreted as a lodgement till (Dr. R. Meehan, *pers. comm.*).

A saturated sandy SILT, SAND/GRAVEL or shallow bedrock horizon was present at depth in each of the five shallow boreholes, which was damp or wet on drilling and had a water table during at least some part of the monitoring period. The SAND/GRAVEL was rounded to subrounded at Sites 1, 2 and 4 indicating that it was water-lain. At Site 3, it was angular and subangular which is more indicative of shallow bedrock. The depth to bedrock was found to be >4 m in all holes except Site 3 where it was found to be at 1.3 m based on the drilling returns. The geophysics (2-D resistivity – Figure 7.3) indicated that depth to rock was of the order of 1–10 m across the site. The presence of some artificial fill (terracotta chips) beneath the soils on the steeply sloping ground at Site 3 suggests that, historically, this may have been the location of a farm track. This meant that the soils at Site 3 were artificially dry but they were nevertheless considered to be representative of shallow soil conditions in upland catchment areas and so were a useful addition to the programme.

Using the Geological Survey of Ireland vulnerability mapping assessment method (Fitzsimons et al., 2005), it is considered that on the basis of the subsoil characteristics (Swartz et al., 2003) and the presence of the rushes (Figure 7.4), which are indicators of poor drainage (Lee, 1999), the permeability of the SILT/CLAY and CLAY horizons was low. The resistivity profile highlighted the presence of two east-west palaeochannels to the north and south that align with the Mattock river valley and Lambert's tributary (Figure 7.1), respectively, and, based on the borehole data, contain more permeable deposits at depth. This is consistent with five other similar profiles measured across the river valley throughout the catchment (Wilson et al., 2012), as discussed in Section 5.1.1.

[9] Throughout the chapter, although the soils at the deepest level in the profile at Site 4 were classed as a SILT/CLAY texture in the field, they had the characteristics of the lodgement tills and are therefore referred to as CLAYs in the discussion for convenience so that they are correctly equated with the equivalent lodgement tills at the other sites.

Figure 7.4. View looking northwards along the transect from Site 4, prior to installation. Rushes provide evidence that the soils are poorly drained.

7.2.2 Soil moisture content

The soil moisture sensors (SM1–SM3) were installed at the three measurement depths at Site 1 from November 2011 to November 2012. The data show that the soil moisture in the deeper CLAY horizon (SM3, 80 cm) remained relatively constant all year round, with a mean volumetric water content of 48% (Figure 7.5). Water contents were typically highest and fluctuated most with rainfall in the topsoil (SM1, 20 cm depth; mean, 57%; range, 47–64%). The SILT/CLAY (SM2, 50 cm) had a higher moisture content (51%) than the CLAY but was always less than the topsoil. The higher soil moisture content in the upper soils is likely due to higher organic content, which is more effective at retaining soil moisture (Hillel, 1982). During the recession periods, the SILT/CLAY drained sharply to an average of 44% but replenished quickly with the onset of rain. For example, on 25 March 2012, the soil moisture content drained by 4.26% in 13.25 h. Further discussion on the reasons for this change is provided in Section 7.3.3.

At Site 2, soil moisture was monitored, again at the three depths, from November 2012 to September 2013, which included a very dry summer period. The data show that the soils at all levels were generally lower in soil moisture content than at Site 1, as expected because the site is located further upgradient. Soil moisture content in the deepest monitoring point in the CLAY (SM3, 120 cm) remained relatively constant at an average of 46% until the extended very dry period between July and September 2013 when there was a dramatic reduction to 19%. This corresponded with a period of very low stream flow.

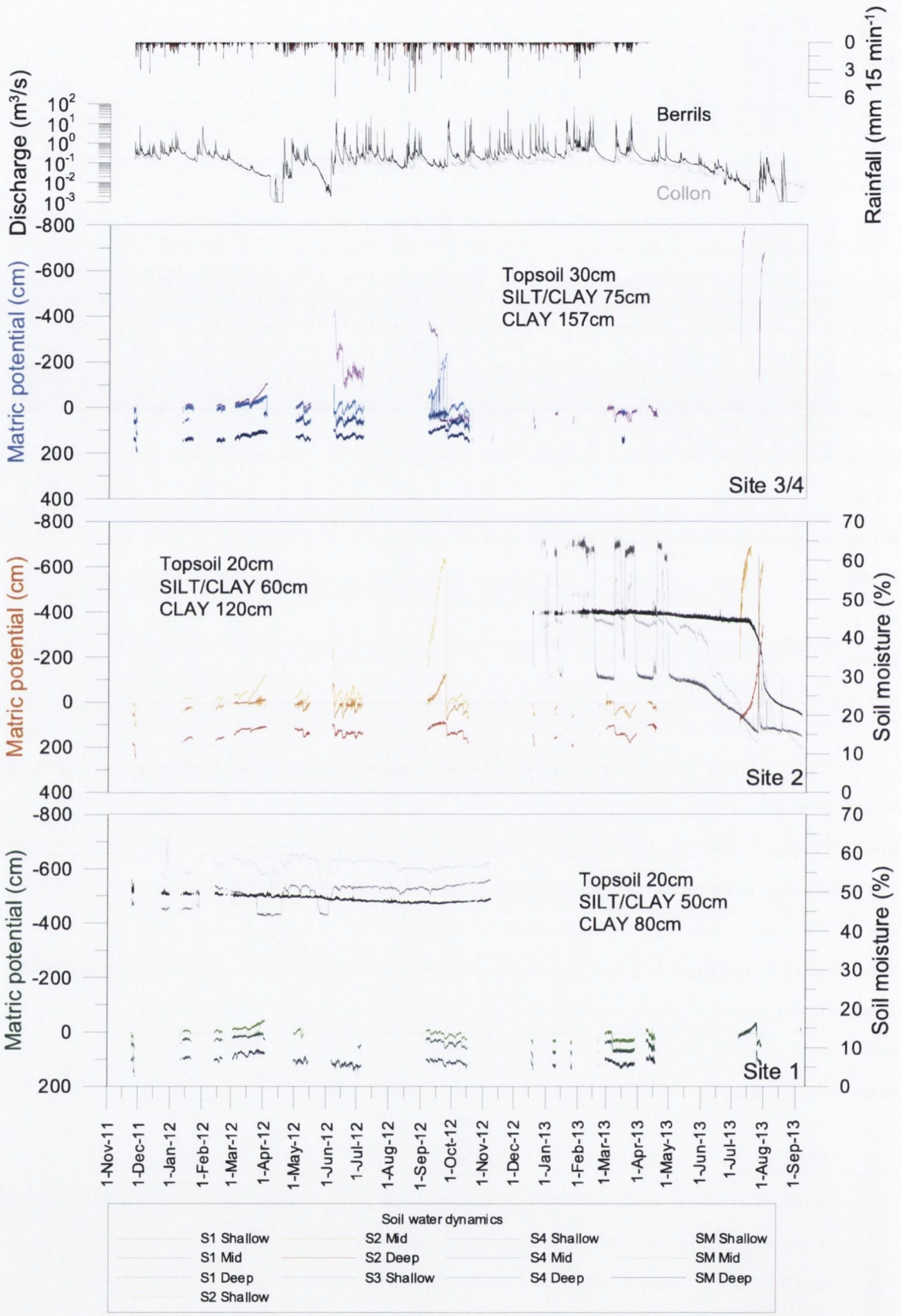

Figure 7.5. Matric potential and soil moisture content for the four sites during the study period, with stream discharge, rainfall and dates when pathways sampling was carried out. Sites 3 and 4 are shown on the same graph for convenience; they are not presumed to be connected hydraulically.

In the SILT/CLAY layer at Site 2 (SM2, 60 cm), the soil moisture content responded quickly with rainfall and fluctuated from 14 to 65%, the largest range of all six monitoring points. In a pattern similar to Site 1, the soil moisture content remained relatively constant for extended periods at 30% and 64%. The sharp decline in soil moisture in the SILT/CLAY during the extended dry period in July 2013 occurred 1.5 days after the upper soils (SM1, 20 cm), suggesting a good hydraulic connection, but approximately 1.5 months before the underlying CLAY.

The upper soils at Site 2 (SM1, 20 cm) generally responded closely to rainfall, but remained at 43–44% for extended periods. The lowest soil moisture content recorded at any of the sites (11% by volume) was in these soils in September 2013. This was confirmed by the gravimetric analyses carried out on 5 September (refer to Section 4.3.2). Soil moisture was not recorded at Sites 3 and 4.

7.2.3 Matric potential

Collection of a reliable continuous matric potential dataset was challenging. There were issues with the power supply, the logger and the set up of the equipment in the field, all of which contributed to an incomplete dataset that required extensive quality control procedures. As it was difficult to separate good quality data from data that were unreliable, a conservative approach was adopted and data were excluded for time periods for which there were any doubts as to their reliability. This has resulted in the functional dataset being less comprehensive than anticipated. The issues that arose are outlined in Appendix 1 and the lessons learned are summarized in Section 7.5.4.

The available matric potential data, although admittedly biased towards the lower tension values (i.e. higher matric potential), nevertheless suggest that the deepest horizons measured at Sites 1 (S1 Deep, 80 cm), 2 (S2 Deep, 120 cm) and 4 (S4 Deep, 157 cm) remained saturated, i.e. zero or positive matric potential, all year round (Figure 7.5, Figure 7.6), with the exception of a limited period in the dry summer of 2013 when the deep subsoils at Site 2 dried out. This is consistent with the interpretation of these subsoils as low permeability lodgement tills.

In the mid-level SILT/CLAY layer at all sites, the soils were also largely saturated for most of the year. There were longer periods of unsaturated conditions and lower matric potentials in the drier summer months at Site 2 (S2 Mid, 60 cm), however, which accompanied the reductions in soil moisture content and are likely due to the drainage.

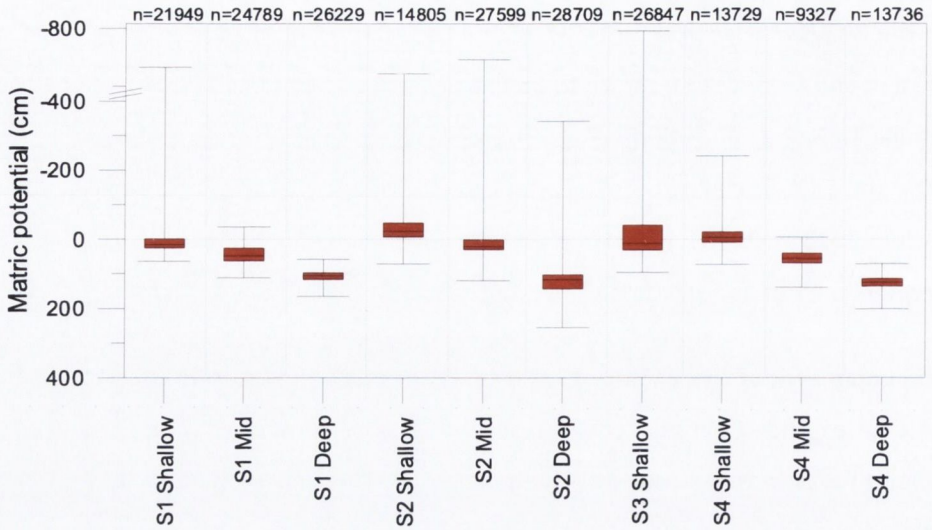

Figure 7.6. Matric potential at each of the soil monitoring horizons. Note the available data are biased towards the higher matric potentials because of quality control issues. The zero line representing saturation is highlighted.

The upper topsoil layers at Sites 2 (S2 Shallow, 20 cm), 3 (S3 Shallow, 20 cm) and 4 (S4 Shallow, 30 cm) were typically unsaturated during the study period with mean matric potentials of –70.2, –54.5 and –15.6 cm, respectively, based on the available data. At Site 1 (S1 Shallow, 20 cm), however, the topsoils were largely saturated for the majority of the monitoring period, consistent with it being the most downgradient site near the river. The lower matric potentials generally at Site 2 are likely to be due to the effective subsurface drainage affecting the site. Site 3 had the lowest recorded matric potentials due to the presence of the well-drained, steeply dipping shallow bedrock layer at a shallow depth at the site.

7.2.4 Groundwater levels

Groundwater levels were measured at least monthly from 3.5–4 m deep piezometers at each site, except at Site 3 where a depth of only approximately 2 m could be achieved with the drilling rig. Continuous water level monitoring was also carried out at Sites 1 and 2 for a limited period using some borrowed water level monitoring equipment (Schlumberger mini divers).

Permanent water tables were evident in the piezometers at Sites 1 and 2 throughout the 2 years of data collection, reflecting their lower positions in the landscape (Figure 7.7). Water was present at Site 3 on only two occasions during mid-winter due to the steep slope and permeable zone at the base of the piezometer. The water level at Site 5 behaved consistently with Site 2, which is just 18 m downgradient, although it was dry between July and September 2013 due to its shallower depth. There was a slightly different water level regime at Site 4 near the catchment divide, however; there was a significant lag time in the recession in comparison with the other sites, and the piezometer was dry for longer periods throughout the year. It is considered that this

may be a consequence of the water level regime being controlled by the palaeochannel to the south in the Lambert's tributary valley (Figure 7.3) in a manner similar to that described in the EPA monitoring holes in the southern part of the catchment (Section 5.1.3.2).

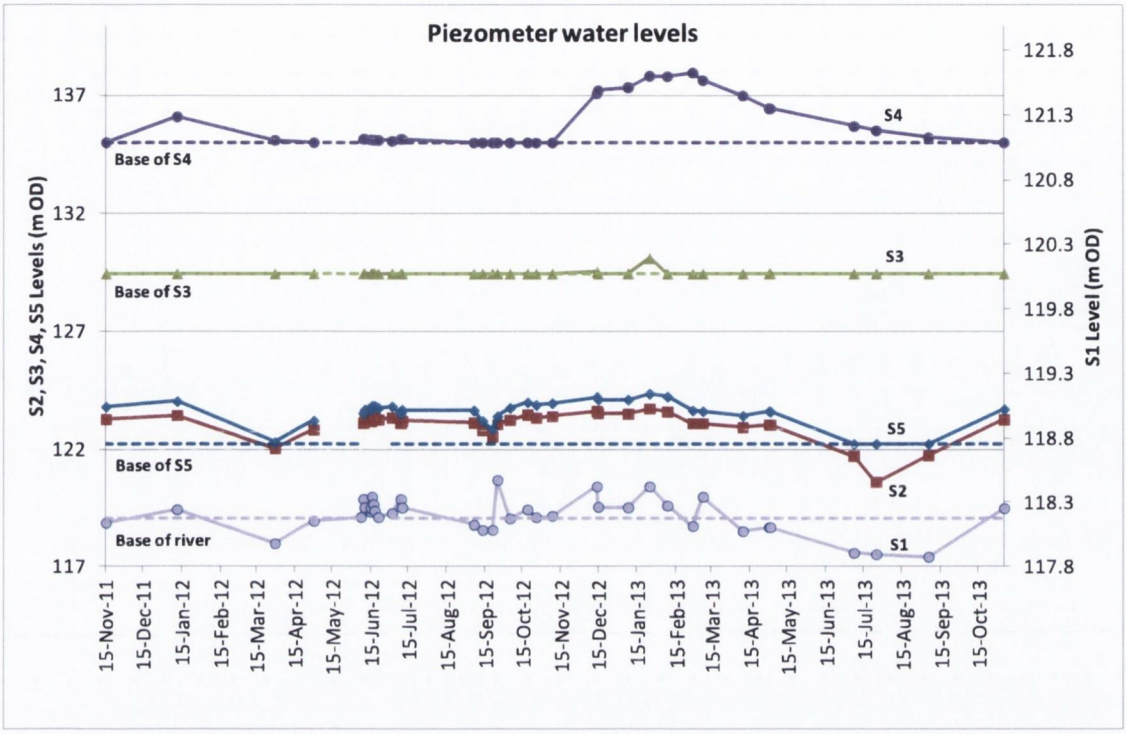

Figure 7.7. Water levels (m OD) in the piezometers at Sites 1–5 during the study period. Fluctuations at Site 1 are shown on the secondary y-axis. Dashed lines indicate the bottom of the piezometers at Sites 3, 4 and 5 so that sampling periods when the holes were dry are indicated. The dashed line for Site 1 is the depth of the nearby stream bed.

Comparison of continuous water level data for Sites 1 and 2, with river flow data, over a 1-month period in June 2012 (Figure 7.8), shows that the groundwater level at Site 1 corresponds more closely with the changes in river level. There was a lag time of 3.5 h evident for the first of the three measured events, which took place after several weeks of dry weather, but for the second and third events, the responses were essentially simultaneous. The groundwater at Site 1 therefore appears to be very well connected hydraulically to the river, once the substrate has been wetted, despite being some 9 m distant. The mean groundwater gradient between Site 1 and the river is very low, of the order of 0.001, reflecting the high permeability of the sand and gravel deposits. In contrast, the mean gradient between Site 5 and Site 2 away from the river channel, is an order of magnitude higher at 0.013.

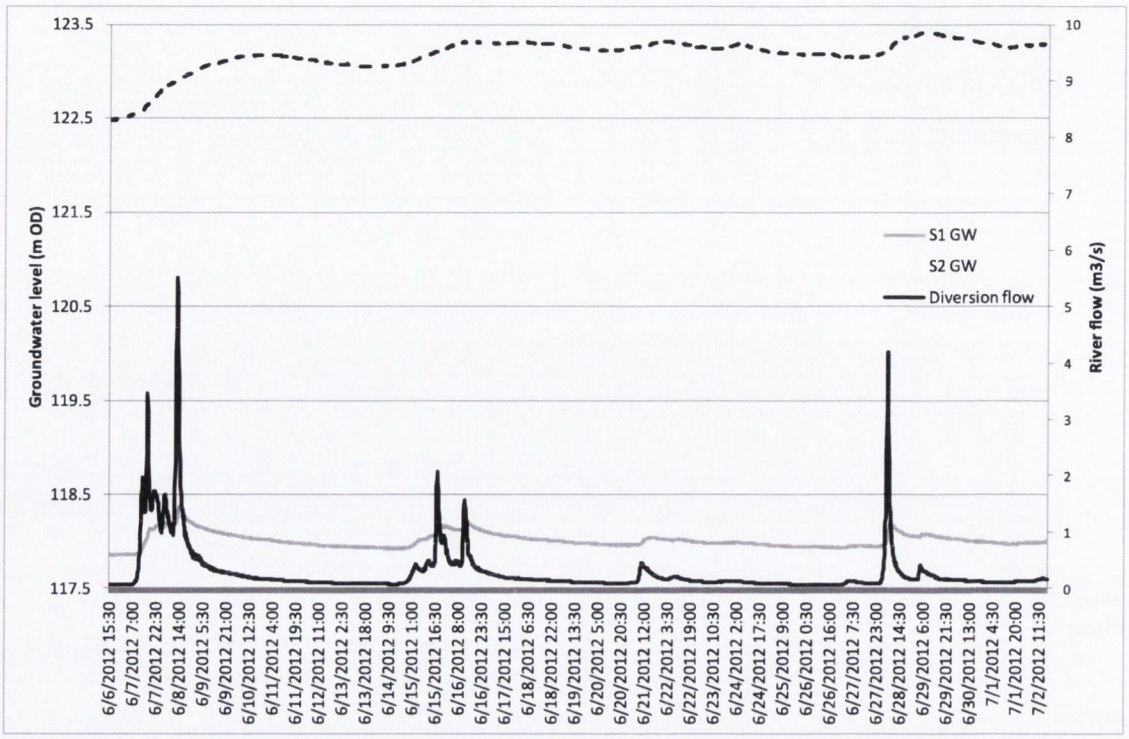

Figure 7.8. Groundwater level fluctuations at Sites 1 and 2 with river flow at the Diversion just downstream.

7.3 Contribution of soil water to stream flow

Soil moisture and matric potential data were used to generate soil moisture characteristic curves for each soil depth at Sites 1 and 2 to gain insights into the drainage characteristics of the soils. These were compared with the evidence of drainage obtained from measuring flows in the land drains at different antecedent conditions. The matric potential data were also converted to total water potentials to understand the hydraulic gradients, and therefore water transfer between the soil layers, between sites and to the stream.

7.3.1 Soil moisture characteristics

Soil moisture characteristic curves were generated using the paired soil moisture and matric potential data for the soils at the three depths at Sites 1 (Figure 7.9) and 2 (Figure 7.10). The relationship between tension and soil moisture at each site was complex, which is a reflection of the extent of hysteresis due to the differences in soil moisture content during wetting and drying (Hillel, 1982), and the limitations with the dataset as described in Appendix 1.

7.3.1.1 Porosity

The soil moisture characteristics show that the soils at depths at Site 1 were frequently saturated, with high moisture content. The porosity, which is considered to be equal to the soil moisture

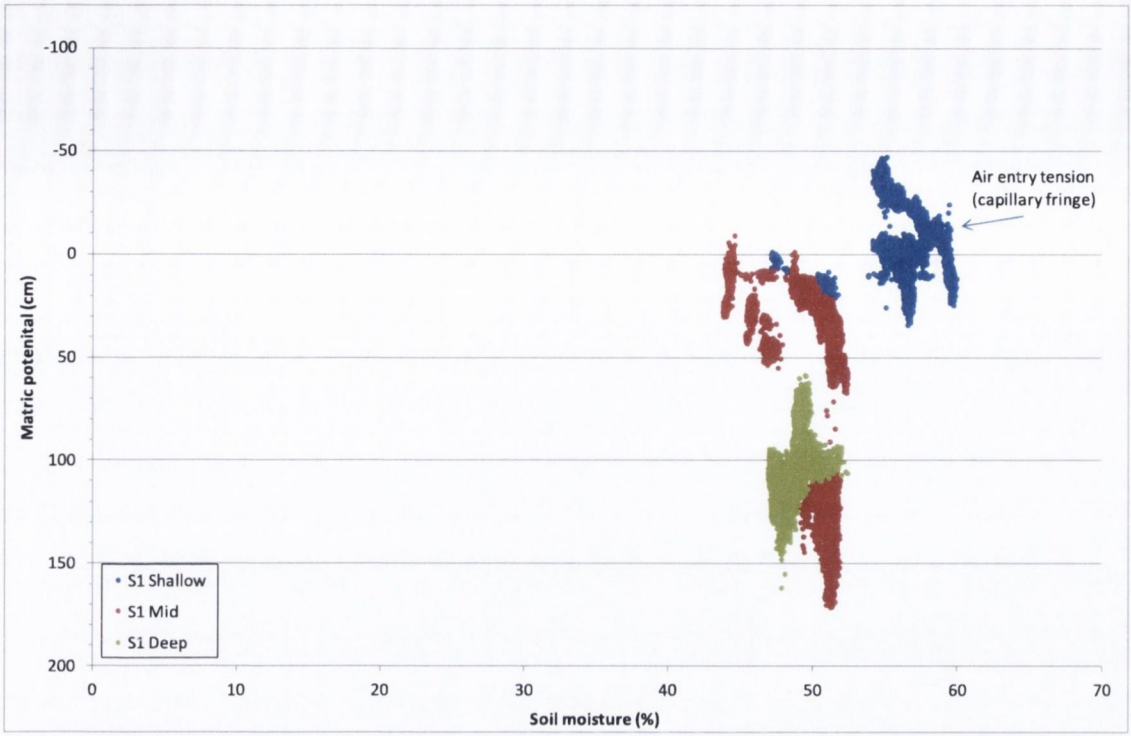

Figure 7.9. Soil moisture characteristic for the three monitoring horizons at Site 1 (Shallow = 20 cm; Mid = 50 cm; Deep = 80 cm). The black dashed line indicates the point of saturation. Note that the majority of data points are below the line indicating that water drains readily from the soils. The air entry tension or capillary fringe in the upper soil layer is indicated by the change in slope in the curve from vertical and corresponds to a matric potential of approximately –15 cm.

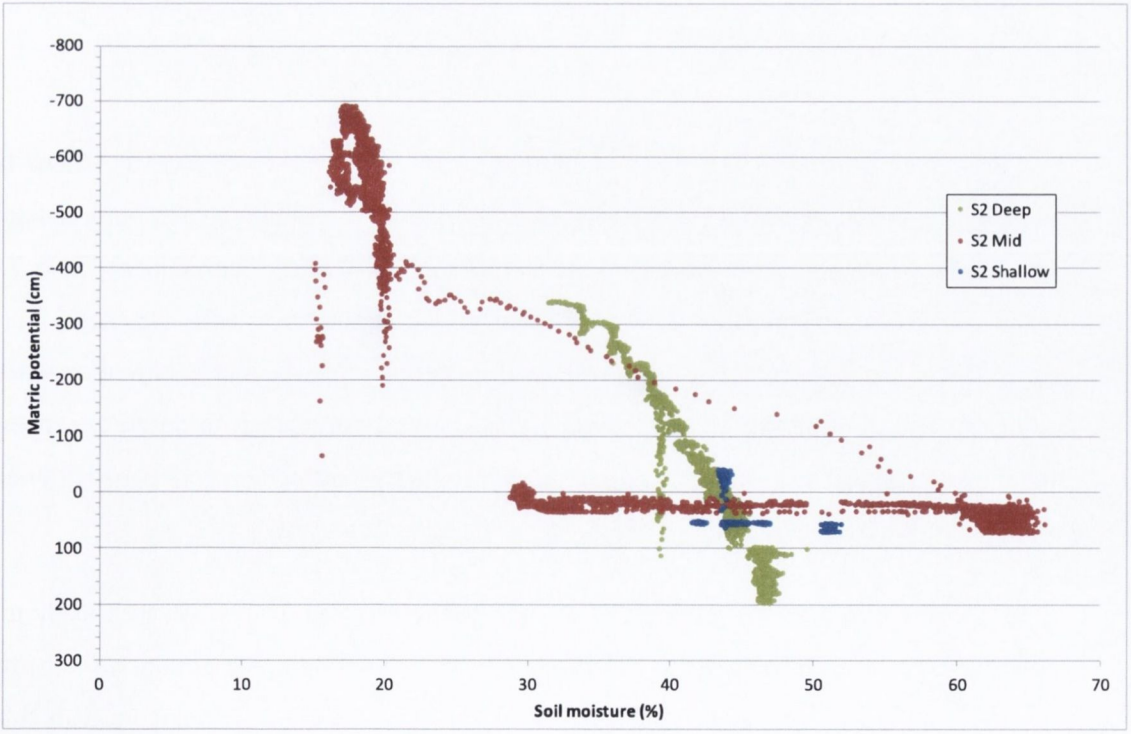

Figure 7.10. Relationship between soil moisture and matric potential at the three monitoring horizons at Site 2 (Shallow = 20 cm; Mid = 60 cm; Deep = 120 cm). Black dashed line = point of saturation.

content at zero tension (Hillel, 1982), ranged from 47–59% in the topsoil (SM1 Shallow, 20 cm) to 43–49% in the SILT/CLAY (SM1 Mid, 50 cm). The range in values in each horizon, and the relatively high upper limits in comparison with average clay soils (Dingman, 2002), is likely to be due to the presence of macropores increasing the porosity in excess of that provided by the soil matrix. This dual porosity, which can sometimes also mean dual permeability, has also been observed elsewhere in other studies (Gärdenäs et al., 2006).

At Site 2, there was a large range in soil moisture content at saturation at all depths, but especially in the mid-depth soils. Porosity ranged from 39–44% in the CLAY (SM2 Deep, 120 cm) to 29–64% in the SILT/CLAY (SM2 Mid, 60 cm), which again suggests dual porosity with a greater extent of preferential flowpaths and drainage at the mid-depth. This is consistent with the rapid increases and decreases observed in the soil moisture content (Section 7.2.2).

7.3.1.2 Capillary fringe

A capillary fringe depth of 15 cm was evident in the topsoil at Site 1 at 20 cm depth, which is the point at which the slope of the soil moisture characteristic curve near saturation moves away from the vertical, indicating a reduction in soil moisture with increasing tension. The capillary fringe depth was within 5 cm of the ground surface indicating that the extent of the unsaturated soil horizon was typically small. This suggests that overland flow is likely to be common in these soils in the lower landscape position. The data for Site 2 were less clear; this may be because there was no capillary fringe due to better drainage.

7.3.1.3 Field capacity and drainage

The distinctive changes in soil moisture content in the topsoils and mid-level SILT/CLAY layers at both Sites 1 and 2 (Figure 7.11) were reviewed with the corresponding matric potential data from the soil moisture characteristic curves, to determine the drainage conditions (Table 7.2). The upper consistent soil moisture contents occurred when the soils were saturated, i.e. matric potentials >0 cm. The lower consistent values all occurred when the matric potentials were <0 cm and therefore the soils were unsaturated. These characteristics are considered to represent the soil moisture conditions when the majority of the soil water in the macropores had drained away, and that which remained was held against gravity, i.e. field capacity.

Field capacity was lowest for the SILT/CLAY at Site 2 (SM2 Mid, 60 cm) which is likely to reflect better drainage due to the presence of adjacent land drains. This would be supported by the large fluctuations in soil moisture content. Anecdotal evidence from the landholder suggests that this is the layer into which the field drainage was developed in the 1950s, which would be supported by

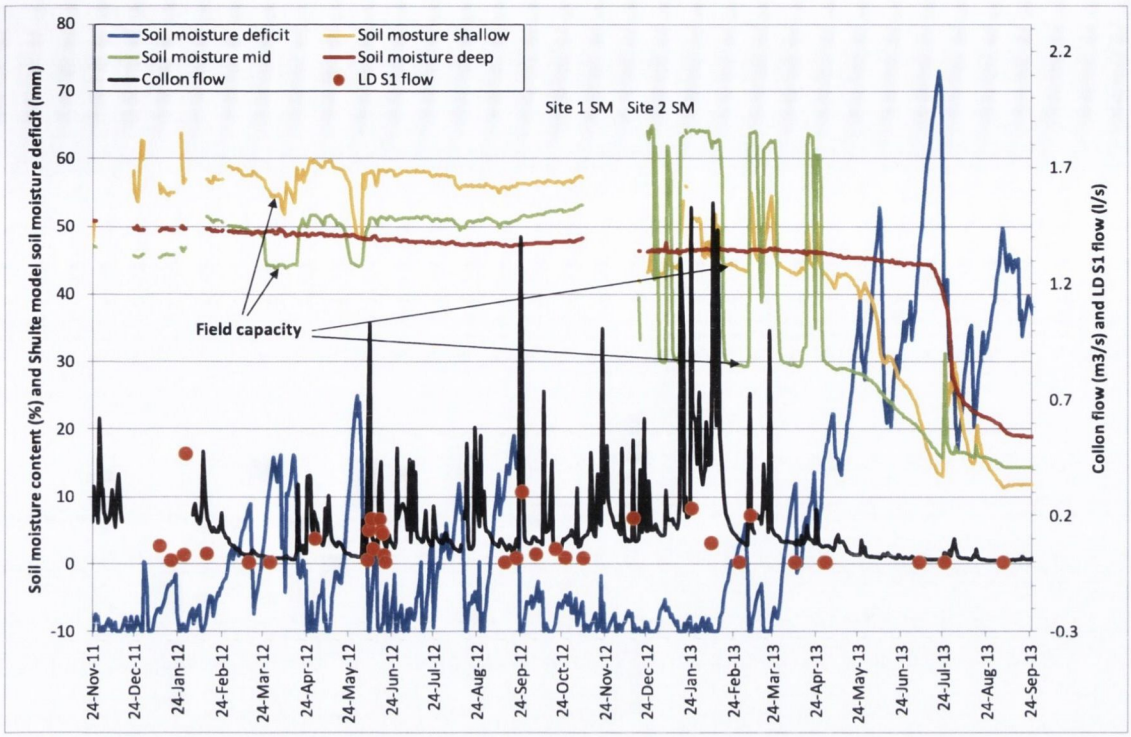

Figure 7.11. Daily stream flow, soil moisture content, and flow in the land drain at LD S1, with the SMD from the Schulte model (Met Eireann). Soil moisture content data are from the three measured depths at the soil water dynamics site at Site 1 (left) and Site 2 (right). The vertical dashed line indicates the period when the soil moisture monitoring equipment was transferred from Site 1 to Site 2 and therefore the datasets before and after reflect different soils. The horizontal dashed line represents zero stream and land drain flow, and zero SMD, i.e. field capacity. FC = field capacity estimated based on the soil moisture characteristic curves from the research site. Note the relationships between the measured soil moisture content and the modelled SMD; and land drain flow and SMD.

Table 7.2. Summary of the soil moisture characteristics at Sites 1 and 2 at saturation and field capacity.

Site	Soil horizon	Depth (cm)	Saturation		Field capacity	
			Soil moisture (%)	Matric potential (cm)	Soil moisture (%)	Matric potential (cm)
1	Topsoil	20 (Shallow)	58	Up to 25	54	-47
	SILT/CLAY	50 (Mid)	52	20–171	44	-9
2	Topsoil	20 (Shallow)	51	56–70	44	-40
	SILT/CLAY	60 (Mid)	64	15–70	30	-18

observations of the depths of four of the five monitored land drains in the field. The first set of holes drilled at Site 2 into this layer also had to be abandoned as a flowing land drain was encountered.

In the topsoils at both sites, the higher soil moisture content and lower matric potential at field capacity, suggest that these soils retain more moisture, due potentially to their higher organic content. Although the field capacities of the topsoil at Site 2 and the SILT/CLAY at Site 1 were the same, their matric potential at field capacity was very different which reflects their different permeabilities and texture. The field drainage was also effective at quickly reducing the soil

moisture content of the topsoil layers, as indicated by the rapid drainage response times and the similar duration of reduced soil moisture content as in the SILT/CLAY, which suggest a good hydraulic connection between them. The reduced fluctuations at Site 1 in comparison to Site 2 is likely to be due to the longer periods of saturation and greater upward gradients at the lowermost end of the transect. The deeper CLAY layers, at 80 cm (SM1 Deep) and 120 cm (SM2 Deep) depth, remained largely saturated for most of the study period. The data thus suggest that the drainage is most effective in the SILT/CLAY and topsoils, and that Site 2 appears better drained than Site 1.

7.3.1.4 Land drain flow and soil moisture characteristics

The spot flows measured in the land drains were compared with the soil moisture content data for the topsoils and SILT/CLAY at Sites 1 and 2 (Figure 7.12). The purpose of the comparison was to determine whether there was a relationship between land drain flow and field capacity, to support the estimates of field capacity, and because as noted by Beven and Germann (2013), flow can be independent of field capacity where macropore flow is significant. The estimates of porosity and the large fluctuations in soil moisture content at Site 2 suggested that macropore flow might be important in this catchment.

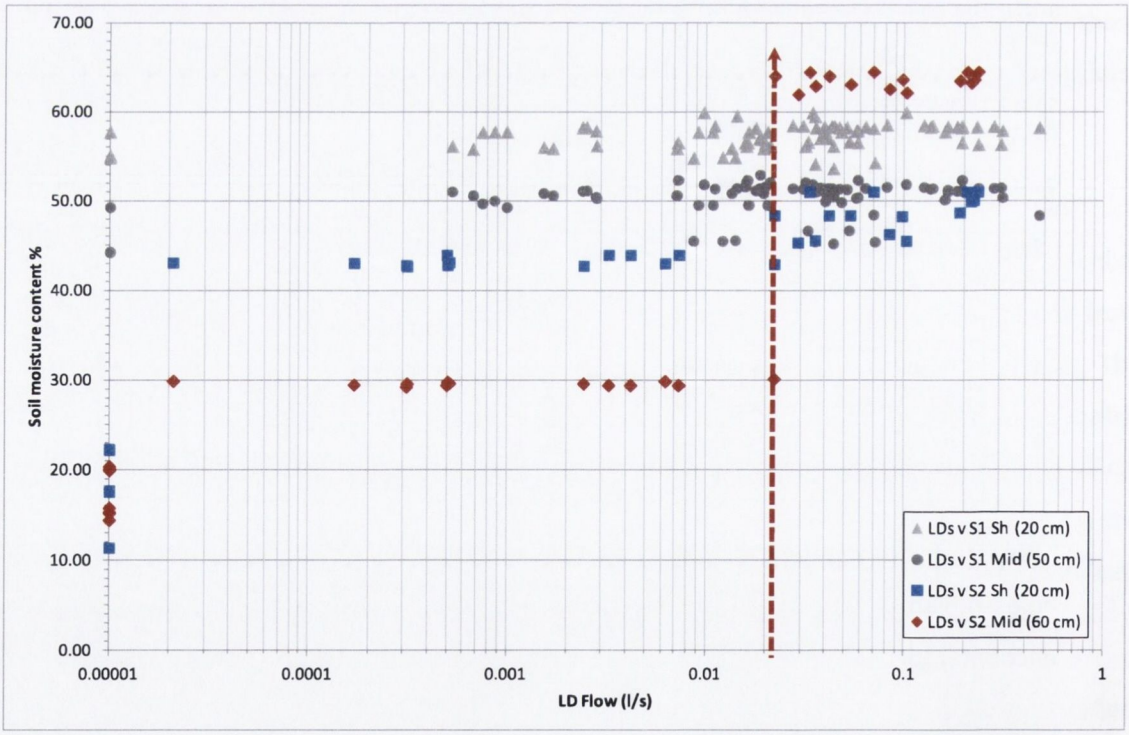

Figure 7.12. Land drain flow and soil moisture content for the topsoil and SILT/CLAY layer at Sites 1 and 2. Field capacity for each soil is highlighted by the horizontal dashed line of the same colour. Vertical dashed line shows an increase in soil moisture content in the SILT/CLAY at Site 2 (60 cm) which corresponded to an increase in flow in the land drains. Zero land drain flow is taken as 10^{-6} l/s for plotting purposes.

The data suggested that the land drains did not flow when the soils were below field capacity, which is consistent with the definition of field capacity given by Schulte et al. (2005). The relationships between soil moisture content and land drain flow varied for each soil layer, however. There was a distinct increase in land drain flow when the soil moisture content increased in the SILT/CLAY at Site 2 (Figure 7.12, red points) and, to a lesser extent in the overlying topsoils at that site (blue points). The soil moisture content/flow relationships at Site 1 however, were less clear, as there was a large variation in flows in the land drains at similar soil moisture contents (grey points). This may have been due to the soils at Site 1 being almost permanently saturated.

The land drain flows were also compared with matric potential data for each soil layer (Figure 7.13). The data highlighted that that the soils at Site 1 at both depths were rarely unsaturated, but despite this, there was a large range in land drain flows, although higher land drain flows of more than 0.02 l/s did correspond with increases in matric potential at both depths. This suggests that it was not only the soils close to the stream that were governing the drainage. At Site 2, the soils were unsaturated at both depths more often. The land drains continued to flow, and often at relatively high flow rates, when the soils at Site 2 had matric potentials that were lower than

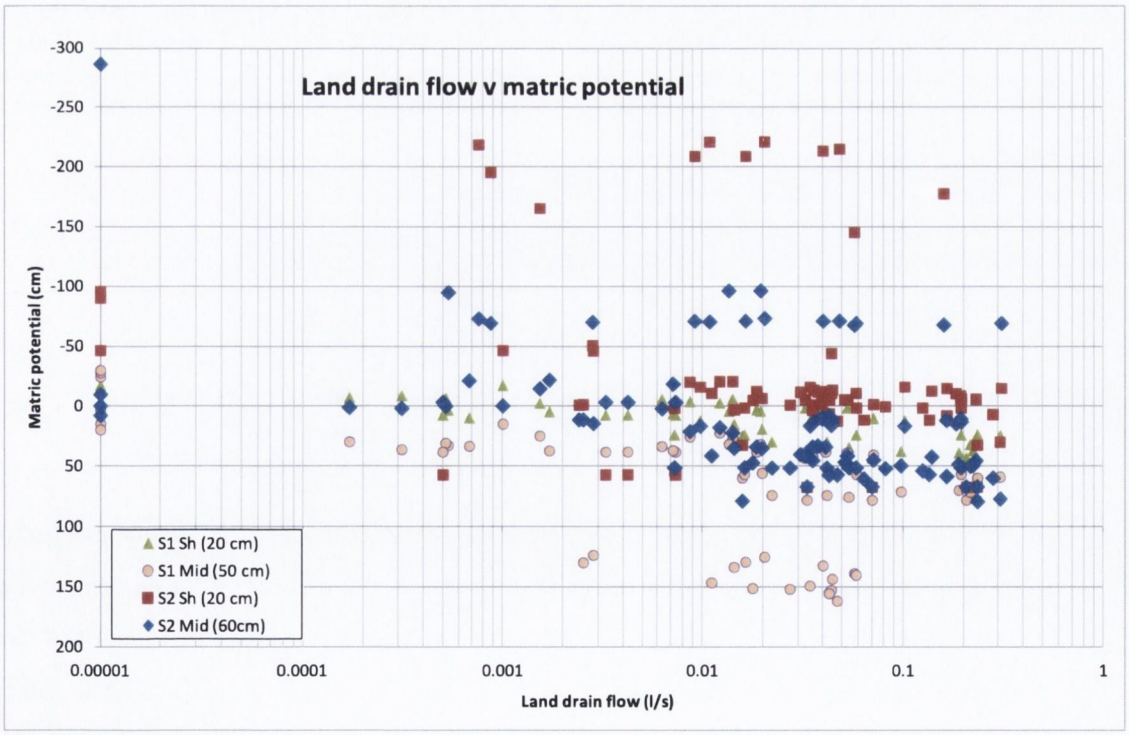

Figure 7.13. Land drain flows with matric potential data for the topsoils and SILT/CLAY layers at Sites 1 and 2. Dashed lines highlight the matric potential at field capacity for each soil layer. Note land drains still flowed when the soils at Site 2 were at lower matric potentials than field capacity.

those associated with field capacity. Despite soil moisture being tightly bound at Site 2, there were land drains still flowing which means either the land drains were being supplied from soils with different types of soil moisture regimes in other parts of the catchment, and/or there was macropore flow occurring; both are considered likely.

To review the relationships more closely, a statistical analysis of the correlations between the flow in each of the five land drains where flow was monitored, and matric potential (Table 7.3) and soil moisture (Table 7.4) in each soil horizon. The locations and characteristics of each land drain are discussed in detail in Chapter 8.

Table 7.3. Correlation coefficients for flow in five different land drains (and all land drains together) and tension at each of the monitored depths at each site. The numbers in bold indicate the relationships that were statistically significant with p values <0.05 (Student's two tailed t test). The grey cells indicate the strongest correlations that were statistically significant between flow and tension for each land drain.

Land drain	Land drain flow versus tension									
	Site 1			Site 2			Site 3	Site 4		
	Shallow	Mid	Deep	Shallow	Mid	Deep	Shallow	Shallow	Mid	Deep
LDS1	-0.286	**-0.797**	**-0.518**	**-0.360**	-0.265	**-0.170**	**-0.005**	-0.471	**-0.145**	**-0.015**
LD Forest	-0.397	-0.714	**-0.735**	-0.577	-0.496	-0.459	**-0.793**	n/a	n/a	n/a
LD Track	-0.275	**-0.720**	**-0.531**	**-0.398**	-0.675	**-0.336**	**-0.250**	-0.323	**-0.683**	**-0.352**
LD Hill	-0.352	**-0.670**	**-0.545**	**-0.175**	-0.131	**-0.231**	**0.291**	-0.514	**0.082**	**-0.045**
LD pipe	-0.398	-0.828	**-0.685**	n/a	-1.000	-0.348	-0.952	n/a	n/a	n/a
LD all	-0.244	**-0.226**	**-0.468**	**-0.284**	-0.309	**-0.224**	**-0.041**	-0.344	**-0.250**	**-0.128**

Table 7.4. Correlation coefficients for flow in five different land drains (and all land drains together) and soil moisture content at each of the measurement depths at Sites 1 and 2. Numbers in bold indicate statistical significance with p values <0.05 (Student's two tailed t test). The grey cells indicate the strongest correlations that were statistically significant between flow and soil moisture content for each land drain.

Land drain	Land drain flow versus soil moisture content					
	Site 1			Site 2		
	Shallow	Mid	Deep	Shallow	Mid	Deep
LDS1	**0.308**	**0.121**	**-0.087**	**0.697**	**0.901**	**0.399**
LD Forest	n/a	n/a	n/a	**0.613**	**0.892**	**0.340**
LD Track	**0.180**	**0.322**	**-0.173**	**0.659**	**0.885**	**0.373**
LD Hill	**0.391**	**0.174**	**-0.103**	**0.625**	**0.941**	**0.379**
LD pipe	n/a	n/a	n/a	**0.572**	**0.941**	**0.289**
LD all	**0.229**	**0.151**	**-0.077**	**0.523**	**0.725**	**0.291**

There were statistically significant, strong, negative correlations between flow in each of the land drains and the matric potential in all cases at at least one of the soil monitoring points (Table 7.3), i.e. the greater the tension (or the more negative the matric potential), the lower the land drain flow[10]. The strongest correlations were typically with the soils at the mid (S1 Mid, 50 cm) and deep (S1 Deep, 80 cm) horizons at Site 1, closest to the stream. LD Forest, which is located in a

[10]Note that tension, which is the matric potential expressed as a positive, has been used in this analysis for convenience in the calculations.

mid-slope area, was correlated best with the tension in the shallow soils at Site 3 (S3 Shallow, 20 cm), which is in a similar mid-slope position, but there was also a similarly strong significant correlation with the deep level soils at S1 (S1 Deep, 80 cm). The land drain flow at all sites was very well correlated with the soil moisture content at the mid-level at Site 2 (SM2 Mid, 60 cm) (Table 7.4). These relationships suggest that the soil water dynamics at different locations in the landscape and at different depths influence the drainage in different ways. It is hypothesized that they may reflect in this catchment that the water in the drains are sourced from environments such as that at S2 Mid, which fill and empty most frequently, but that the rate of discharge is controlled by the hydraulic head in the mid and deeper level soils closer to the river. The relationships between the different land drains, and flow and nutrient transport, is explored in further detail in Chapter 8.

7.3.1.5 Land drain flow and soil moisture deficits

To take a more general overview, the land drain flow data were also compared with the estimates of the daily soil moisture deficit (SMD) for poorly drained soils generated by Met Eireann using the Schulte Hybrid model (Figure 7.11). The Schulte modelled SMD data are widely available and applicable nationwide, so it was considered to be a useful exercise to determine whether there were any relationships that could be applied more widely in the development of the catchment management support tools.

In the Schulte model, the soils are assumed to be at field capacity when the SMD is zero (refer to Section 3.4.5). Based on the available data, it appears that the predictions of zero SMD from the model compare favourably with the estimates of field capacity provided by the soil moisture characteristics at the site (Figure 7.11), thus initially supporting the definition that no drainage occurs when the SMD is zero (SMD_0), i.e. field capacity.

Review of the spot flows for the land drains in relation to the modelled SMD (Figure 7.14) showed that land drains still flowed, albeit at a low rate, when there was an SMD of up to 16 mm[11] which supports the hypothesis that macropores in the soils drain into the land drains. The maximum flow when there was an SMD was approximately 0.025 l/s; this represents a general flow threshold between unsaturated and saturated flow conditions at these sites, whereas all flow had ceased when the SMD was >16 mm. These flow thresholds are further explored in relation to nutrient transport in Sections 8.3 and 8.5.

[11] It must be considered that the SMD data are daily values and the land drain flows are spot values, which means they are not directly comparable, but nevertheless there appears to be a consistent trend. The Schulte model has also been developed based on the climatic conditions at Dublin airport, some 40 km to the south, and although they are at a similar position in relation to the sea, and hence evapotranspiration would be expected to be similar, the timing of the rainfall events may be different by a few hours.

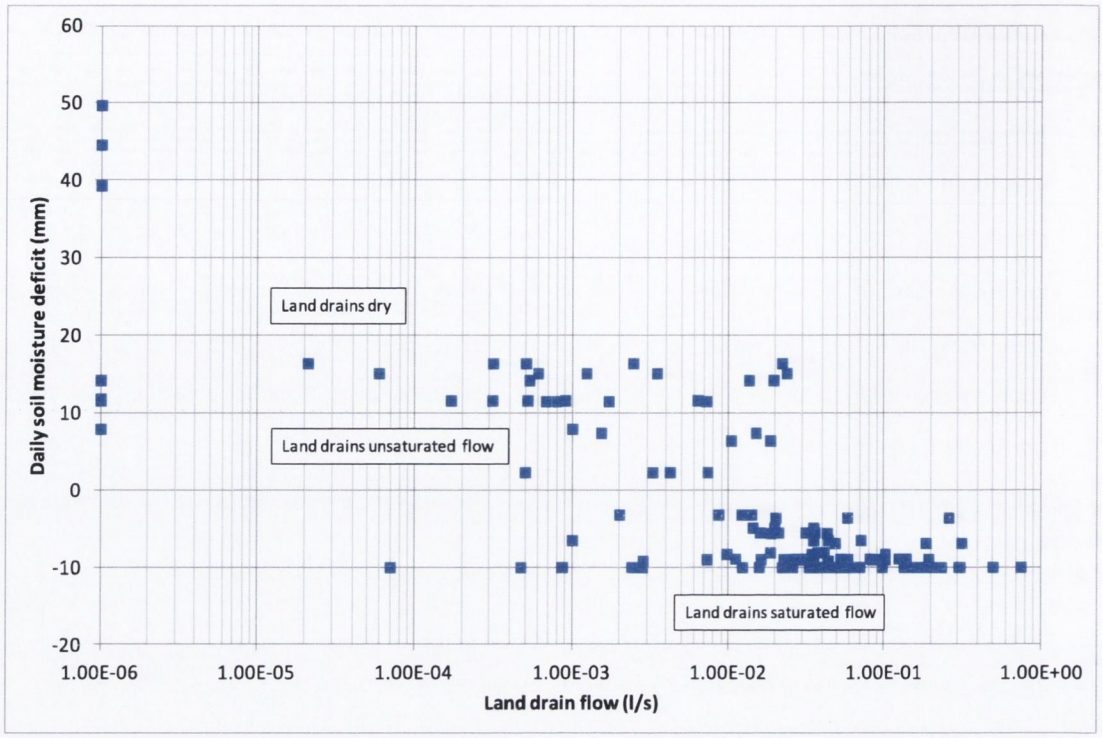

Figure 7.14. Land drain flow (spot data) and daily SMD modelled using the Schulte model (Met Eireann data). Dashed lines represent the SMD limit beyond which there is no land drain flow (horizontal), and the maximum land drain flow when there is an SMD (vertical). Note the log scale on the x-axis; zero flow was taken to be 10^{-6} l/s for plotting purposes.

The highest flow occurred when there was excess soil moisture (SMD = −10 mm; SMD_{min}) as expected, but high flows were still possible when SMD_{min} had not yet been reached. There were also periods when the land drains flowed at low rates at SMD_{min} when conditions were apparently wet, but these measurements were taken in the morning before significant rainfall events which influenced the daily SMD estimate. Further discussion on the applicability of the SMD model is provided in Section 7.5.4.

7.3.2 Total water potential

Total water potential, or hydraulic head, was calculated for each layer at each site by adding the gravitational potential above an arbitrary datum to the matric potential (Figure 7.15). Ordnance datum was selected so that the data could be compared with the groundwater levels from the underlying saturated sands and gravels. Figure 7.16 shows the changes in head over time, together with the geological profiles at each of the sites. Site 3 was not included as matric potential data were only available for the upper soil layer. Note that the groundwater hydraulic heads are much lower than those in the soils at Sites 1 and 4 so they are shown on the secondary y-axis; they do not therefore relate directly to the geological profiles pictured.

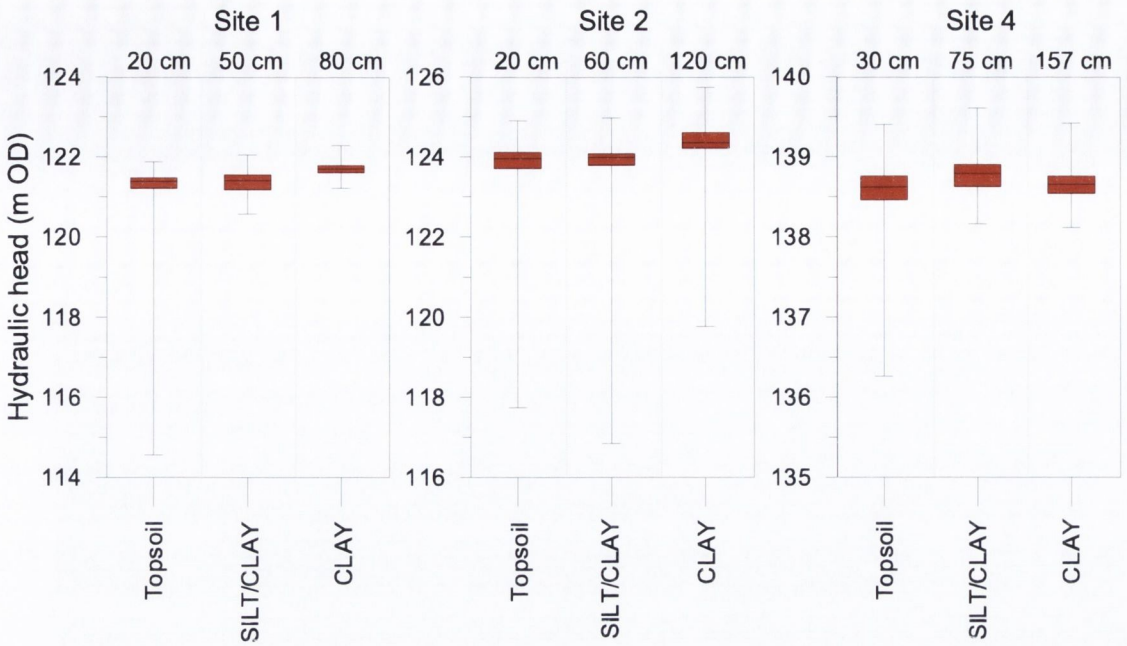

Figure 7.15. Total water potential (hydraulic head) above Ordnance Datum at Sites 1, 2 and 4.

The data show that at Site 1, the topsoil (S1 Shallow, 20 cm) and SILT/CLAY (S1 Mid, 50 cm) had similar heads during the study period, which fluctuated between the two horizons, supporting the hypothesis that they likely acted as a single hydraulic unit. The heads in the deeper CLAY (S1 Deep, 80 cm) were slightly higher suggesting upward gradients from the CLAY into the SILT/CLAY and topsoil. There was evidence that the CLAY acted as a hydraulic barrier in the profile because the head in the underlying sand/gravel at Site 1 was much lower and was driven more by the stage in the stream (Section 7.2.4).

At Site 2, there was a similar pattern to Site 1: the hydraulic heads in the topsoil (S2 Shallow, 20 cm) and the SILT/CLAY (S2 Mid, 60 cm) were comparable and there was also an upward gradient from the underlying CLAY (S2 Deep, 120 cm). During the drier periods, however, the heads dropped below the depth of the SILT/CLAY layer suggesting that the topsoils and SILT/CLAY may have been dewatered. Groundwater in the underlying sandy SILT was confined by the CLAY with upward gradients except during dry periods.

At Site 4, the available data tentatively suggest that the heads may have been the highest in the SILT/CLAY (S4 Mid, 75 cm) and that drainage of this layer was therefore less effective in the upper catchment. The monitoring point for the SILT/CLAY at Site 4 was deeper than at the other sites however, i.e. 75 cm, in comparison to 50 cm and 60 cm at Sites 1 and 2, respectively. It must also be acknowledged that the datasets are not entirely comparable because the particular difficulties with the mid-level tensiometer at Site 4 meant that there were approximately 1.5 times fewer data for the SILT/CLAY layer than for the shallow or deep soils/subsoils. The heads at all soil levels

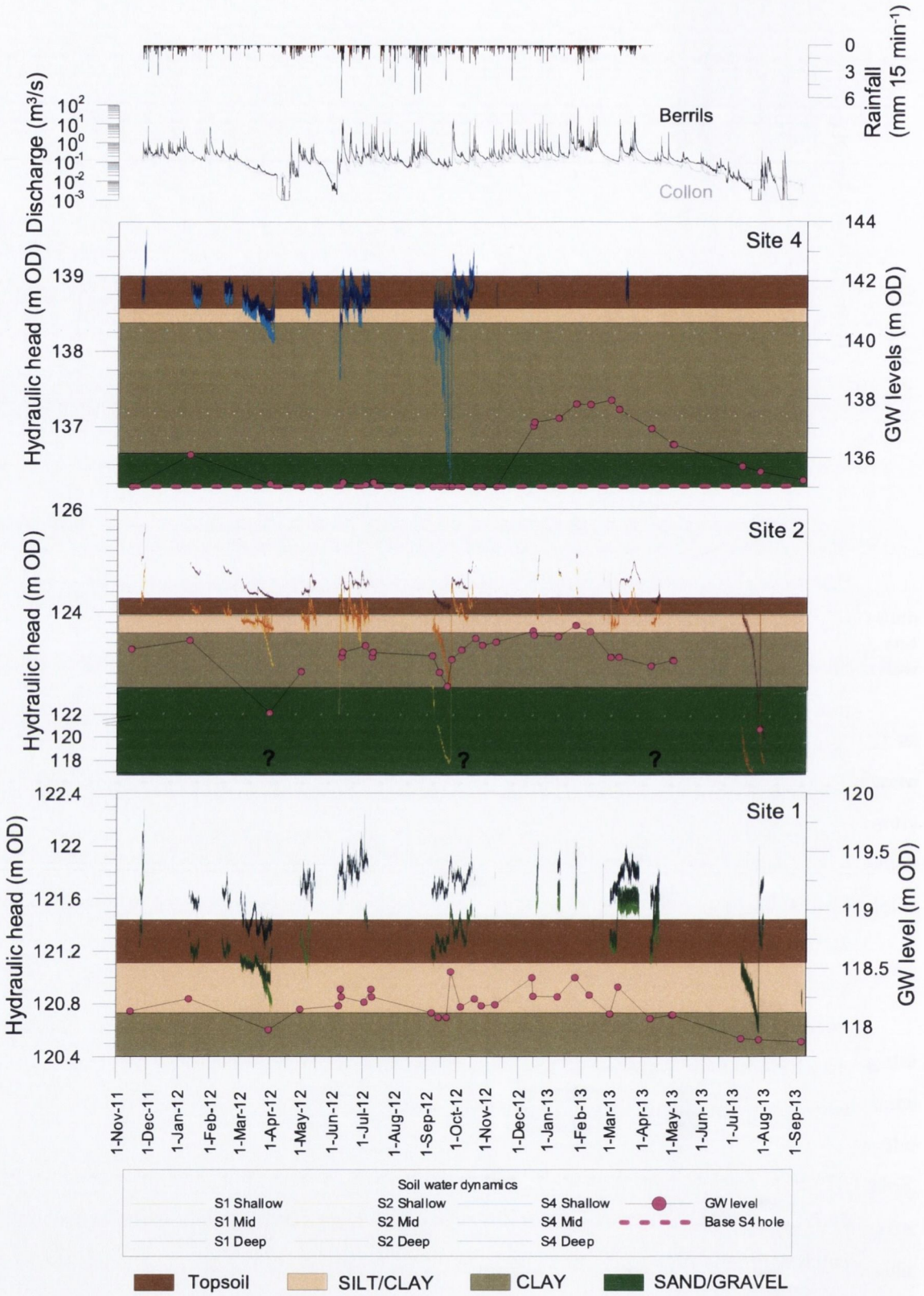

Figure 7.16. Hydraulic head in the soil water and groundwater, with geology, at Sites 1, 2 and 4. Depths of the geological layers are shown on the primary y-axes. Groundwater levels are shown on the secondary y-axes for Sites 1 and 4 and the geology layers therefore do not apply directly as pictured. Note changes in scales on y-axes between sites.

at Site 4 were frequently lower than the ground surface, which suggests that overland flow was less important at this location, as would be expected in the upper catchment.

An estimate of the median hydraulic gradients in the different soil horizons between Sites 1 and 2 was made, taking as an assumption that they were hydraulically linked. The other sites were not considered as they were too far away, and a spring and a ditch cross the transect between them and Sites 1 and 2. The topographic gradient between Sites 1 and 2 was 0.1, which was the same as the median hydraulic gradient in the topsoil. The median gradients in the SILT/CLAY and CLAY layers, however, were slightly smaller at 0.09, which suggests that the lower soil layers cannot readily accept all the infiltration through the topsoil and that some is likely discharged as interflow, or return flow at the surface.

7.3.3 Estimates of flux

An estimate of the flux through the soils can be made by applying Darcy's Law (Eqn. 2.1), taking representative values for the required parameters. The hydraulic gradient was taken to be the gradient between Sites 1 and 2 as calculated from the total water potential (0.09). The cross-sectional area was assumed to be the depth of the topsoil and SILT/CLAY layer (0.65 m) over the length of the stream channel in the upper catchment above the first monitoring point (3.12 km). An estimate of the hydraulic conductivity was also required, however, because it was not measured directly in the field.

The subsoils at the site are classified as low permeability using the Geological Survey of Ireland methodology (Section 7.2.1), which suggests that the permeability was less than 10^{-9} m/s (Swartz et al., 2003). Permeabilities of a similar range (2×10^{-10} m/s) were measured in clayey lodgement tills in the United Kingdom (Cuthbert et al., 2010). This results in an estimated flux through the soils at the site of 4×10^{-6} to 7×10^{-7} m^3/s. This equates to a contribution of 0.004 m^3/s from the soils on both sides of the river in the 3.12 km reach in the upper catchment, which is small in comparison to the median flow of 0.082 m^2/s at the Diversion flow gauge, the upper catchment monitoring point that is closest to the soil water dynamics site (refer to Figure 7.1 for location). However, these permeabilities are matrix permeabilities and there is sufficient evidence from the variability in soil moisture content that preferential flow is also occurring through macropores at the site. An alternative method using the rate of drainage was therefore applied.

During a low flow period on 25/26 March 2012, as discussed in Section 7.2.2, the soil moisture content reduced dramatically in the SILT/CLAY layer at Site 1 by 4.26% over 12 h (Figure 7.17). The matric potential was greater than zero throughout the period, which indicates that the soils were saturated and that the moisture content loss was due to drainage and/or evapotranspiration.

However, the 12 hours was overnight so it is anticipated that the evapotranspiration was very small. There was a corresponding reduction in stream flow at the Diversion of 0.003 m^3/s over approximately the same period, from 0.005 to 0.002 m^3/s, which represents a reduction in stream flow of 60%, or conversely, the soil moisture was providing 60% of the flow in the stream at 0.005 m^3/s immediately before the reduction in soil moisture.

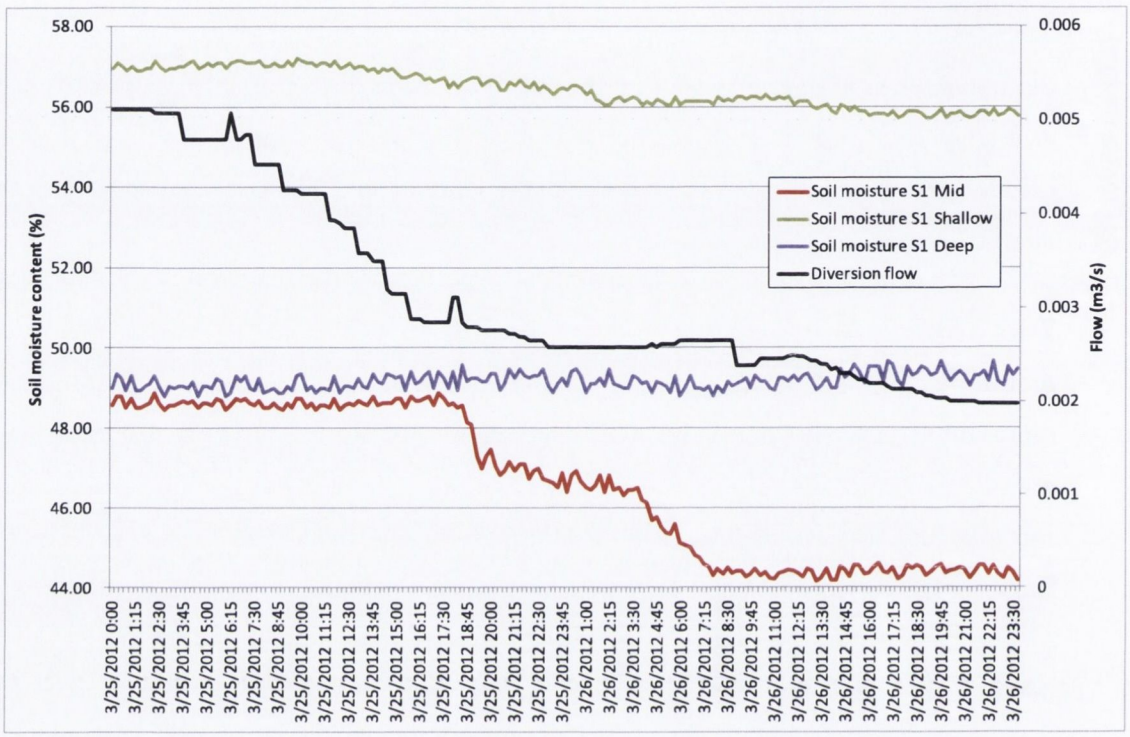

Figure 7.17. Decreases in stream flow and soil moisture content at Site 1, 25/26 March 2012. Note: the apparent small fluctuations in the soil moisture data are due to sampling noise.

This is remarkably consistent with the results of the chemical hydrograph separation method, which estimated that 60% of the flow during low flow periods is contributed to the stream via interflow (Section 6.2.1.7). There is an inherent presumption, however, that the reduction in soil moisture was responsible for the reduction in streamflow, so further exploration of the data was carried out to determine whether this volume of water could actually be delivered via the soils based on the available data.

A crude estimate of the amount of water drained from the SILT/CLAY layer during the 4.26% reduction in soil moisture content was made. If the saturated thickness is taken to be the hydraulic head over the base of the SILT/CLAY layer at the time the moisture drop commenced (0.287 m), then approximately 4.26% x 0.287 m, or 0.012 m of water was drained over the 12 h. Assuming negligible evapotranspiration, the area that would be required to support the flow of 0.003 m^3/s along the 3.12 km of stream channel above the diversion, extends to just 1.9 m either side of the stream channel. This estimate assumes that the drainage takes place evenly through

the soils, but in reality it will be restricted to the areas surrounding the drainage channels. Taking the area of influence around each drainage channel to be 2 m (i.e. 1 m each side) and an average length of drainage channel affected of 10 m, which represents the distance between the river channel and Site 1 where there was evidence of a response, suggests that the drains would need to be spaced approximately 10 m apart to provide the required flow. This drain spacing is a little lower than is likely in practice; mole plough drains in Ireland are typically spaced at 1–2 m, whereas piped collector drains, which would be the ones likely to be still flowing in low flow conditions, are placed approximately 15 m apart in clayey soils in Ireland (Tuohy et al., 2013). However, the first response in the reduction in streamflow commenced some 16 h prior to the response in the SILT/CLAY layer at Site 1, and 11 h prior to that in the topsoils, suggesting that if the reduction in flow was due solely to the elimination of the interflow contribution, the latter was being contributed from a wider proportion of the catchment, further from the river or further upgradient, than the near-stream location at Site 1.

This is corroborated by field observations from two site visits before and after the event. On 14 March 2012, it was observed that two of five main land drains being monitored were still flowing at a steady trickle, whereas the other three were dry. Unexpectedly, the drains that were flowing were LD Hill located near the catchment divide, and LD Track which is in a mid-slope position at a break in slope, which are the farthest of the five that were being monitored from the river (refer to Figure 8.2 for the locations of the land drains). By 29 March, flow at all five monitored land drains had completely ceased. Further discussion on the land drains and how they operate is provided in Chapter 8.

Additional factors to consider include the likelihood of inefficiencies in some places where drains are blocked, and variations in the saturated thickness over the area. Consideration was also given to whether the soil moisture loss could have been due to an exceptionally warm day the day before giving rise to large evapotranspiration. However, the SMD for 25 March based on data from Met Eireann and generated using the Schulte model (refer to Section 3.4.5) was only 3.4 mm, which indicates that the period was not excessively dry. The SMD was also decreasing by just 1.9 mm/d, which is substantially less than the 12.2 mm of soil moisture loss over the 12 h as indicated by the soil monitoring data. Although the estimate obtained is very crude, it is nevertheless in the right range. It therefore seems realistic that the soil moisture drainage could sustain 60% of dry weather baseflow as estimated using the chemical hydrograph separation method (Section 6.2.1.7).

7.4 Soil water dynamics during events

An in-depth review of the soil water dynamics was carried out on the data for two sequential rainfall events in June 2012, the first from June 7 to 10, and the second from the June 14 to 20. These events were selected because they were also intensively monitored for stream and pathways chemistry and therefore have accompanying estimates of the pathway contributions from the chemical hydrograph separation methods (refer to Section 6.2.1). There were unfortunately no soil water data available for any of the events monitored in winter; the equipment had not been installed at the time of the 6-day event in February 2011, and there was a power supply and logger failure during the January 2012 event. Nevertheless, the two sequential June events, which took place under different antecedent conditions, i.e. very dry before the first event and wet before the second, provide useful insights into at least some of the variability that occurred.

The matric potential data were plotted in hourly time-series graphs to review how they changed with depth and time. The matric and total potential data were compared to rainfall, stream discharge, groundwater levels and the estimates of the pathway contributions from the chemical hydrograph separations. The aim was to identify the hydrological conditions during the events under which interflow may have occurred, and to contrast the findings with the quantification of the pathways contributions derived from the chemical hydrograph separations.

7.4.1 June 7–10 event

The soil matric potential data for the first of the events for Site 2 and Site 4 are presented in Figure 7.18 and Figure 7.19, respectively. Data were not available for the upper two tensiometers at Site 1 due to quality control issues, which meant that the scope for analysis at that site was limited. The matric potential data are converted to total potential data in Figure 7.20 and compared with the pathways contributions and other catchment data. Six timesteps (T1–T6) when significant changes in the matric potential data occurred were identified, which, on review, generally coincided with significant changes in stream flow or pathway contributions. A summary of these relationships is provided in Table 7.5. The timesteps are also provided on the three corresponding graphs for cross referencing purposes.

At T1 as rainfall was starting, there was an upward gradient into the topsoils from the deeper soils at both Sites 2 and 4. There was a rapid rise in the head and a shift to saturation in the topsoils at Site 4 (S4 Shallow, 30 cm) however, which suggests that the topsoils may have been tension saturated.

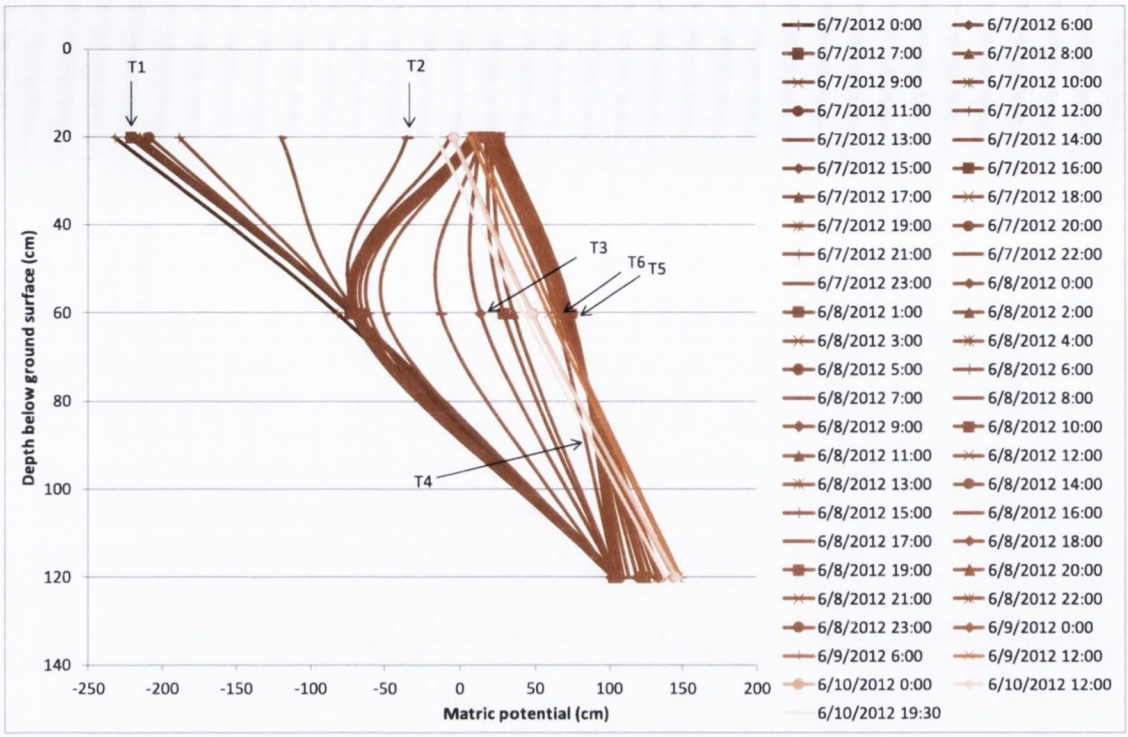

Figure 7.18. Hourly time series of changes in matric potential with depth at Site 2 during the June 7–10 event. Profiles become increasingly lighter in colour with time. Note the later profiles are every 12 h instead of every hour. Specific time periods of interest, which are discussed further in Table 7.5, are labelled T1–T6 for reference. The vertical dashed line represents zero matric potential, which is saturation.

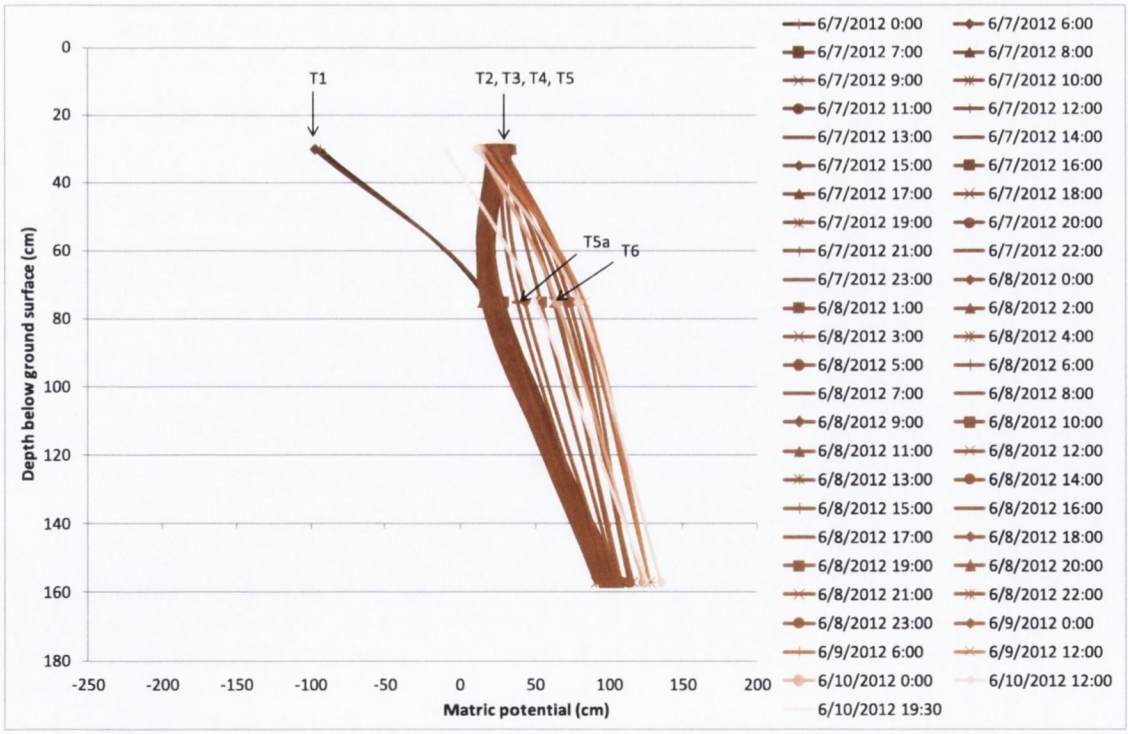

Figure 7.19. Hourly time series of changes in matric potential with depth at Site 4 during the June 7–10 event. Profiles become increasingly lighter in colour with time. Later profiles are every 12 h instead of every hour. Specific time periods of interest, which are discussed further in Table 7.5, are labelled T1–T6 for reference. The vertical dashed line represents zero matric potential, which is saturation.

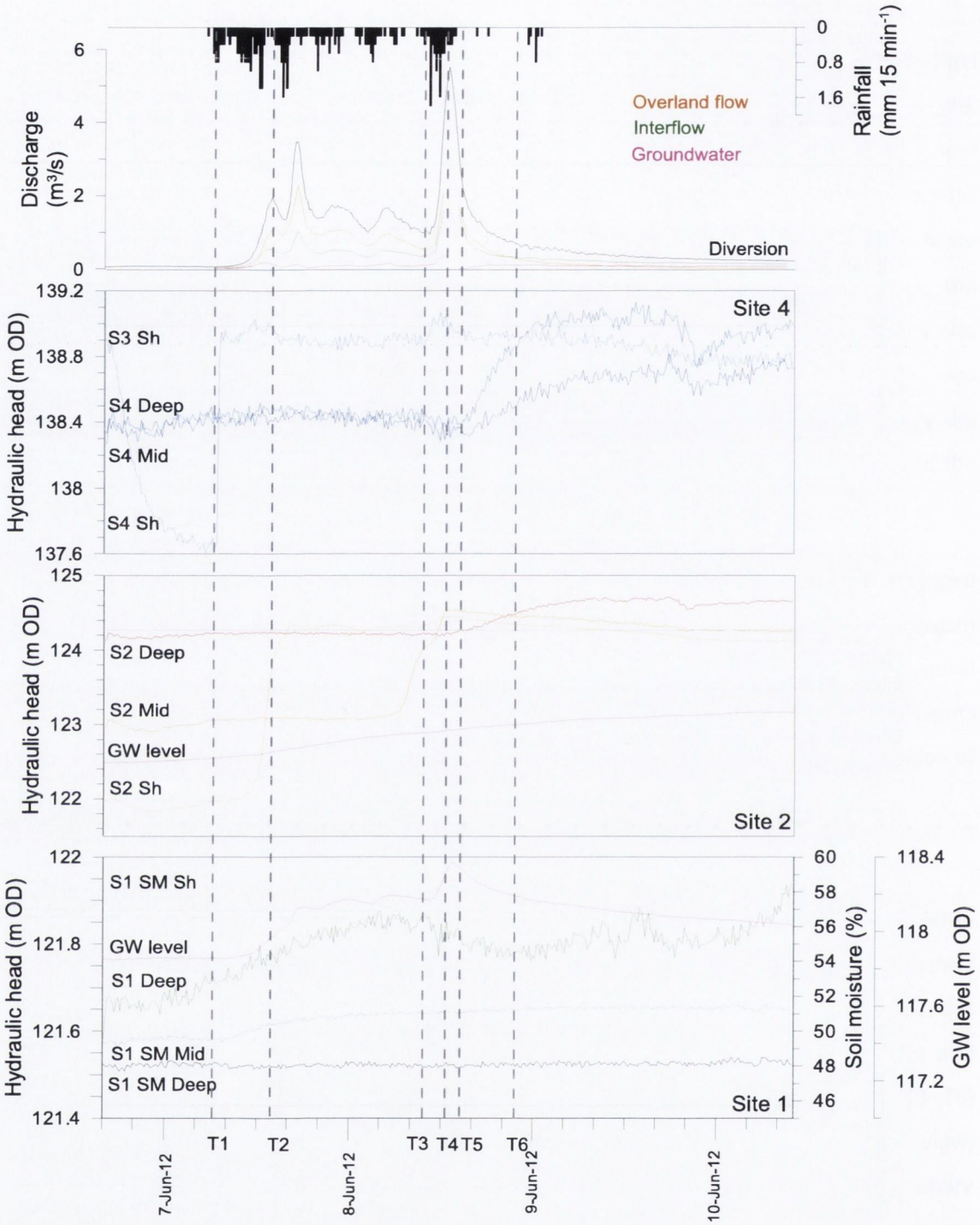

Figure 7.20. Total potentials for Sites 1, 2 and 4, groundwater levels (y-axis), soil moisture (S1 only, y-axis), discharge with pathway contributions, and rainfall during the June 7–10 event. Dashed vertical lines represent specific time periods of interest, T1–T6. Horizontal grey lines represent ground surface. Apparent fluctuations in the total potential data for the soils at Sites 1 and 4 are due to sample noise and are magnified relative to the noise at Site 2 because of the larger scale on the y-axis.

Table 7.5. Summary of key changes in soil moisture dynamics with concurrent stream flow and estimates of the pathways contributing to the flow from the chemical hydrograph separation methods.

ID	Time	Soil water dynamics	Stream flow	Pathways
T1 Rain start	7/6 at 6:00	*Site 2 and Site 4* Upward gradient into unsaturated topsoil. SILT/CLAY also unsaturated at Site 2	Low flow 0.062 m^3/s	IF dominant OF, 23% IF, 55% GW, 22%
T2	7/6 at 14:00	*Site 2* Higher matric potential at 20 cm than at 60 cm but still unsaturated. Saturation at ground surface occurred however, based on field observations, as OF was recorded. Infiltration occurring *Site 4* Similar matric potentials at 30 and 75 cm. Downward gradient	First peak flow 1.97 m^3/s	Switch to OF dominant OF, 64% IF, 30% GW, 6%
T3	8/6 at 9:00	*Site 2* SILT/CLAY saturated and total potential increasing *Site 4* Similar matric potentials at 30 and 75 cm. Downward gradient	Recession	OF reducing OF, 56% IF, 34% GW, 10%
T4	8/6 at 12:00	*Site 2* SILT/CLAY at higher matric potential than topsoil. Highest total potential in SILT/CLAY, also higher than ground surface. Suggests return flow *Site 4* Similar matric potentials at 30 and 75 cm. Downward gradient	Largest peak flow 5.51 m^3/s	Higher relative IF content at peak flow than first peak OF, 51% IF. 39% GW, 10%
T5 Rain stop	8/6 at 14:00	*Site 2* Highest matric potential in SILT/CLAY. Total potential in CLAY higher than ground surface. System full. OF and IF dominant *Site 4* Similar matric potentials at 30 and 75 cm, until 17:00 (5a) when they become greater at depth. Increasing total potentials in lower soils. IF backing up	Recession just commenced	IF increased further OF, 54% IF, 47% GW, 0%
T6	8/6 at 21:00	*Site 2* Matric potential decreasing slowly at all levels. Total potential increasing in the CLAY and lowest in the SILT/CLAY sustaining interflow. Total potentials decreasing uniformly in topsoils and SILT/CLAY suggesting they behave as a single hydraulic unit *Site 4* Total potential in the SILT/CLAY layer highest and above ground surface by 23:00, keeping IF high	Mid-recession	IF dominant OF, 41% IF, 45% GW, 14%

OF = overland flow; IF = interflow; GW = groundwater.

At T2, during the first flow peak in the stream, the matric potential in the topsoil at 20 cm depth at Site 2 (S2 Shallow, 20 cm) increased sharply which corresponded with a switch to overland flow being dominant in stream flow based on the chemistry. The total potential increased above ground surface shortly afterwards. The saturated topsoils ensured the large overland flow contribution, despite the SILT/CLAY (S2 Mid, 60 cm) being unsaturated. At Site 4, there was downward infiltration and little change to the heads as a result of the ongoing rain.

T3 marked an increase in head and a switch to saturation conditions in the SILT/CLAY layer at Site 2 (at 60 cm) due to the continued rainfall, although the stream was in recession. The stream chemistry indicated that the proportion of overland flow was reducing in favour of interflow which would be consistent with this finding. The head conditions at Site 4 remained unchanged.

At T4, at Site 2, the matric potential in the SILT/CLAY (S2 Mid, 60 cm) increased to levels higher than that in the topsoil, and the total potential increased higher than ground surface. This increase in head was coincident with an increase in the relative proportion of interflow in the second (and largest) event peak, in comparison with the first peak. Overland flow was still important however, as the rainfall was only just beginning to ease.

By T5 when the rain stopped, the total potential was at its highest in the SILT/CLAY at Site 2 and at Site 4, the head in the SILT/CLAY in the mid-layer (S4 Mid, 75 cm) had started to increase. The chemistry indicated that the interflow contribution to the stream continued to increase. By T6, the stream was in recession. The total potential in the deep CLAY layer at Site 2 (S2 Deep, 120 cm) was higher than ground level, and higher than the mid and upper level soils, suggesting an upward gradient. The heads in the SILT/CLAY and topsoil (S2 Shallow, 20 cm) drained uniformly suggesting they were hydraulically linked and were draining the soil water. The chemistry indicated that at this point interflow was dominant in the stream. The increased interflow was supported by the high head above ground level in the SILT/CLAY layer at Site 4.

There was no overland flow observed at Site 4 during the event (or at any stage during the research), which suggests that the soil was able to accept the infiltrating water and that it either discharged via the soil layers or was recharged to deeper levels. The water level in the piezometer was 4.08 m below ground surface during two site visits on June 9 and 10 (T6+), which indicated that the deeper groundwater was disconnected (Figure 7.7). The increased heads in the CLAY and SILT/CLAY layers during the recession after the peak event (T6+), which caused the total potential of the SILT/CLAY layer to rise above the ground surface, indicated that the deeper soil water had backed up and was likely released slowly during the baseflow period.

Unfortunately, due to the missing matric potential data at the upper levels at Site 1, the full profile assessment is not possible. However, the total potential did increase slightly at 80 cm depth (S1 Deep) at T1–T3 in the early stages of the event, at a time when there was little change at the deeper depths at the other sites. The total potential was also higher than ground surface even before the event began which, when considered with the soil moisture content data, suggests that the soils were likely to have been fully saturated, prior to and throughout the event, at all depths. This scenario presents favourable conditions for the development of overland flow, which would be supported by general observations in the field that the soils at this site were rarely visibly unsaturated. This was in contrast to the heads at the deeper levels at the other sites, which did not breach ground surface until the rain had almost ceased. A relatively large increase in soil moisture content of 1.5% was also recorded in the SILT/CLAY layer, which suggests that it may have been an important water transport layer.

7.4.2 June 14–20 event

At the time the rain commenced (T7) during the second event, the SILT/CLAY layer at Site 2 (S2 Mid, 60 cm) was saturated, the topsoils (S2 Shallow, 20 cm) were unsaturated (Figure 7.21) and there was an upward gradient from the underlying CLAY (S2 Deep, 120 cm), which had a total potential higher than ground level (Figure 7.23). This suggests that, in contrast to prior to the first event, discharge was likely through the SILT/CLAY. This was confirmed by the river chemistry, which indicated that interflow was providing 60% of the flow in the stream at the same time (Table 7.6). At Site 4, the topsoils were also unsaturated (Figure 7.22) and the total potentials in the SILT/CLAY and CLAY were similar and below ground level, suggesting that discharge through the topsoils was an important pathway. As this is also the root zone, however, evapotranspiration was also likely to have been a contributing factor.

During the first flow peak (T8), the chemistry suggested that interflow was the dominant pathway in the stream (50%). As the equivalent peak in the June 7–10 event was dominated by overland flow, the soil moisture data were reviewed to consider why the differences arose. At Site 2, the total potential in the CLAY layer (S2 Deep, 120 cm) were higher than ground level suggesting an upward gradient, but the total potential in the SILT/CLAY (S2 Mid, 60 cm), which was saturated, was low and below ground surface suggesting that it remained an important discharge layer. At this stage during the first event, the SILT/CLAY was still unsaturated. The gradient between the topsoil and the SILT/CLAY layer was also approximately half that observed during the first event. This was because the rainfall leading up to the peak, although greater overall than during the first event at 24 mm versus 16 mm, was less intense (1.4 mm/h in contrast to 3.8 mm/h). The lower

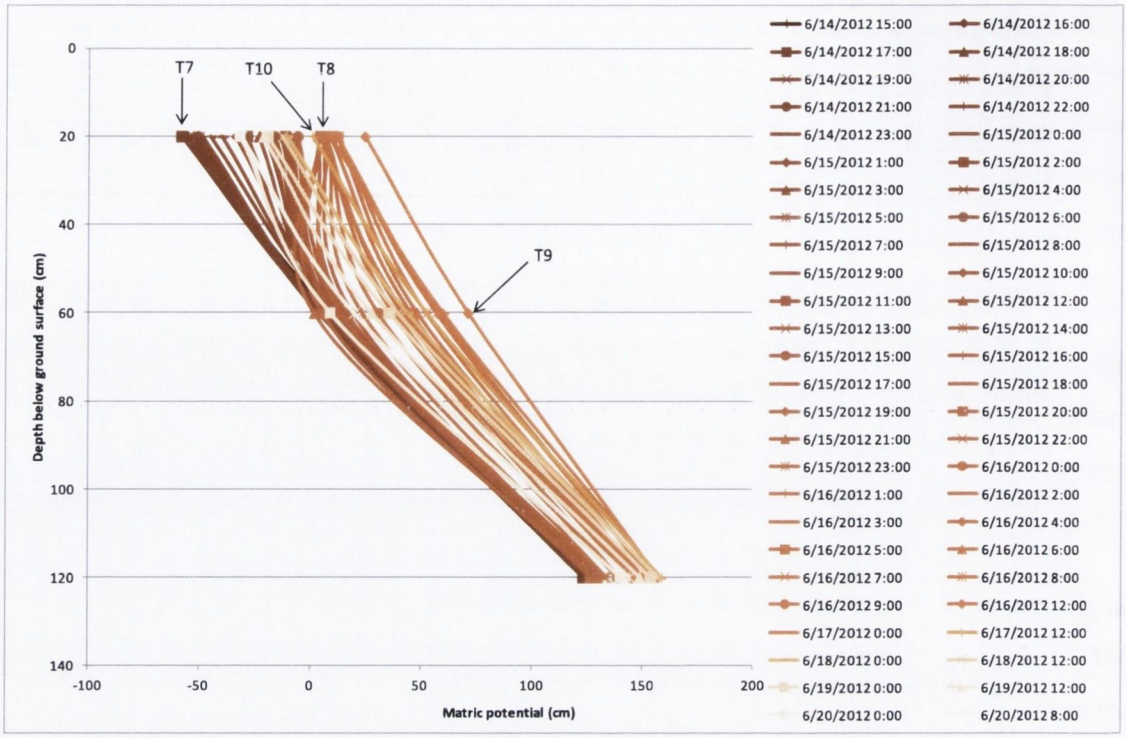

Figure 7.21. Hourly time series of changes in matric potential with depth at Site 2 during the June 14–20 event. Profiles become increasingly lighter in colour with time. Later profiles are every 12 h instead of every hour. Time periods T7–T10 are referred to in Table 7.6. Vertical dashed line, saturation.

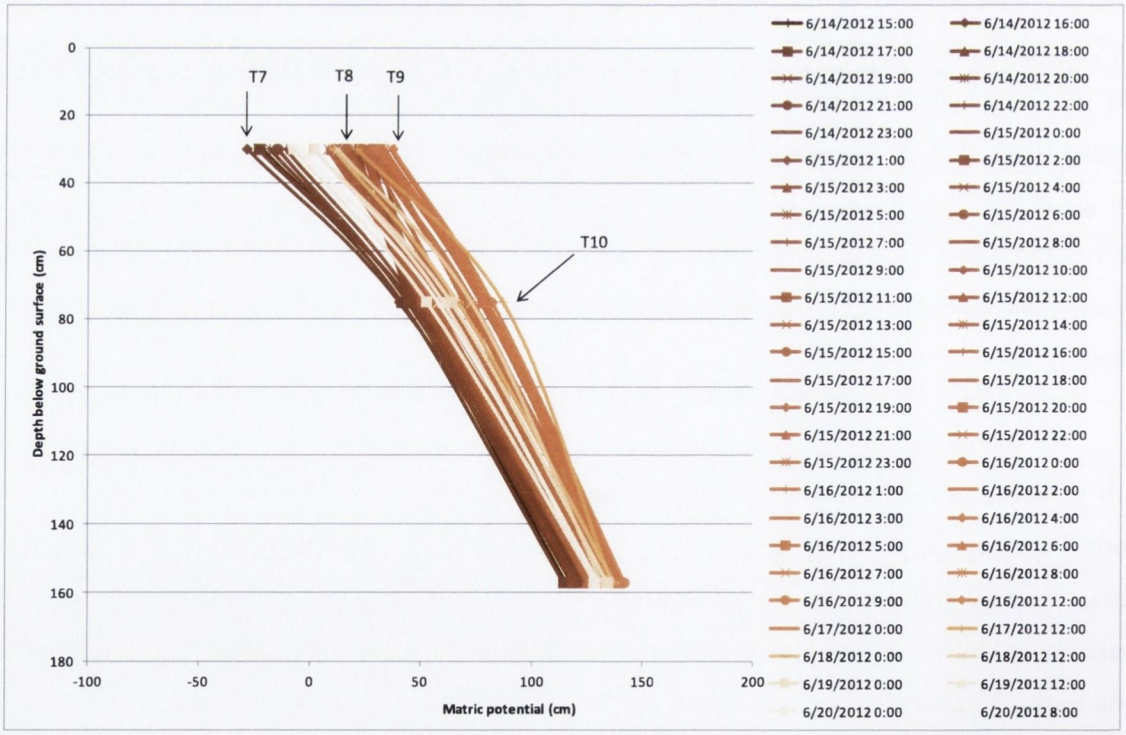

Figure 7.22. Hourly time series of changes in matric potential with depth at Site 4 during the June 14–20 event. Profiles become increasingly lighter in colour with time. Later profiles are every 12 h instead of every hour. Time periods T7–T10 are referred to in Table 7.6. Vertical dashed line, saturation.

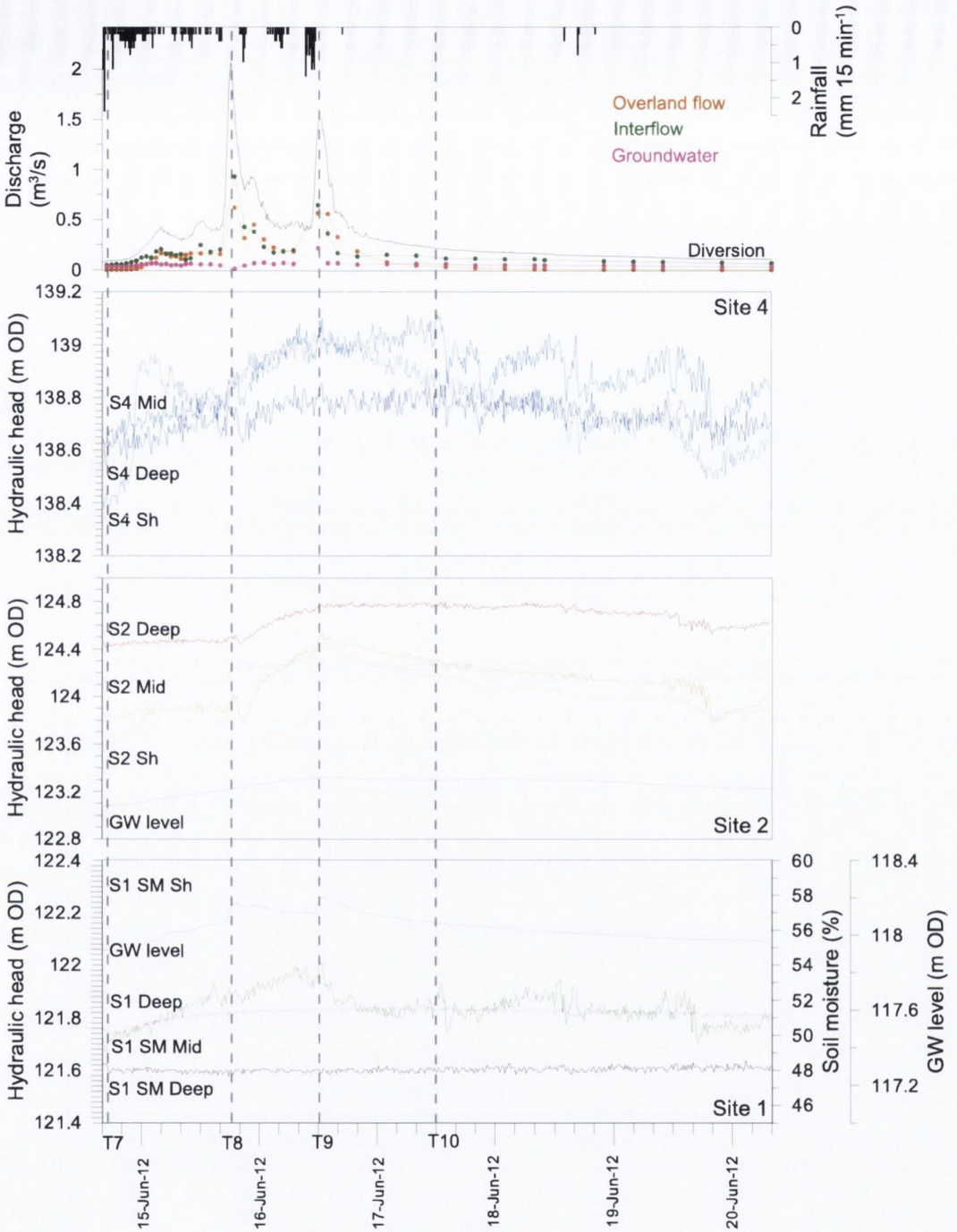

Figure 7.23. Total potentials for Sites 1, 2 and 4, groundwater levels (y-axis), soil moisture (S1 only, y-axis), discharge with pathway contributions, and rainfall during the June 14–20 event. Dashed vertical lines represent specific time periods of interest, T7–T10. Horizontal grey lines represent ground surface. Apparent fluctuations in the total potential data for the soils at Sites 1 and 4 are due to sample noise and are magnified relative to the noise at Site 2 because of the larger scale on the y-axis.

Table 7.6. Summary of key changes in soil moisture dynamics with concurrent stream flow and estimates of the pathways contributing to the flow from the chemical hydrograph separation methods.

ID	Time	Soil water dynamics	Stream flow	Pathways
T7 Rain start	14/6 at 16:15	*Site 2* Topsoils unsaturated. SILT/CLAY saturated in contrast to June 7 event. Total potentials below ground level. Upward gradient from the CLAY. Discharge through the topsoils and SILT/CLAY. *Site 4* Topsoils unsaturated and with the lowest total potential at the site, but wetter antecedent conditions at all depths than first event	Low flow 0.074 m^3/s	IF dominant OF, 0% IF, 60% GW, 40%
T8	15/6 at 18:00	*Site 2* Similar matric potentials at 20 cm and 60 cm suggesting a downward gradient and infiltration. Total potential in SILT/CLAY lower than topsoil or CLAY and below ground surface suggesting that it was an important discharge layer. Downward gradients from topsoil to SILT/CLAY less than during the first event *Site 4* Increase in matric potential at 30 cm. Similar total potentials at 30 cm and 75 cm. Downward gradient and infiltration	First peak flow 2.07 m^3/s	IF dominant in peak flow OF, 39% IF, 50% GW, 11%
T9	16/6 at 12:00	*Site 2* Matric potentials at all levels at their highest during the event. Total potentials all above ground level. Similar heads in the topsoil and SILT/CLAY likely contributed to the similar OF/IF contributions. *Site 4* Matric potential reached highest levels in the topsoils and had a similar total potential as the SILT/CLAY layer, both higher than ground surface	Second peak 1.56 m^3/s	IF still dominant OF, 40% IF, 45% GW, 15%
T10	17/6 at 12:00	*Site 2* Matric potentials decreasing steadily at all levels; topsoil at 20 cm almost at zero tension. Total potential in the topsoil reduced below ground level and remained at the lowest head suggesting it was a likely discharge layer. Total potential in the CLAY layer remained high *Site 4* Higher matric potential in the SILT/CLAY layer which gave rise to the higher total potential above ground surface. Similar pattern as during the first event	Recession	OF reduced, IF and GW increased OF, 16% IF, 57% GW, 27%

OF = overland flow; IF = interflow; GW = groundwater.

intensity rainfall, lower gradients and the saturated SILT/CLAY layer, which would have resulted in higher hydraulic conductivities during the second event, are likely to have been the reasons for the increased relative proportion of interflow.

At Site 4 during the same period (T8), the topsoils became saturated and the total potentials at 30 cm (S4 Shallow) and 75 cm (S4 Mid) increased to similar levels that were higher than the CLAY layer (S4 Deep, 157 cm) but still below ground surface. This indicated that downward gradients and infiltration occurred. It was unlikely therefore that this part of the catchment had any role to play in the generation of the overland flow.

During the second peak (T9), the matric potentials at Site 2 at all levels were at their highest and the total potentials were all above ground level. Similar heads in the topsoil (S2 Shallow, 20 cm) and SILT/CLAY layer (S2 Mid, 60 cm) probably contributed to the similar proportions of overland flow and interflow in the stream. At Site 4, the matric potential in the topsoils (S4 Shallow, 30 cm) was at its highest, but the total potential in the upper two layers was similar, suggesting downward infiltration.

At T10 at Site 4, in a pattern similar to the recession period during the first event, the total potential in the SILT/CLAY layer (S4 Mid, 75 cm) was the highest of the three layers and was above ground level, which could indicate that there was discharge occurring through the topsoil layer that helped sustain the relatively high proportion of interflow (57%) as indicated by the chemistry. Some infiltration to the deeper soils may also have been occurring, but it was likely to have been slow based on the CLAY soil texture. At Site 2, the matric potentials were decreasing steadily at all levels and the topsoil at 20 cm (S2 Shallow) had almost returned to zero tension, which would have been a factor in reducing the overland flow. The total potential in the topsoil reduced below ground level and remained the lowest of all the layers at this site suggesting that it was a likely discharge layer.

7.5 Discussion

7.5.1 Evidence for interflow

This research has found that there is sufficient evidence in the soil water dynamics to consider interflow as an important pathway for the delivery of flow in the Mattock catchment. Rapid changes in soil moisture content, the range of soil moisture at zero tension, and flow in the land drains when there was a soil moisture deficit, all suggest that drainage occurs through macropores and preferential flowpaths. The flux through the soil matrix is otherwise a minor contribution to stream flow. This is consistent with research carried out by Richards et al. (2005)

in an Irish karstified limestone site who noted, using tracers, that there was both rapid breakthrough and slower matrix flow.

Uniform decreases in total potential in the topsoil and SILT/CLAY layers during the recessions, with coincident increases or stable high potentials in the CLAY layer, groundwater fluctuations at depth that do not respond well to rain, and high hydraulic heads in the CLAY layer corroborate the evidence from the trial pits that suggests that the CLAY is an effective barrier to infiltration. The head data at Site 4 suggest that there is some infiltration occurring through the CLAY layer but based on the delayed responses in the piezometer, it is likely to be slow. This is consistent with this subsoil being slightly more dilatant in field tests than the lodgement tills at the other sites. This suggests an interflow mechanism consistent with that described by Ahuja and Ross (1983) of downslope flow in soils above a low permeability layer.

The mid-level SILT/CLAY is a key discharge horizon at Sites 1 and 2. The matric potential in this layer at Site 2 also reaches relatively low levels, which suggests that it is drier for longer than at the other sites. The topsoil appears more important as a discharge layer at Site 4 based on the head data but it must be considered that the instrumentation in the SILT/CLAY layer at Site 4 was installed at 75 cm depth in comparison with 50 cm and 60 cm at Sites 1 and 2, respectively, which may have a bearing on the apparent effectiveness of the SILT/CLAY as a drainage layer. The topsoil is also important at sites lower along the transect when the antecedent conditions are wet and the heads are high. The uniform reduction in heads during recessions in the topsoil and SILT/CLAY layers at Sites 2 and 4 suggest that they drain as single hydraulic units. Therefore, there is evidence from this study that interflow occurs at greater depths in the SILT/CLAY layers (at 60 cm and 75 cm), which are deeper than the key interflow development zones found at 10–45 cm depth in other studies (Tunney et al., 2000, Diamond and Sills, 2001). However, it is likely that the depth at which the drainage system is installed, and the proximity of the sampling site to that drainage system, are likely to be key factors.

7.5.2 Near-surface pathway contributions from different positions in the landscape

On the basis of the available data, it would seem likely that the soil water at Site 4 in the upper catchment played a lesser role in short-term overland flow generation than at Site 2, but contributed more to the longer-term contribution of interflow after the event. This is because the hydraulic heads at all levels remained below the surface for much of the events, and the head in the SILT/CLAY layer remained high long after both events. This is consistent with its location towards the top of the hill.

Site 1 was saturated with relatively high matric and total potentials throughout the events, as expected due to its location towards the bottom of the slope. However, it is anticipated that, because the soils are almost permanently saturated and the heads are frequently higher than ground level, the scope for increased interflow discharge with rainfall at this location is likely to be limited by the hydraulic conductivity, which will already be at its maximum due to the high moisture contents. These soils are likely to be more important as sources of overland flow while delivering a consistent but important background component of interflow.

Site 2 showed the most variability and therefore scope to respond to the rainfall, and it is considered to have had the greatest bearing on the changing interflow dynamics at the scale of the event. This may be a consequence of its position in the landscape, being close enough to the downslope end of the transect to have saturated soils at depth, but not so close that they were permanently saturated. The drainage at the site, which would have facilitated the discharge of the infiltrating water and created a better throughput, is also likely to have played a significant role. It is difficult to comment in detail on the role of the soils at Site 3 as it was artificially dry and there were no head data at depth to compare gradients.

7.5.3 Conditions under which interflow occurs

In general, there was good support from the soil monitoring data for the pathways understanding derived from the chemical hydrograph separations, particularly from the data for Site 2 as described above. A stronger conceptualization of the development of interflow during events was achieved by combining the two approaches.

Peak flows were dominated by overland flow that originated at the surface when the topsoils were saturated, but the relative heads in the different soil layers also played a role. In dry antecedent conditions, the topsoil became saturated while the underlying SILT/CLAY was unsaturated, gradients between the layers were high and the head in the topsoil was higher than ground level. In wetter antecedent conditions, when the heads in the underlying soil layers increased above ground surface, the relative proportion of overland flow decreased in the peak flows due to the increased proportion of interflow. The overland flow contribution still remained high, however, as the soils were fully saturated and the heads in the topsoils were high.

Interflow contributed more to the peak flows in wet antecedent conditions when all heads were higher than ground surface and when the head in the CLAY layers was higher than in the SILT/CLAY and topsoils. Towards the later stages of the events, the topsoils and SILT/CLAYs drained at a similar rate suggesting they acted as a single hydraulic unit.

Diamond and Shanley (1998) suggested that hourly rainfall intensity is a suitable indicator of overland flow. This may be true from a delivery pathway perspective, in that more runoff from the catchment to the stream occurs during heavier rain, but the origin of the water may be predominantly from deeper in the soils than surface water that cannot infiltrate due to topsoil saturation. Although this is not important from a flood risk perspective, it does have implications for nutrient management because nitrate and phosphorus tend to accumulate in different geological horizons, as discussed in Chapters 5 and 6.

Researchers in other countries have found that the initial soil moisture content, i.e. the antecedent conditions, is one of the most important factors dictating stream flow generation processes (Hino et al., 1988, Zehe et al., 2005). Over much of Ireland, the soils and subsoils have been derived from the Lower Palaeozoic rocks and are clayey with low permeability. The Irish climate, with its long-duration, low-intensity rainfall (Rohan, 1986), means that these soils can be almost permanently saturated for significant portions of the year (Diamond and Shanley, 1998), and when they are not, as in the first of the June events analysed in this research, they return to saturated conditions quickly. It was found in the Mattock catchment that the matric potential and hydraulic head data were more useful than the soil moisture content in distinguishing the different pathway responses.

7.5.4 Field capacity, soil moisture deficits and land drain flow

It has become apparent through the course of this research that, as noted by a number of authors (Hillel, 1982, Schulte et al., 2005, Cavazza et al., 2007, Doody et al., 2010), the term field capacity is poorly defined and is used in different ways in the literature. Some take it to be the moisture content at a tension of 0.3 bar (Dingman, 2002); others consider a moisture content at 0.1 bar more appropriate (Haise et al., 1955, Shaw et al., 2011); some regard it as the moisture content 2–3 days after rain or irrigation ceases (Dingman, 2002); and others consider it to be the maximum amount of water that can be stored in the soil when excess water has drained away (Veihmeyer and Hendrickson, 1949), although 'excess' is not defined. These definitions would appear to be inconsistent in the context of the Mattock catchment; for instance, on the basis of the available data, the clayey soils do not drain sufficiently after rain in 2–3 days to reach a tension of 0.3 bar. This is perhaps because the rate of drainage is also affected by other factors not considered in the definitions, such as antecedent moisture conditions, depth to an impermeable layer, type of clays and the presence of organic matter (Hillel, 1982), and because of the low-intensity, long-duration rainfall patterns in Ireland (Rohan, 1986), which maintain saturated conditions for longer. Although the concept of field capacity is useful, it clearly means

different things to different practitioners. It is perhaps a better approach to rely on the soil moisture accounting approach, or the soil moisture characteristic curve.

In this study, the Schulte soil moisture deficit model proved to be a useful tool in broadly categorizing the flows in the Mattock catchment at different moisture levels, particularly as the data are readily available and can be used in ungauged catchments. However, it was found that in this catchment, the land drains still flowed at an SMD of 16 mm, whereas it is an assumption in the model that drainage only occurs when there is zero SMD. This highlights that the model should be used with caution in catchments that have been artificially drained. In addition, the SMD is calculated at a daily time step, whereas the flows in the land drains have been found to change significantly over a matter of hours. This limits the use of the SMD as an accurate predictor of land drain flow, but it nevertheless proved useful within its limitations.

7.5.5 Lessons learned in relation to collection of matric potential data

Collecting continuous matric potential data rather than relying on manual measurements, an approach often used in Irish studies (Gill et al., 2009, Premrov et al., 2010), was critical for analysing data on the scale of rainfall events, but the added complications that arose with the loggers and power supply were disappointing. The complications were accentuated because the 160-m distance between Site 1 and Site 4 was very long in comparison to other studies where tenisometers are more usually placed in a small localized block. For example Diamond and Sills (2001) placed their tensiometers 50 cm apart in rows 70–90 cm apart, and Cuthbert et al. (2010) and Kerebel et al. (2013) had study sites that were <12 m^2 and 10 m^2, respectively. Regrettably, much of the data logged at the lower matric potential levels had to be discarded as they were considered to be unreliable. Lessons learned for future studies include the following:

- Short cable lengths should be maintained, with multiple loggers if necessary.
- Cables should be buried if possible. (This would be more achievable with shorter cable lengths).
- Tensiometer lengths should be kept to a minimum to maintain the highest effective operating limits. Alternative methods could also be considered such as electrical resistance blocks.
- Cheaper loggers should not be favoured over the more reliable brands.
- A trickle charger and large solar panel(s) should be factored into the cost of establishing a site as a necessity.
- During dry summers, the frequency of maintenance visits should be increased to every few days, particularly if the effective limits of the tensiometers are short.

7.5.6 Future research

This aspect of the research has focussed on comparing insights from the soil moisture dynamics with estimates of the pathways contributions from chemical hydrograph separation methods. A strong link between the matric potentials at Site 2 and the pathways derived from the chemistry has been found. It is unfortunate that equivalent soils data for Site 1 were lacking and therefore a comparable assessment of the soils near the river was not possible. Although further sampling is not possible as the sites have to be dismantled shortly by agreement with the landholder, further exploration of the available matric potential data and the spot-sampled chemistry data that have already been collected could be carried out with a view to further analysis of the linkages between these data, both for Site 1 and for all sites in different antecedent conditions.

Additional exploration of the available soil moisture and matric potential data may also reveal further information about other aspects of the role of soil moisture dynamics in stream flow in this catchment, such as the role of the capillary fringe and the groundwater ridging effect (Sklash and Farvolden, 1979, Gillham, 1984, Waswa et al., 2013).

Further analyses to relate reductions in soil moisture drainage to reductions in stream flows at different, especially higher, flow levels would also be useful. The 25/26 March flow event was selected initially because the stream flow reduced to almost zero, which meant that the spatial extent of the land drains and other preferential flowpaths contributing to the flow was at a minimum. Investigations at higher flow levels would have the extra unknown variables of changing spatial extents and efficiencies of the contributing land drains, but it would nevertheless be an interesting exercise. Different methodologies could also be applied, such as use of the Dupuit-Forchheimer equation for estimating unconfined flow (Wooding and Chapman, 1966), and use of a local value for unsaturated soil permeability that could be estimated using the Brooks-Corey empirical relationship derived from the soil moisture characteristic (Milly, 1987).

This research was focussed on a hillslope which had been artificially drained and the results have demonstrated that the interflow pathway contributions are heavily influenced by the artificial land drainage network. It would provide an interesting contrast if the experiment could be replicated in two adjacent fields with the same geological characteristics, but where one was drained and the other was not. In practice, as was found in the Gortinlieve catchment, where land drains are not present in these poorly drained conditions, the soils and subsoils quickly fill to capacity and water is discharged at the surface as return flow. Interflow is more likely to be significant in hydrological events where there is a land drain (or the transition zone) present to speed up the lateral transport processes.

It is acknowledged that a large number of replicates are required in soil moisture flux studies before assumptions can be made about representivity and capturing the degree of variability (Western et al., 1998). With the limited infrastructure used in this research, it is unlikely that these requirements have been satisfied. The installation did have utility, however, in adding confidence to the hydrograph separation methods and it has provided useful information to further the development of the conceptual model. Perhaps its greatest strength is as an indicator of when and how the soil moisture changed in different parts of the catchment with different hydro(geo)logical regimes, and in different geological units. In particular, it has provided insights into the mechanisms driving interflow in this catchment and the influence of artificial drainage. Further discussion on the role of artificial drainage is provided in Chapter 8.

8 The role of artificial drainage

8.1 Introduction

From the literature review (Section 2.7), it was identified that there was a need to understand better the role of artificial drainage as a pathway in the delivery of flow and nutrients to streams. It was highlighted that this should be carried out on drainage systems on working farms in their current state, so that their likely current impacts on the nutrient dynamics in streams could be assessed. To this end, a sampling campaign was carried out in land drains and ditches in the Mattock catchment to complement the chemical hydrograph separation (Chapter 6) and soil water dynamics (Chapter 7) studies. A variety of land drains and ditches were sampled around the catchment, with a focus on the soil water dynamics site, to determine the spatial and temporal variability in chemistry and nutrient concentrations in the drainage system, and understand their relationships with the hydrogeological setting.

For the purposes of this research, land drain is the term given to describe buried subsurface in-field drains that are constructed with pipes or stones; they are often called tile drains or pipe drains (Figure 8.1). Artificially constructed open channels located around field boundaries, which may be ephemeral or permanent, are termed ditches. These are also known as dykes by the farming community. They are distinguishable from natural tributaries because the fields they bound have a regular shape and it is evident from the topographic maps that they were constructed around the fields, rather than the other way around (Figure 8.1).

Figure 8.1. Typical land drain (left) and ditch (right), Gortinlieve catchment.

8.2 Characteristics of the land drains sampled

Eight land drains were sampled regularly. Four drained the same two interconnected fields in which the soil water dynamics transect was located (Figure 8.2): one was located in the upper part of the hillslope (LD Hill), one was in the mid-slope area (LD Forest), and two were located in the lower hillslope adjacent to the stream (LD S1, LD Usual). This ensured the following:

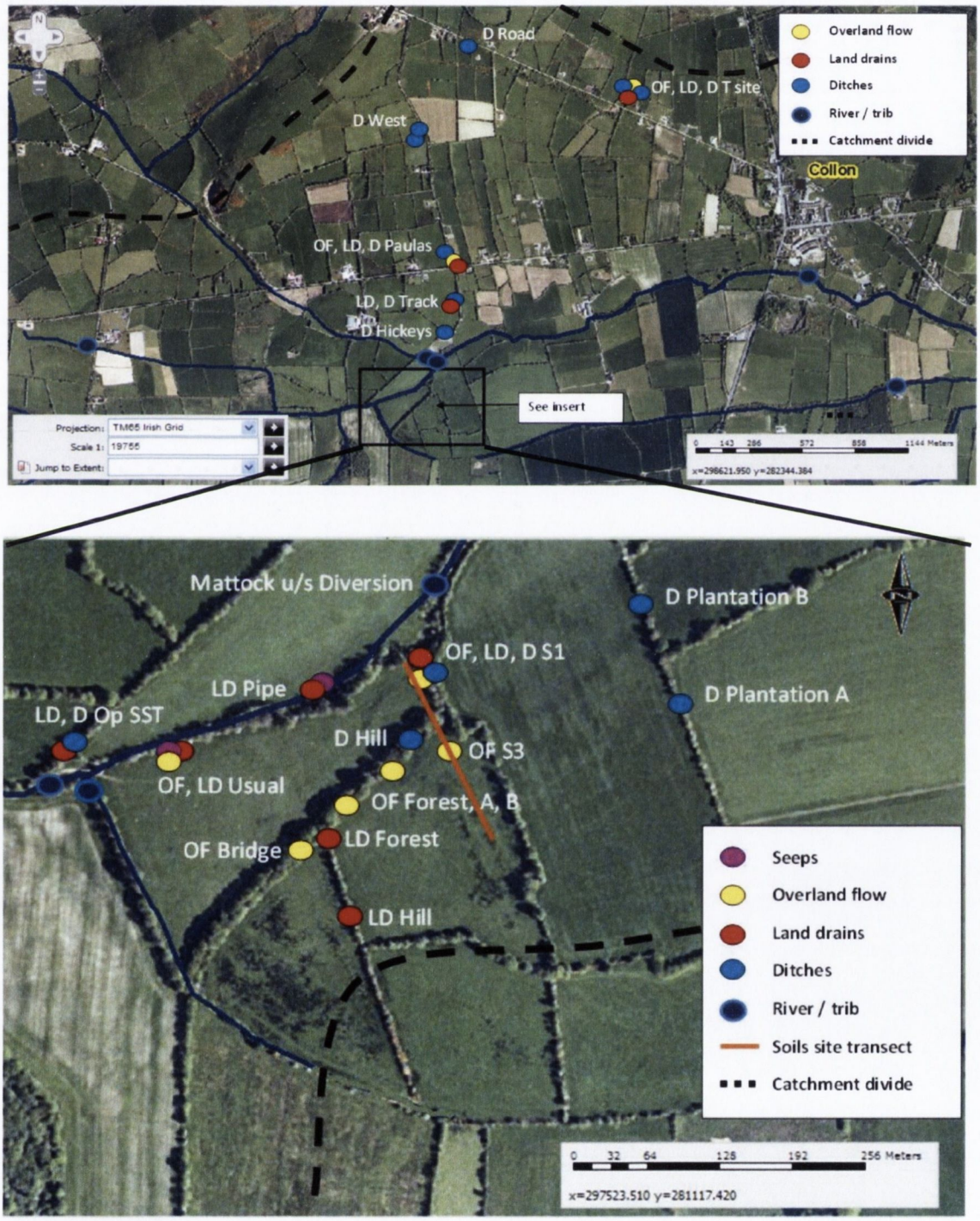

Figure 8.2. Artificial drainage sampling sites. OF = overland flow; LD = land drain; D = ditch. The Collon flow monitoring site is indicated by the blue circle located in the river to the south of the village.

(a) that findings from the soil water dynamics site would be comparable;

(b) that a range of hydrogeological regimes were being sampled, including the upper, mid and lower hillslopes; and

(c) that all four land drains would be under the same land-use regime so that potential biases due to different nutrient management practices could be eliminated.

Four additional sites in equivalent landscape positions but on a larger scale (LD T Site, LD Track, LD Pipe, LD Opp SST) were included from the northern side of the Mattock catchment to bring a comparative spatial aspect to the research. LD Pipe, LD Forest, LD Opp SST and LD T Site were added later in the project and so have fewer available data, and LD Paulas was covered over in drainage works and so became inaccessible early in the project.

8.2.1 Construction

The drains were typically of clay pipe construction, which were commonly found in all the study catchments (Figure 8.3). There were no pipes evident at three of the sites, although pipes may have been present but hidden from view, and flow discharged through a bed of stones or a soil cavity. LD Track flowed through a 12-inch concrete culvert pipe buried into the hillslope, which was likely to have been just a protective cover. With the exception of LD Usual and LD Pipe, which discharged directly into the stream channel, all land drains were connected to the stream via field boundary ditches.

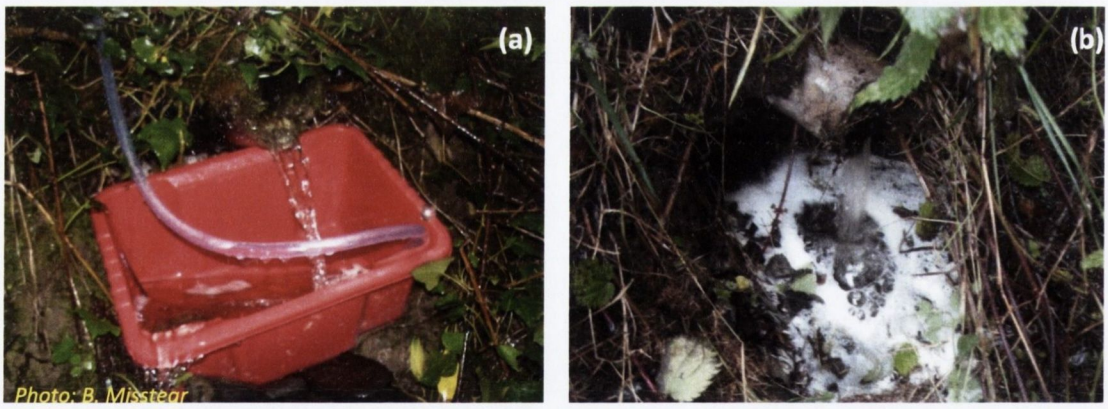

Figure 8.3. (a) LD S1, collection of samples with the autosampler. (b) LD Hill.

8.2.2 Drainage problem

Five of the drains were located in areas identified on the GSI maps as having thick low permeability tills >5 m, which suggests that they were installed to alleviate a surface water drainage problem in the soils and subsoils. In contrast, three of the drains were located in areas where rock was close to the surface and therefore high water tables overlying the poorly productive rocks were considered likely. The origin of the land drain water is discussed further in Section 8.3.1. Table 8.1 summarizes the characteristics of the eight land drains.

Table 8.1. Characteristics of the monitored land drains.

Land drain name	Landscape position	Construction	Hydrogeological setting	Mean flow* (l/s)	Max flow (l/s)
Southern catchment					
LD Hill	Upper slope	2 inch clay pipe	Low K soil and till, >10 m	0.03	0.14
LD Forest	Mid slope	2 inch clay pipe	Low K soil and till, >10 m	0.02	0.05
LD S1	Lower slope	4 inch clay pipe	Alluvium over low K till, 8 m	0.12	0.75
LD Usual	Lower slope	Stones, no pipe visible	DTB <3 m	0.14	0.5
Northern catchment					
LD T Site	Upper slope	Stones, no pipe visible	Low K soil and till, 5–10 m	n/a	n/a
LD Track	Mid slope	12 inch concrete, likely to be a protective cover	DTB <2 m	0.07	0.32
LD Opp SST	Lower slope	Soil cavity	Low K soil and till, 5–10 m	n/a	n/a
LD Pipe	Lower slope	2 inch plastic perforated pipe	DTB <2 m	0.02	0.05

*Mean flow does not include zero flows. K = permeability; DTB = depth to bedrock. Flows could not be measured effectively at two of the drains due to their construction.

8.2.3 Land drain flow

The flows in the drains varied over five orders of magnitude from zero to 0.8 l/s (Table 8.1). The highest flows were measured at LD S1 on 25 October 2011, the day after the heaviest rainfall event during the project, when 47 mm of rain fell in the catchment over 11 hours. This event was a 1 in 20–25 year event for daily rainfall in Dublin, but was a 1 in 80 year event with respect to rainfall intensity (MacCarthaigh, 2011). The measured flow is therefore likely to be towards the upper end of the likely flow range of the land drains monitored. (Further discussion on land drain flow in relation to soil moisture content, matric potential and soil moisture deficits was provided in Sections 7.3.1.4 and 7.3.1.5).

8.3 Land drain chemistry

8.3.1 Origin of the land drain waters

During the chemical hydrograph separation exercise, it was determined that the silica and SAC of the land drain waters varied widely (Figure 6.1). There were some land drains that appeared similar to overland flow (high SAC, low Si), some that were more like bedrock groundwater (low SAC, high Si), and some that were more uniquely a subsoil signature (low SAC, low Si). Review of the data for individual land drains revealed that each drain had its own distinct signature (Figure 8.4), and that all land drains could be loosely grouped into four different categories reflecting the origin of the waters they drain. For instance, LD Hill and LD Forest were typically more closely aligned with the signature of overland flow. Their mean electrical conductivity values of approximately 240 µS/cm and their locations in organic soils in the upper and mid-slope areas, respectively, suggest that they drain rainwater infiltrating from the surface. In contrast, LD Pipe has a much higher mean conductivity (>400 µS/cm), high Si and low SAC which is a signature more

closely linked to bedrock groundwater. This land drain is located in the lower slope area where rock is close to the surface and it is likely that it drains shallow groundwater. During a rainfall event in March 2013, however, the Si was significantly reduced and the SAC increased, suggesting that infiltration from the soils and subsoils is also a factor in wet weather.

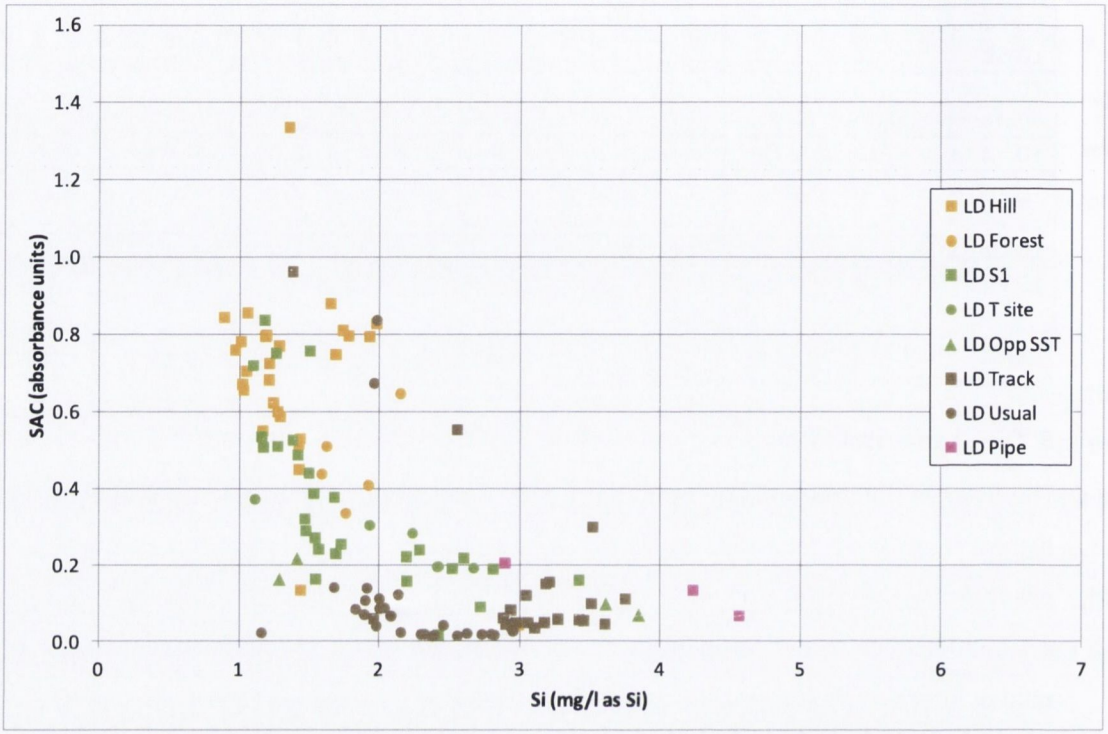

Figure 8.4. Mixing model using the end member tracers to identify the origins of the land drain flow. Orange = upper soils; green = soils and subsoils; brown = transition zone from surface infiltration; pink = transition zone from groundwater upwelling. Symbol shape designates the relative importance of the land drain for delivery of flow in each category: square = highest flow; circle = medium flow; triangle = lowest flows. Refer to Figures 6.1 and 6.2 for comparison with the other end members and the river.

LD Track and LD Usual are both also located in places where rock is close to the surface, but they are higher up in the landscape; LD Usual is at a higher elevation than LD Pipe and LD Track is at a break in slope but is still some distance from the river. The chemistry at these sites is still relatively high in Si, but low in SAC and low in electrical conductivity, suggesting relatively short residence times with some filtration of the organic matter. It is considered likely that these land drains drain the transition zone. LD S1, LD Opp SST and LD T Site show the signature of the subsoil although, in this category, there is still a relatively wide variation reflecting their different positions in the landscape and the variability with antecedent conditions. The average chemistry of the land drains in their four categories is summarized in Table 8.2.

Table 8.2. Average chemical characteristics of the eight regularly monitored land drains.

Land drain	EC	Si as Si	SAC	NO_3 as N	SRP as P	NO_3 load	SRP load	Origin (interpreted)
	µS/cm	mg/l	Abs units	mg/l	mg/l	mg/s	mg/s	
LD Forest	241	1.86	0.469	1.2	0.022	0.057	0.001	Soils
LD Hill	246	1.40	0.690	0.5	0.013	0.018	5×10^{-4}	Soils
LD S1	135	1.81	0.362	0.5	0.015	0.069	0.002	Subs
LD Opp SST	236	2.54	0.138	0.1	0.014	n/a	n/a	Subs
LD T site	263	2.13	0.258	0.2	0.035	n/a	n/a	Subs
LD Usual	83	2.20	0.110	1.1	0.014	0.430	4×10^{-4}	TZ/Subs
LD Track	167	3.03	0.145	3.5	0.016	0.570	0.002	TZ/Subs
LD Pipe	409	4.00	0.136	0.2	0.003	0.006	7×10^{-5}	TZ/GW

EC, electrical conductivity; SAC, spectral absorbance coefficient; TZ, transition zone; Subs, subsoils

8.3.2 Nutrient delivery

Nitrate and soluble reactive phosphorus (SRP) levels in the land drains were typically relatively low, with median concentrations across all measured land drains of 0.67 mg/l as N and 0.008 mg/l as PO_4, respectively, although there were high SRP levels at almost all sites on occasion (Figure 8.5). There were some differences between the individual land drain sites, however. Comparison of the four southern land drains, which were subject to the same relatively low pressure land use and fertilizer application regimes, suggests that the origin of the water being drained was an important factor in the delivery of nitrate. LD Usual, which drains the transition zone, had consistently higher nitrate than the other sites draining the soils, subsoils and groundwater. The median values of SRP were typically low across the four sites, which likely reflects the low intensity land use in these fields. LD Forest often had higher levels of nitrate and SRP than the other three sites, which may be due to its location near a highly trafficked crossing point between the two fields.

On the northern side of the catchment, very high levels of nitrate (up to almost 20 mg/l as N) were observed in LD Track suggesting that a nearby contamination source was likely. High SRP concentrations were not observed, but nitrate and SRP loads increased together with increases in flow (R^2 = 0.93). This land drain is located 120 m downgradient of a row of four single dwelling houses with domestic waste water treatment systems, and a farmyard across the road. Review of the County Council planning files revealed that at least one of these has a secondary treatment system; these are known to be less efficient in the removal of nitrate than phosphorus (Gill et al., 2009). It is hypothesized that nitrate from these sources infiltrated to the shallow bedrock / transition zone, from where it was transported laterally and collected in the land drain which is located immediately downgradient, at the break in slope.

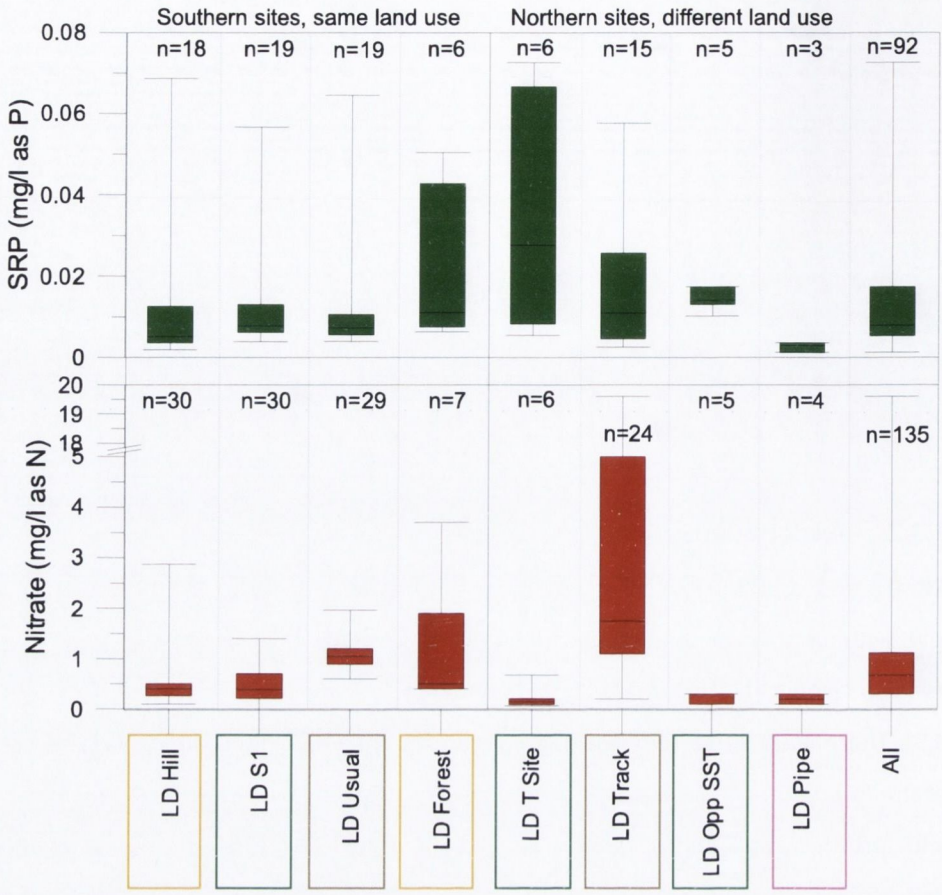

Figure 8.5. Nitrate and soluble reactive phosphorus (SRP) in the land drains. Note the break in the y-axis for nitrate. Coloured boxes on the x-axis represent the origin of the water as per Table 8.2.

For the remainder of the sites on the northern side, nitrate values were very low at the two subsoil land drains (LD T Site and LD Opp SST), and at LD Pipe, the groundwater drain, which was especially low in both nutrients. SRP was high at the subsoil LD T Site, but not at LD Opp SST. Although the sample size was similar, the samples were taken at different times; the higher SRP values at LD T Site were taken during rain events, whereas the LD Opp SST samples were taken during recessions, which may be the reason for the differences.

8.3.3 Nutrient changes with flow

The concentrations of SRP (Figure 8.6) and nitrate (Figure 8.7) in the land drains increased when the saturated/unsaturated flow threshold of 0.025 l/s, as illustrated in Figure 7.14 (Section 7.3.1.5), was exceeded, although it was apparent that some land drains provided higher proportions of the load than others.

SRP concentrations increased dramatically with flow in the soil and subsoil land drains, and in LD Track (transition zone), but not in LD Pipe (GW). There were few flow data available for LD Usual

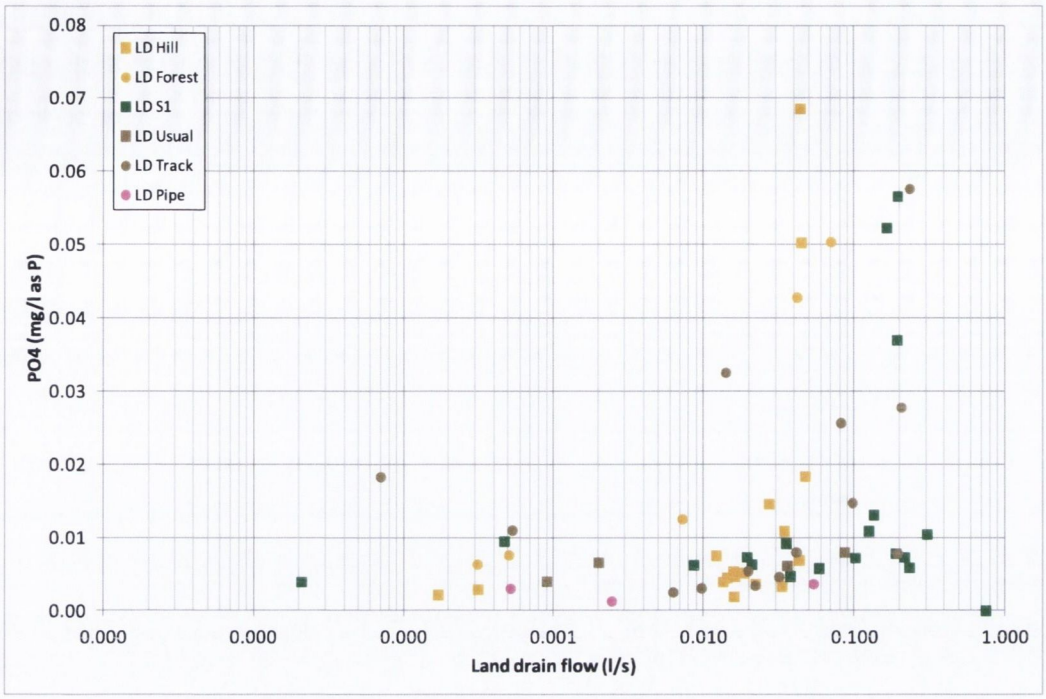

Figure 8.6. SRP concentrations in land drains at different flow levels. Note the log scale on the x-axis. Red dashed line indicates the 0.025 l/s saturated/unsaturated flow threshold illustrated in Figure 7.14.

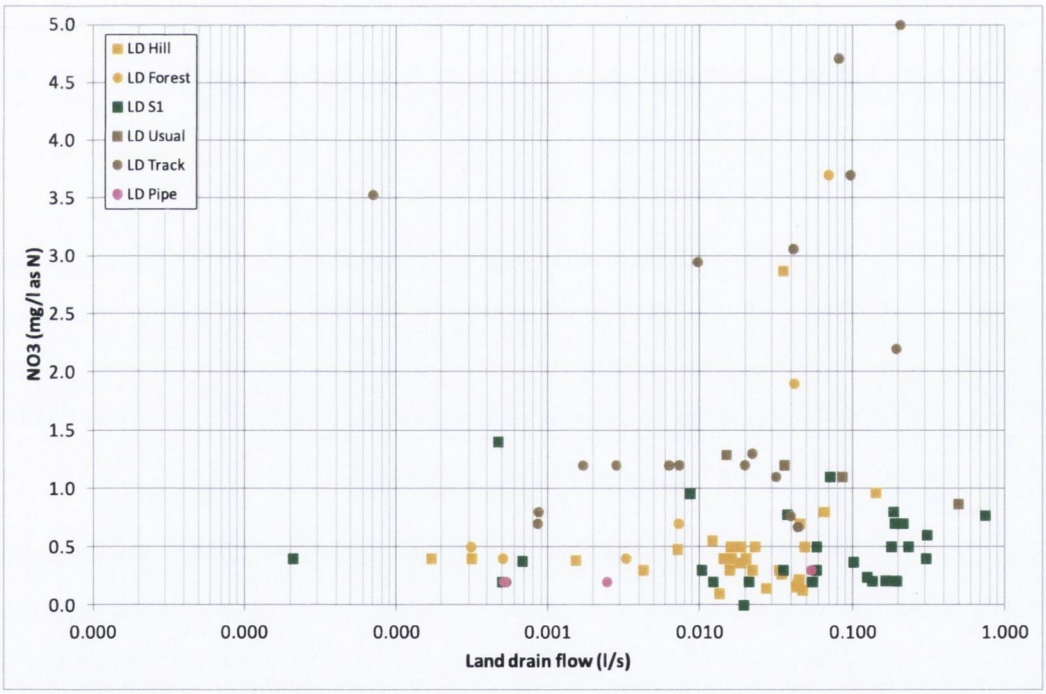

Figure 8.7. Nitrate concentrations in land drains at different flow levels. Note the log scale on the x-axis. Red dashed line indicates the 0.025 l/s saturated/unsaturated flow threshold illustrated in Figure 7.14.

(transition zone) but it is clear from the chemistry data for sampling dates when flows in other land drains were high, that SRP did increase with flow. This suggests that the saturation of the soils had a significant impact on SRP delivery. The source of SRP was likely to be an influx of nutrients from the upper soils through macropores in the deeper soils and subsoils during wetter conditions, because it is known that much of phosphorus is bound in the upper soil horizons

(Sharpley et al., 1996, Tunney et al., 2000). The absence of high SRP at high flows in the groundwater land drain may be due to a piston effect in the groundwater discharge zone where the water being discharged is not directly linked to the nutrient source at the scale of the event. However, there are few data available for the groundwater pathway, so it is difficult to be definitive.

The greatest increases in nitrate with flow (Figure 8.7) were in LD Track (transition zone), which appears to be affected by domestic waste water treatment plants, and LD Forest, which is derived from the soils but may be being affected by increased loads in the heavily trafficked area between fields, although admittedly there were only two relatively high values. This suggests that rainfall had flushed stores of nitrate from within the soil horizons. This would be consistent with the finding in Chapter 5 (Section 5.1.5) that there were significant stores of nitrate in the subsoil boreholes. Similar flushing effects were observed by Schilling and Helmers (2008) who likened the delivery of nutrients in tile drains to that of a karst system, with nitrate being delivered with the diffuse flow and phosphorus via the conduits. In the intervening periods between rainfall events, denitrification may be a contributing factor in keeping nitrate levels reduced overall in the poorly drained and frequently saturated soils and subsoils, because the sources of carbon (and hence electrons) in the water infiltrating from the surface should present favourable conditions for denitrification to occur (Jahangir et al., 2012).

The data indicate that there are strong positive power law relationships between land drain flow and nitrate load (R^2 = 0.84), and SRP load (R^2 = 0.85) (Figure 8.8). The relationships improve further when the land drains are considered separately, but even as a group, the relationships are still strong. This is despite the influence of the small point source at LD Track (R^2 = 0.92), which would have been expected to be diluted in high flows because it is a point source. Further discussion on small point sources is provided in Section 8.7.3.

These results support the findings in Chapter 5 that the transition zone is a key pathway for the transport and delivery of nutrients, particularly nitrate. The land drains draining infiltrating surface water were found to be generally relatively low in nitrate, except in areas where there was a higher input load (e.g. LD Forest), but nitrate increased with flow during rainfall events. These land drains were also high in SRP during rain events. This is consistent with infiltration of nutrients through macropores in wetter weather but removal of much of the nitrate in these poorly drained soils through plant uptake and denitrification. There is reasonable evidence to suggest from the land drain data, therefore, that the type of drainage has a bearing on the likely potential for nutrient delivery.

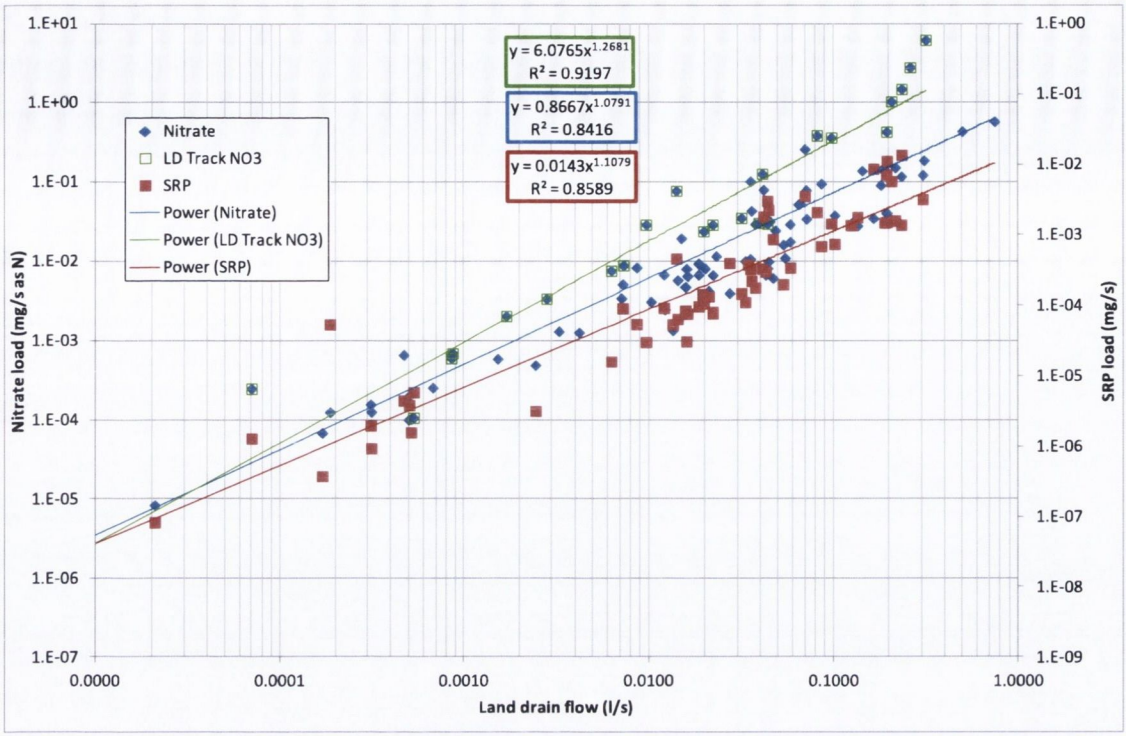

Figure 8.8. Increases in nitrate and SRP loads with flow in all land drains. Trend lines indicate the strong power law relationships across all land drain types. Nitrate loads in LD Track, which are suspected to be affected by domestic waste water treatment systems, are highlighted separately to indicate their high contributions to the load.

8.4 Contribution from the ditches

8.4.1 Introduction

Ten ditches around the catchment were visited regularly during the study period, although some flowed more regularly than others so the sample frequencies are not the same. The majority of the ditches selected were also the receiving waters for the land drains that were sampled (hence the similarity in the names), which facilitated comparison of different delivery mechanisms at the same sites. Overland flow was also collected at two of these paired sites and the data are included in the comparative analysis in Section 8.4.3. Flows in the ditches were not measured.

8.4.2 Origin of the ditch waters

Signatures of waters from different origins were also evident in the ditches, and it was possible to differentiate them on the same basis as the land drains into waters predominantly from the soils, subsoils, transition zone and groundwater (Table 8.3, Figure 8.9). In general, the ditches draining the shallow soils and subsoils (D Hill and D S1) had the lowest electrical conductivity values, indicating the shortest residence times, and they ceased to flow first in dry periods. For example, D Hill was located in the upper catchment area and consequently rarely flowed, which resulted in just three samples being taken. When it did flow, the average conductivity was just 96 µS/cm [73–108 µS/cm], which indicates that it was supplied predominantly by overland flow and soil water.

In contrast, and as would be expected, ditches that were supplied by groundwater sources with longer residence times had the highest electrical conductivity values (>400 µS/cm on occasion) and remained flowing the longest. For example, D Hickeys and D Track were the only ditches still flowing in July 2013.

Table 8.3. Average chemical characteristics of the regularly monitored ditches. The standard deviation is given in brackets.

Ditch	Number samples	EC uS/cm	Si mg/l Si	SAC Abs units	NO3 mg/l as N	SRP mg/l as P	Origin
D Hill	3	96 (20)	1.2 (0.7)	0.670 (0.043)	1.3 (0.4)	0.088 (0.003)	Soils
D S1	26	174 (53)	2.0 (1.0)	0.567 (0.224)	0.7 (0.4)	0.021 (0.017)	Soils
D T Site	10	191 (79)	1.8 (0.6)	0.377 (0.111)	0.4 (0.3)	0.038 (0.013)	Subsoils
D West	6	209 (78)	2.7 (0.7)	0.245 (0.135)	0.4 (0.1)	0.043 (0.010)	Subsoils
D Plantation	7	215 (67)	2.8 (0.7)	0.448 (0.205)	1.0 (0.8)	0.023 (0.015)	Subsoils
D Opp SST	6	351 (108)	2.4 (1.2)	0.319 (0.121)	0.8 (0.6)	0.039 (0.013)	Subsoils
D Road	10	356 (39)	2.8 (0.4)	0.062 (0.059)	8.9 (5.5)	0.007 (0.003)	TZ/Subs
D Paulas	7	313 (111)	4.8 (2.1)	0.248 (0.223)	1.1 (0.3)	0.065 (0.025)	Groundwater
D Hickeys	25	341 (72)	3.7 (1.1)	0.246 (0.215)	3.4 (1.5)	0.081 (0.107)	Groundwater
D Track	25	349 (112)	4.3 (1.6)	0.268 (0.256)	2.0 (0.7)	0.063 (0.024)	Groundwater

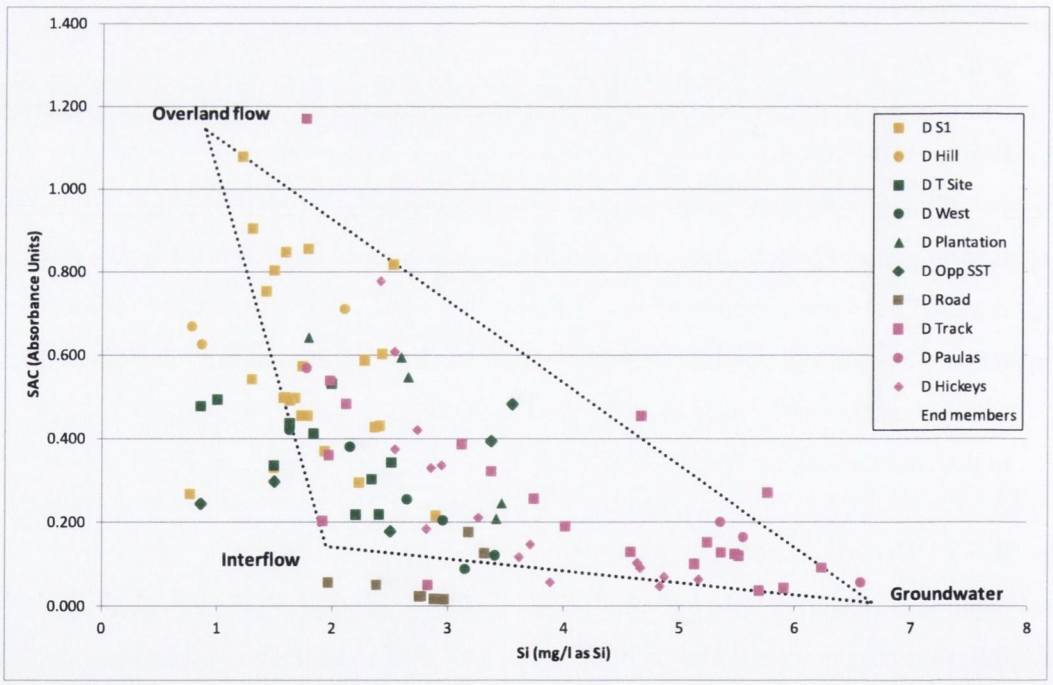

Figure 8.9. Signatures of the water sampled from the ditches. The river mixing model triangle is also included for reference. Pink ditches originate from sources dominated by groundwater; green from subsoils, and orange from soils. Note the degree of overlap in the ditch chemistries in the interflow region of the mixing triangle.

The temporal changes in ditch chemistry were much greater than in the land drains, which meant there was significant overlap in their signatures using the end member tracers (Figure 8.9), particularly in the interflow region of the triangle. This is because during rainfall events, the

ditches collect water from different pathways as they traverse the landscape on their way to the stream. For example, the temporal variations in chemistry of the water in D Track are shown in Figure 8.10. During dry conditions, the ditch had a signature very close to that of the bedrock groundwater. In wetter antecedent conditions, there was an influx of water from LD Track, which is supplied by the transition zone, as well interflow and overland flow sources. This resulted in mixed water with a signature that was as dilute as overland flow on occasion.

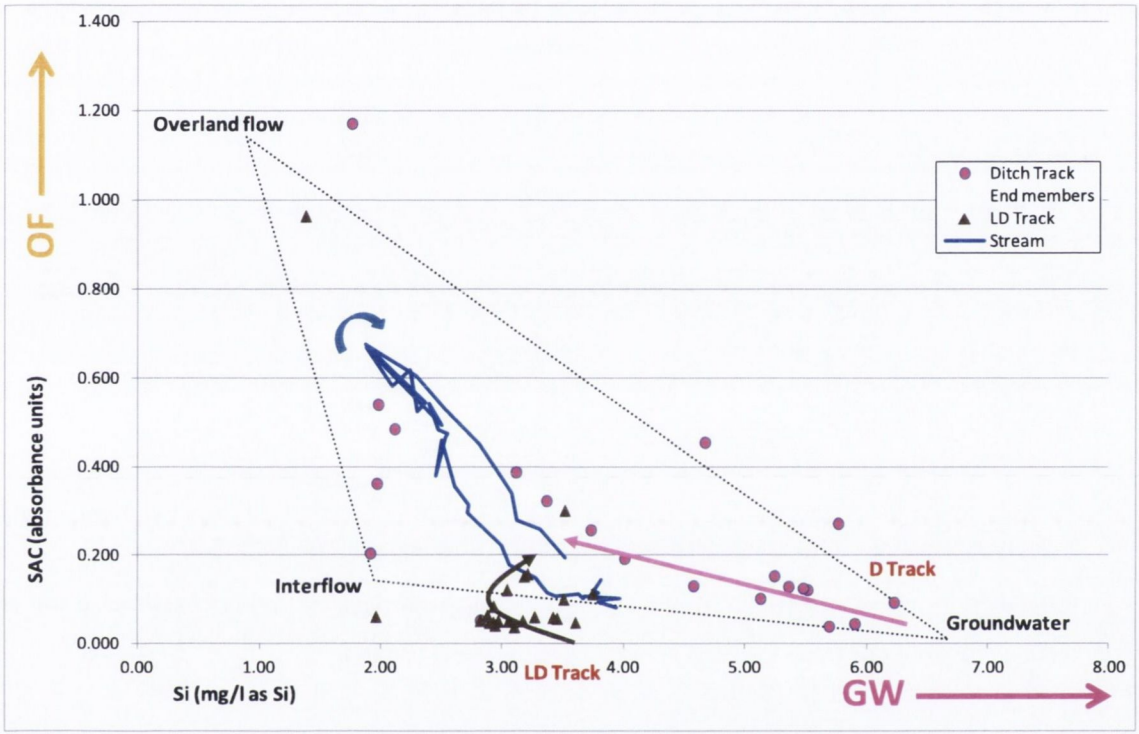

Figure 8.10. Evolution of the chemistry of the water in Ditch Track. In dry antecedent conditions, the water is predominantly of groundwater origin. In wetter conditions, LD Track (transition zone) flows into the ditch, where it, and other dispersed sources of water from the soils and subsoils, dilute the ditch water. The influence of overland flow is also evident at other times. The progression of the stream chemistry at the catchment outlet and the end member mixing triangle are also shown for reference.

8.4.3 Nutrient delivery

There were large variations in nutrient concentrations in the ditches; nitrate ranged from close to zero to more than 22 mg/l as N, whereas SRP concentrations ranged from 0.004 to 0.35 mg/l as P. Similar to the land drains, however, there were trends in individual ditches that were consistent with the origin of the waters supplying them (Figure 8.11).

In the soil and subsoil ditches, nitrate was typically low at <2 mg/l as N, and SRP was consistently between 0.01 and 0.06 mg/l as P, except in the small number of samples from D Hill where it was much higher. As mentioned above, this ditch rarely flowed and when it did, it was mostly supplied by overland flow from the upper catchment area, which would have delivered SRP from the

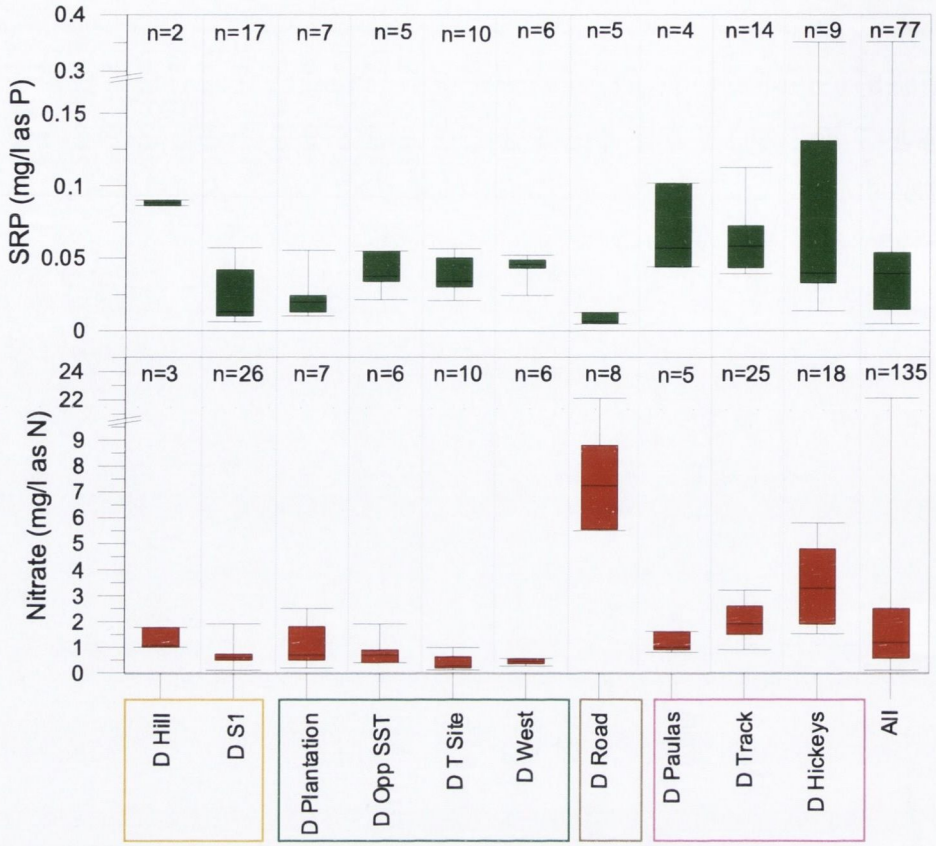

Figure 8.11. Nitrate and soluble reactive phosphorus (SRP) in the ditches. Note the break in the y-axes. Coloured squares on the x-axis represent the origin of the water as per Table 8.3.

surface. In addition, the ditch was shallow and in the shade, and was accessible to the sheep so they congregated there on occasion, hence increasing the load.

In D Road in the transition zone, nitrate concentrations were very high but SRP was very low. This site is located in the upper catchment area on the northern side of the catchment, in the vicinity of a number of houses with older style septic tanks and newer package treatment plants. Samples were taken in the ditches on both sides of the road at this site and combined to reduce the likelihood of sampling a direct discharge but both sides were similar. It is considered likely that this site operates in a manner similar to LD Track and transports effluent that has collected at the top of the bedrock that is washed through with rain.

The three ditches fed by groundwater were all typically higher in nutrients than the others. D Paulas is a road-side ditch which is upstream of, and flows into, D Track, and it may be being influenced by the domestic waste water treatment units from the houses located along the road. Nitrate concentrations are slightly higher in D Track suggesting there may be general increases in diffuse nitrate concentrations moving downgradient, but the SRP was reasonably similar. D Hickeys is located adjacent to, but slightly downstream of, a farmyard and is almost certainly being affected by farmyard activities. The highest concentration of SRP of all sampling sites was

measured in this ditch at the end of September 2012, following the first major rainfall event after the summer suggesting that there was a first flush effect from the yard. The water quality observed in the three groundwater-fed ditches may therefore reflect impacts from small point sources. It is unclear whether this is as a result of direct discharge pipes, which could be remediated to improve water quality, or whether, being relatively permanent, the ditches discharge more widely spread diffuse contaminants from these and other sources. Stream and ditch profiling from other parts of the catchment suggest that it is likely to be both (Finn, 2012).

8.4.4 Comparison of nutrient delivery from ditches and land drains

Comparison of the median land drain and ditch water quality at five paired sites shows that the water quality in the ditches was always poorer than in their associated land drains, for both nutrients (Figure 8.12). Overland flow at the two paired sites where it was also sampled (and in other locations where it was sampled – not shown) was lower in nitrate and higher in SRP than either the land drain or the ditch, except D Hill where the SRP was very high as discussed above but there were a limited number of samples. As expected, this highlights that the SRP is from the upper soils, whereas nitrate is primarily from subsurface pathways.

On occasion, SRP concentrations were higher than the 0.035 mg/l as P threshold limit, which represents the boundary between Good and Moderate status, in all land drains except LD Forest and LD Opp SST. These land drains had the smallest number of samples and SRP spikes may simply have been missed. Median SRP concentrations were >0.035 mg/l as P in 7 of the 10 ditches. Nitrate was generally only higher than the interim surrogate level of 1.8 mg/l as N in land drains and ditches supplied by the transition zone or groundwater. This highlights that the artificial drainage network is an important contributor of nutrients to the stream, both from diffuse sources and small point sources.

8.5 Responses in the river

The river flows, and nutrient concentrations and loads, under each of the three land drain flow scenarios described in Section 7.3.1.5, i.e. land drains dry (SMD >16 mm/d), unsaturated flow (SMD 0–16 mm/d) and saturated flow (SMD <0), were reviewed to determine whether there were any significant associated changes in the river that might be attributed to changes in land drain contributions.

8.5.1 Flow

The daily flow data for Collon (Figure 8.13, refer to Figure 8.2 for the location of the gauge within the catchment) show that there also appeared to be equivalent flow thresholds in the river. When the land drains were dry, the flow in the river was typically <0.07 m^3/s. When the land drains were

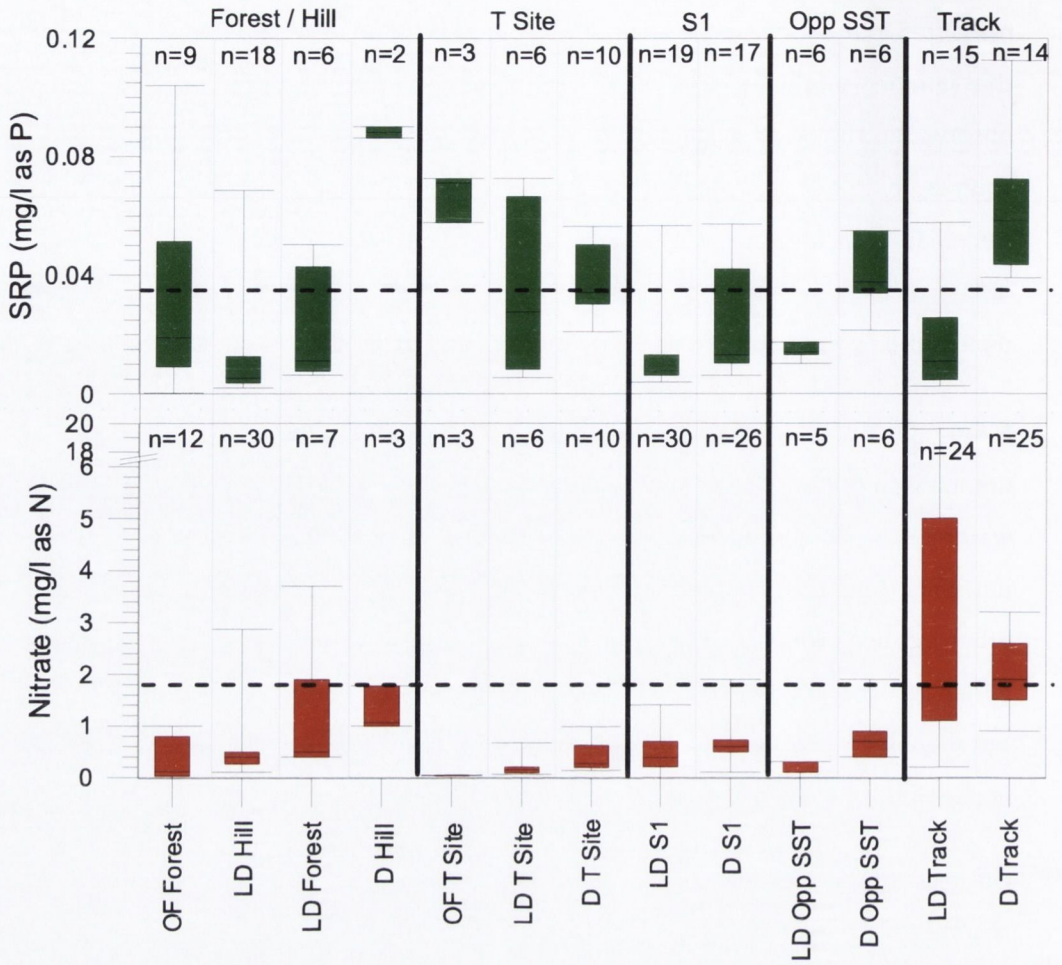

Figure 8.12. Comparison of nitrate and SRP concentrations in pairs of ditches and land drains, i.e. at the same location, with overland flow where measured. Note the concentrations of both nutrients are higher in the ditches than in the land drains, and overland flow is low in nitrate but high in SRP. LD Hill and LD Forest both flow into D Hill. Dashed lines indicate ecological water quality threshold limits, i.e. 0.035 mg/l as P for SRP and 1.8 mg/l as N for nitrate.

flowing under unsaturated conditions, the river was typically flowing at <0.12 m^3/s at Collon (or 0.15 m^3/s at the catchment outlet). At these flow levels, the subsoils in the upper borehole in the transect were also dewatered (Figure 5.4). As expected, when the land drains were flowing under saturated conditions, the flows in the river were at their highest.

These flow thresholds are also evident on the flow duration curve (Figure 8.14). Although the land drains cease to flow at about the 57% flow exceedance level in the stream, there is still a contribution from the soils and subsoils as slower interflow. The additional significant change in slope on the curve at the 70% exceedance level (0.025 m^3/s) is the flow level at Collon at which a significant reduction in soil moisture content in the SILT/CLAY layer at Site 1 at the soil moisture monitoring transect occurred on 25–26 March 2012 (Section 7.3.3.). The moisture data indicated that at this level, the interflow ceased and the groundwater pathway became dominant.

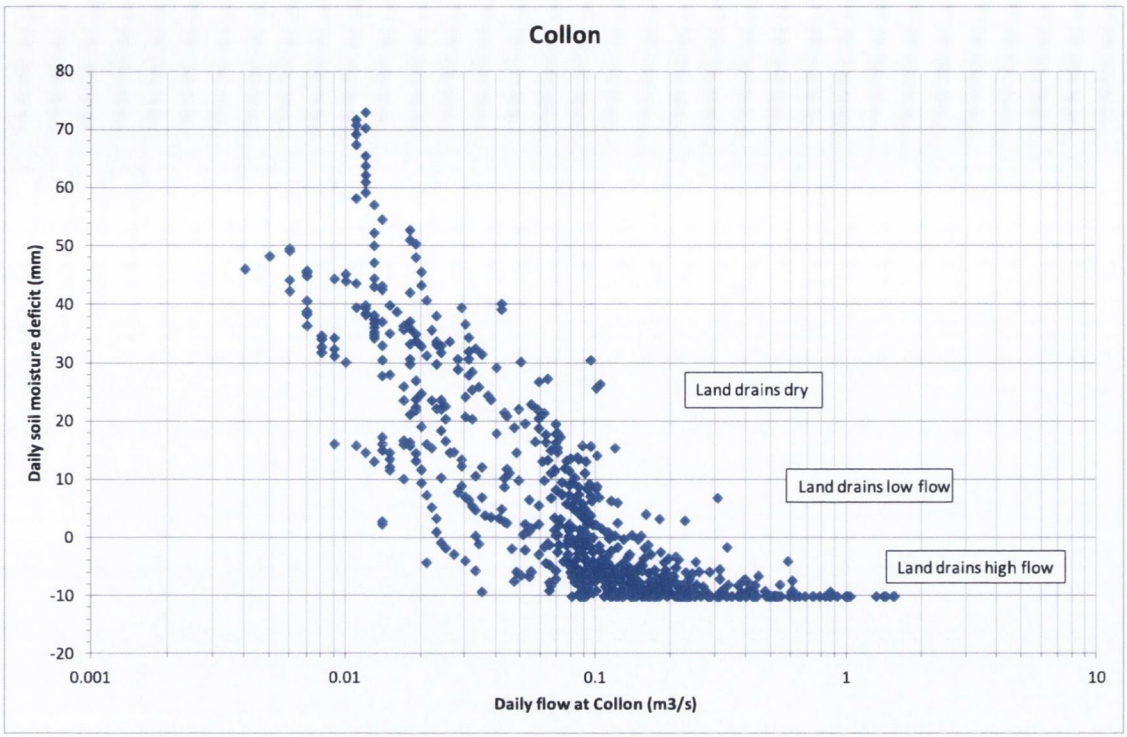

Figure 8.13. Daily flow at Collon (Nov 2011 to Oct 2013) with daily modelled SMD, highlighting the coincident flow conditions in the land drains from Figure 7.14. Two river threshold flows are identified: vertical dashed lines at 0.07 and 0.12 m^3/s, which represent maximum flow when the land drains are dry, and maximum flow when there is an SMD, respectively.

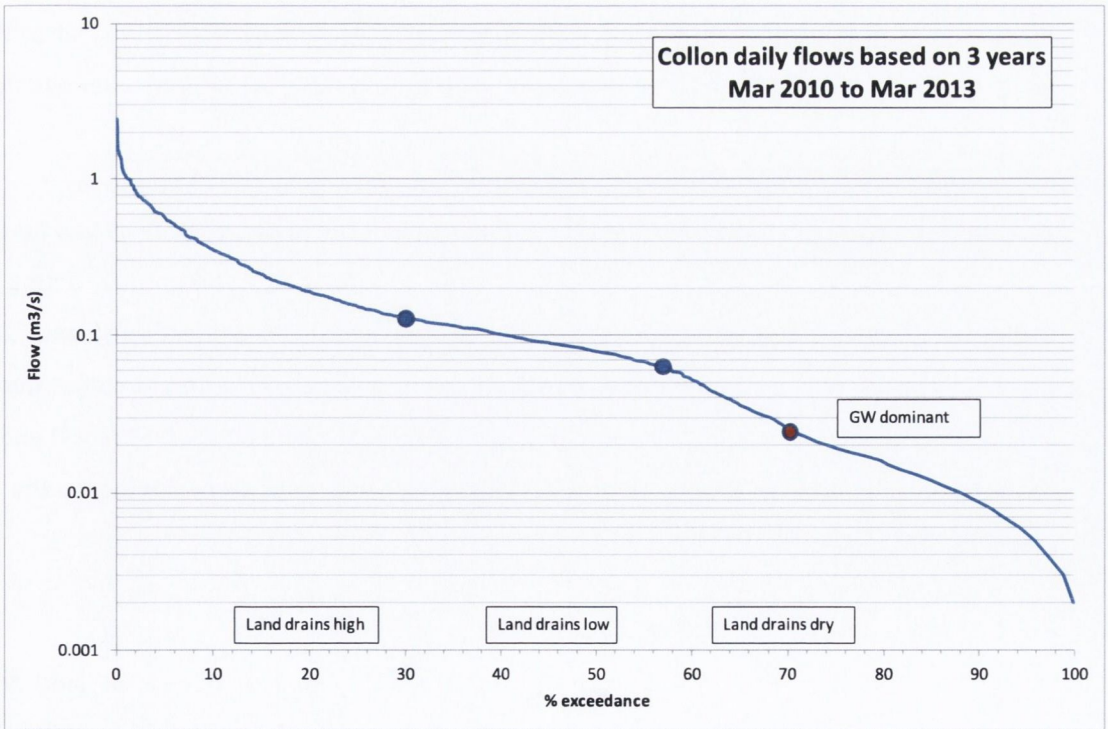

Figure 8.14. Flow duration curve for the Mattock at Collon indicating the changes in the land drain pathway contribution as determined by the significant changes in slope on the curve. At the additional change point at approximately 70% exceedance, the interflow pathway ceases to flow in the upper catchment as determined by the soil moisture data.

8.5.2 Nutrients

It was previously highlighted in Section 6.6 that there was a discrete change in nitrate concentration dynamics in the river at flow levels at this same flow threshold of 0.12 m^3/s at Collon. At lower flows, the concentration of nitrate increased with flow, whereas at higher flows, nitrate concentrations were diluted with increasing flows. Maximum nitrate concentrations in the river were reached at this threshold point (Figure 6.18). This was attributed to the increasing dominance of overland flow at high levels diluting the subsurface contributions. However, it was also demonstrated in Section 6.2.1.7 (Figure 6.4) that the proportion of overland flow in the event peaks decreases (and interflow increases) as antecedent conditions become wetter. So how then can these be reconciled?

Review of the nutrient data as loads instead of concentrations, with flow, revealed that both the nitrate (Figure 8.15) and SRP (Figure 8.16) loads increase with increasing flow in the river, with strong power law relationships ($R^2 = 0.85$ and $R^2 = 0.91$, respectively). This suggests that although there is dilution when overland flow is occurring, the loads are still increasing as the proportion of interflow increases. This is consistent with the power law increases in nutrient loads in the land drains. It was also noted that the loads of nitrate in the river were very low when the land drains were dry, and that they only started to increase significantly once the land drains had crossed the 0.025 l/s flow threshold, signifying that the soils were becoming saturated and interflow was becoming significant. The response in the SRP loads was later at higher flow levels, when the soils were fully saturated, confirming that the largest contribution of SRP came from overland flow.

8.6 Land drain contributions during events

The changes in land drain flow and chemistry, and the ditch chemistry, were reviewed for the two June 2012 events to consider how artificial drainage contributes to stream flow during rainfall conditions (Figure 8.17). Spot sample data for LD Hill (soils), LD S1 (subsoils) and LD Track (transition zone), for flow, nitrate and phosphate, were available at different stages during the events. Nitrate and phosphate data were available for three of the ditches: D S1 (soils) and two of the groundwater ditches, D Hickeys and D Track. Phosphate data were limited to the second event only for logistical reasons.

8.6.1 First event, dry antecedent conditions

During the first of the storms, the soil land drain (LD Hill) was the first of the land drains to increase in flow. The increase occurred in immediate response to the rainfall and coincided with a rapid increase in hydraulic head in the shallow soils at 30 cm depth at Site 4, at the top of the

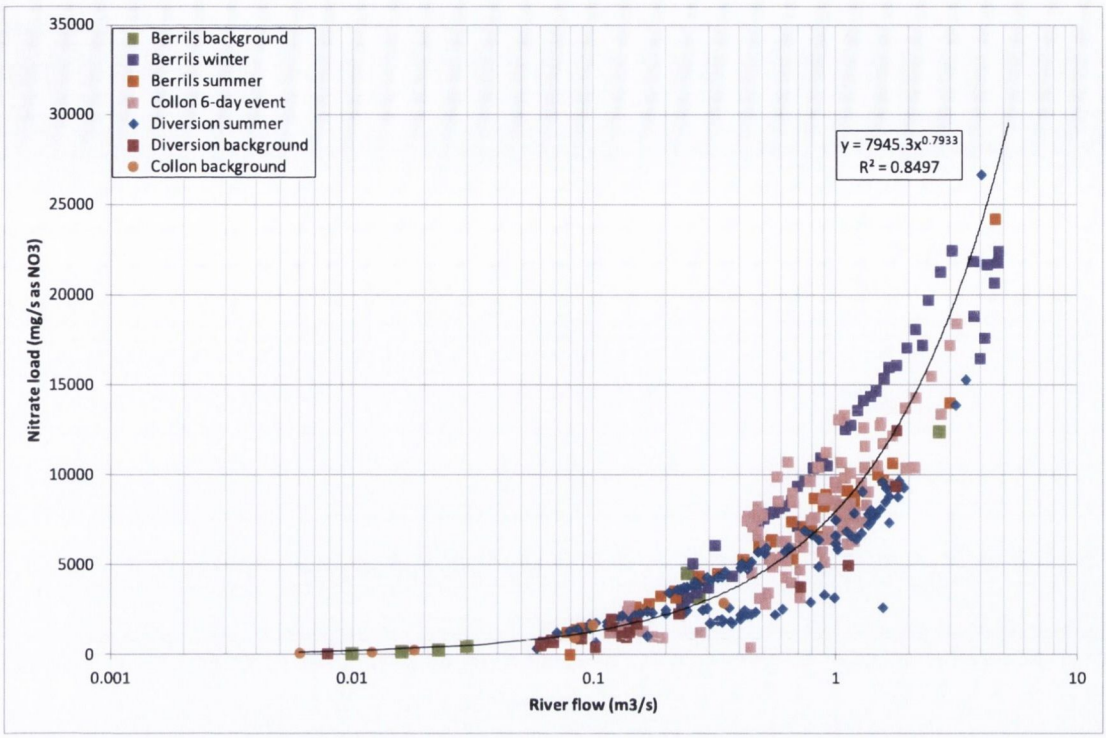

Figure 8.15. Changes in nitrate load in the River Mattock with increases in flow. Dashed red lines represent the 0.07 and 0.12 m^3/s flow thresholds identified in Figure 8.13.

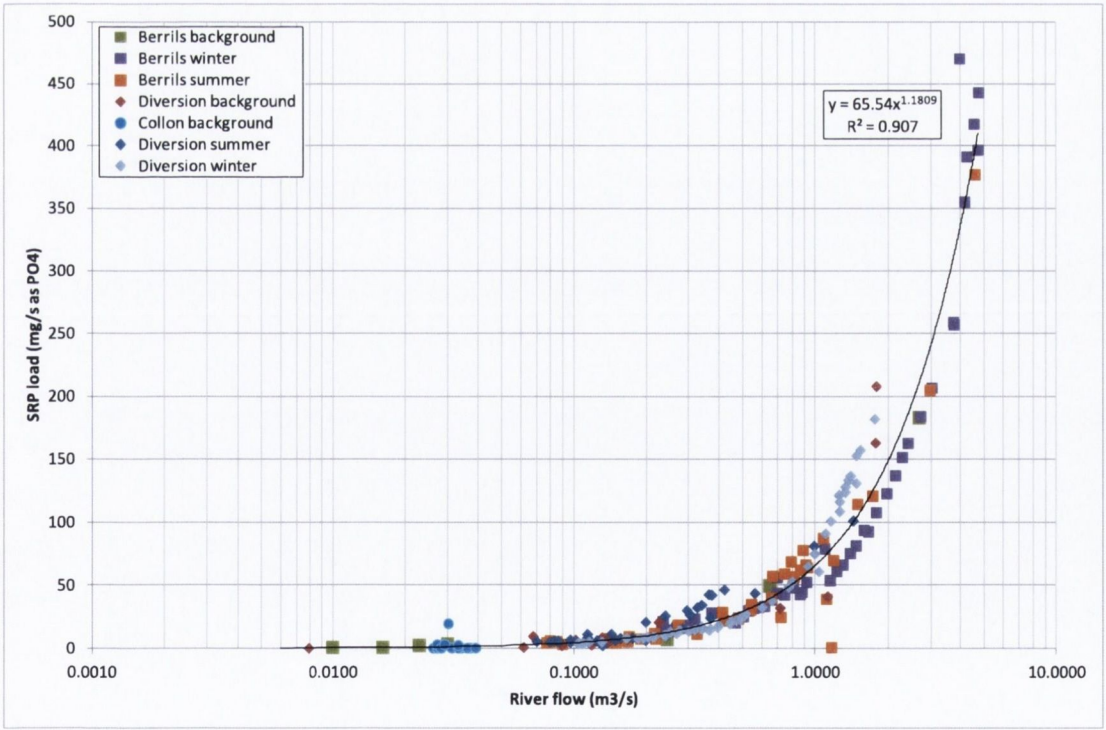

Figure 8.16. Changes in SRP load in the River Mattock with increases in flow. Dashed red lines represent the 0.07 and 0.12 m^3/s flow thresholds identified in Figure 8.13.

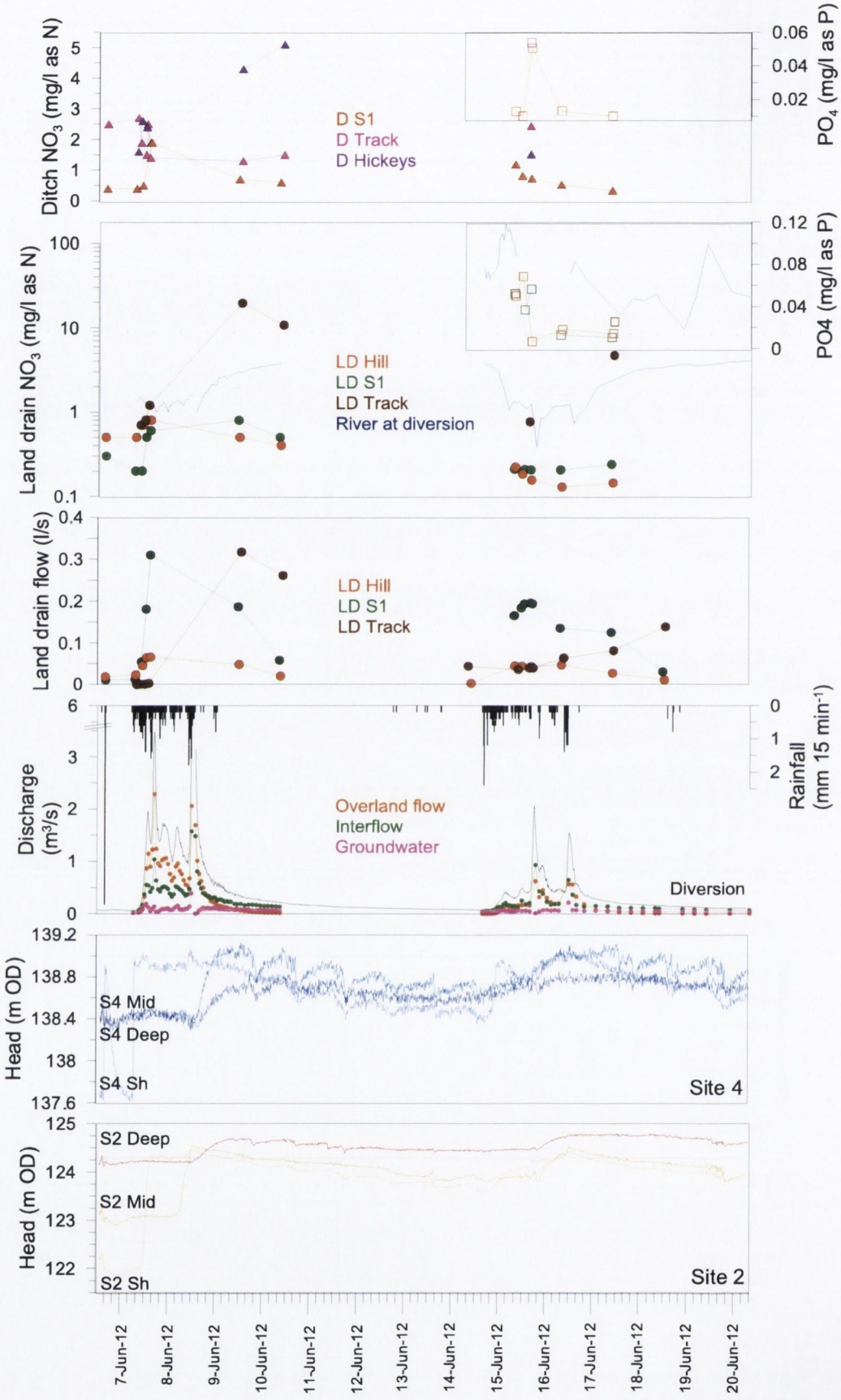

Figure 8.17. Hydraulic head at Sites 2 and 4, pathways separations, land drain flow, and nutrient concentrations for the two June 2012 events. Note the log scale for nitrate concentrations.

hillslope. This change in head was due to a large change in matric potential of over 110 cm between two measurement periods which were 15 min apart. This suggests that the soils were likely to have been tension saturated, i.e. there was a significant capillary fringe. The addition of rainfall almost instantaneously reduced the tension, which resulted in the rapid increase in head, and subsequent release of flow into the land drains.

This was followed shortly afterwards by an initial increase in flow in LD S1 in the subsoils. The rising limb of the stream hydrograph started to increase, corresponding with large increases in head in the shallow soils (20 cm) at Site 2 and in flow at LD S1. LD S1 is located at the bottom of the slope and has a larger contributing area upslope than LD Hill which resulted in the higher flows at that site overall during the event.

LD Track (transition zone) was much slower to respond to the rain than the other two land drains, and reached its highest flow level after the rain had stopped, when the river and the other land drains were in recession. The flow response was more closely aligned with the changes in head in the mid and deep soils at Sites 2 (60 and 120 cm) and 4 (75 and 157 cm). This is consistent with the source of the water being deeper in the soils at the transition zone.

Nitrate concentrations generally increased with flow in all land drains, although there were exceptions in the early stages of the event at all three sites. Nitrate concentrations remained low during the first small increases in flow in LD Hill and LD S1. This may be because there was a piston effect with pre-event water that had been denitrified, being pushed out of the land drains first before the nitrate-rich water from the soils was flushed in. In LD Track, the nitrate concentration increased slightly, despite a negligible increase in flow, but once the flow increased significantly, so too did the nitrate, and to a very high level of 19.6 mg/l as N. While there was clearly a larger source of nitrate in the soils and transition zone at LD Track, the conditions in the transition zone were not likely to have been favourable for denitrification to occur prior to the event. LD Track was dry prior to the rain, in contrast to LD Hill and LD S1, and the higher permeabilities in the transition zone in these rock types than in the clayey tills derived from them (Comte et al., 2012) suggest that it was likely that it would have been too aerated for dentrification to occur. In the river, the nitrate concentration increased with flow which suggests that there was a first flush effect after the long dry period. The push from aerated environments such as the transition zone may therefore have been dominant at the catchment scale.

The nitrate concentration in LD Hill (soil) reduced with the decrease in flow, but at LD S1 (subsoils) it remained high for a period during the land drain flow recession. This is consistent with a greater source of nitrate gaining access to LD S1 over its larger contributing area. In the later stages of the

event, the nitrate in LD Track responded closely with flow which is likely to reflect a close relationship between the expanding and contracting saturated area and nitrate stores in the subsoils.

In D S1, the soils ditch, the changes in nitrate concentrations reflected the changes in the soil and subsoil land drains, in that nitrate increased with flow. In the two groundwater ditches however, the pattern was different. Nitrate was at a higher concentration to begin with, and with the onset of rain the nitrate was diluted. At D Track, nitrate remained at the dilute level for the remainder of the event, suggesting that source of nitrate was deeper pathways that were being diluted with overland flow. At D Hickeys, however, nitrate concentrations increased with increasing flow as the event progressed, highlighting that new sources were being added to the ditch with rainfall; these may have been contributed by the adjacent farmyard.

8.6.2 Second event, wet antecedent conditions

During the second event, the antecedent conditions were wetter and the rainfall was less intense. The pattern of changes in flows at the three land drains was similar to during the first event, with increases in flows being later at LD Track than in LD Hill or LD S1, and lower increases at LD Hill than at LD S1.

Despite similar flow levels in LD Hill, the nitrate concentrations were lower suggesting that the source was becoming exhausted with its limited area of supply, but nevertheless the loads at all land drains still increased with flow. LD Track increased significantly in nitrate once again indicating the discharging waters had access to continued new nitrate stores in the transition zone. There were limited data available for the ditches but nitrate concentrations appear comparable, if slightly lower than the first event.

The nitrate concentrations in the river were diluted with the event which is the more typical nitrate response, and although the loads increased in a similar pattern as during the first event, they were almost two orders of magnitude less. While this is undoubtedly related to the lower rainfall in the second event, it also highlights the importance of the first flush effect after a period of dry weather. Similar first flush effects were observed in the Gortinlieve catchment during the August 2010 event (Section 5.3.4.2).

Phosphate was sampled in LD Hill, LD S1 and D S1 (which all drain the soils and subsoils) during the second event and different responses were observed to those for nitrate. Phosphate concentrations in the land drains peaked with the highest land drain flows, but then rapidly decreased suggesting the source had been washed out. The lower concentrations in the land

drains coincided with increases in phosphate in the ditch. This is consistent with a source from the upper soil layers in the field, which infiltrated with the rainfall through preferential flowpaths into the land drains and then into the ditches. This source was reduced with the decrease with rain.

8.7 Discussion

8.7.1 Contributions of artificial drainage to nutrient delivery

It has been determined through this research that the interflow pathway, and particularly the artificial drainage as a transport mechanism for interflow, contributes significantly in terms of flow during events. For example, the proportion of interflow was higher than overland flow at peak flow during the second of the June events. The research has also found that nutrient loads in the drainage network increase with increasing flow. This results in interflow providing a significant contribution to the overall load in the stream. However, this research has also provided evidence that the origin of the drainage water, specifically its hydrogeological setting, has a significant bearing on the dynamics of the nutrient contributions.

Drainage waters collected nitrate from stores that were perched above a lower permeability layer, for example, in LD Hill from the soils above the SILT/CLAY layer; in LD Track from the transition zone above the more competent bedrock; and in MK Subs 1 and 3 in the borehole transect site, in the subsoils overlying the bedrock. These nitrate stores were high when there was a significant load above the low permeability barrier, such as the domestic waste water treatment units at LD Track, and animals congregating at the field crossing at LD Forest. High nitrate stores were also observed in the transition zone boreholes in the middle cluster at Gortinlieve (Figure 5.31), which is next to a farmyard. Away from the higher nutrient loading points, the soils and subsoils were better able to cope with the level of nitrate in the landscape from agricultural practices and nitrate concentrations were generally low. Denitrification may have assisted in this process as the low permeability soils present favourable conditions. However, the first flush effect was significant and led to increases in nitrate with flow in the river. Nitrate loads also increased in all land drains, with increased land drain flow, only becoming exhausted in wet antecedent conditions at the land drain with the smallest contributing source area but remaining high elsewhere.

Phosphorus was high in all land drains and ditches on occasion although the mechanisms of its delivery were very different. There was evidence that it was washed through the soils and subsoils from the surface into the drainage system, via preferential flow paths, and that it was delivered from small point sources directly into ditches or via the transition zone. Phosphorus was less important where the drainage intercepted rising groundwater.

Thus, understanding the nature of the drainage problem should help to predict the likely nutrient dynamics and will be a useful addition to the toolbox in delineating the critical source areas for management purposes. Three categories of drainage have therefore been identified that summarize the links between the hydrogeological setting and nutrient transport: surface water drainage in the soils and subsoils, transition zone drainage and groundwater drainage. These are discussed further in Section 8.8.3.

8.7.2 End member signature selection for the interflow pathway

As discussed in Chapter 5, the ditches are an important delivery mechanism for waters from different origins, but they are not considered to have a discrete signature of their own; they are simply extensions of the stream network delivering the same mixtures of water otherwise observed in the stream. The mixture of chemistries in the ditches in the interflow region of the mixing triangle is replicated in the land drain mixing triangle, although there it is biased slightly more towards the overland flow end member reflecting their shallower depths. This highlights the difficulties in identifying a discrete signature for the interflow pathway for chemical hydrograph separation and emphasizes the need for a strong conceptual model to identify the origins of the near-surface samples being used in the analyses.

The signature for the interflow pathway that was used in the end member mixing analysis in this research was the median of the tracer data for all land drains sampled, but LD Hill was excluded because it was very high in SAC and was considered to be unrepresentative of the wider interflow conditions around the catchment. The dataset thus included samples from land drains from the soils, subsoils and transition zone. Without the conceptual model to highlight the range in hydro(geo)logical environments contributing to interflow, which enabled the confident selection of a diverse set of land drains that encompassed that variability, it is plausible that the end of the study may well have been reached with a land drain dataset that would only have been representative of one hydro(geo)logical setting. The mixing triangle would not then have bound the samples and the mixing analysis would have been incomplete. Alternatively, a different interflow end member signature might have been selected, or it might have been concluded that there were only two significant end members (overland flow and groundwater; refer to Section 6.2.1.5), which would have resulted in a very different interpretation of the role of the interflow pathway.

As there is a certain degree of subjectivity in the chemical hydrograph separation approach, from initially choosing the right end members to sample in the field, to selecting the right tracer concentrations to represent the pathway or source of interest, it is important that the results are tested using a range of different and supplementary techniques. However, this is rarely carried

out in practice in the literature. For example, Garrett et al. (2012) collected data for five end members and subsequently discarded data for two of them on the basis that they did not consider them to represent the extremes. However, the resulting end members did not bound the stream samples which they attributed to end member variability. They concluded that incorporating pre-event sampling and associated water chemistry into the EMMA calculations would produce more accurate results. Soulsby et al. (2006) suggested that combining spatially distributed soil and topographic information with tracer data had huge 'potential utility' in understanding catchment hydrology. The application of several different techniques in this research, including the development of the conceptual model, the flow modelling, chemistry analyses and soil moisture water dynamics, has been found to be important for properly conceptualizing the catchment and confirming the interflow contributions determined from the end member mixing analysis.

8.7.3 The contributions from small point sources

It is a fundamental assumption of load-apportionment models that point source loads are relatively fixed and are independent of rainfall, such that their impacts are diluted in winter but are more prominent in summer baseflow (Bowes et al., 2008). Loads from diffuse sources, on the other hand, are known to increase with rainfall as variable source areas expand connecting new sources of contaminants (Thompson et al., 2012). However, small point sources, such as septic tanks and farmyards, fall into an intermediate category between point and diffuse. They are typically poorly understood and are rarely modelled because of their temporal and spatial variability (Edwards and Withers, 2008). In the River Chitterne catchment in the United Kingdom, which has relatively low agricultural and population densities, Jarvie et al. (2006) found that SRP and boron (an indicator of sewage) both increased with flow, which was in contrast to the majority of the 54 lowland monitoring sites studied where there was significant dilution of these parameters. They attributed this effect to the flushing of sewage into the river as groundwater levels rose and intercepted septic tank soakaways. However, the catchment was underlain by a chalk aquifer where the pathway would most probably have been groundwater, and the study did not look at the contribution of nitrate.

This research has provided evidence from the land drains and ditches in the Mattock catchment that the concentrations and loads from small point sources delivered via the subsurface pathways in poorly drained catchments increase with flow, and that they therefore do not behave as point sources. In fact, the load increases in LD Track were at a higher rate than land drains draining the diffuse agricultural sources, perhaps because of the higher point source loading beneath the contaminant site(s) which were only flushed through during the heavier rainfall events. This

research therefore supports the inclusion of a third category for small point sources in poorly drained catchments for the management of nitrate as well as phosphorus. However, further conclusive evidence that the loads in LD Track and D Road are from human sources, using for example, human-specific tracers such as caffeine, pharmaceuticals or personal care products (Lapworth et al., 2012), or microbial source tracking (Murphy et al., 2013), would be useful to support this recommendation.

8.8 Development of a land drain map for Ireland

8.8.1 Introduction

This research has identified that artificial drainage plays an important role in the delivery of nutrients to Irish streams, yet the majority of the drainage schemes have been in place for many decades and there are no maps available indicating their locations. Similar findings and mapping problems have also arisen in other countries and there are several reports in the literature of attempts to predict and map their locations using GIS and remote sensing, e.g. Germany (Hirt et al., 2005), mid-western United States (Naz et al., 2009) and the United Kingdom (Davison et al., 2008).

The first draft of two national land drain maps has been developed as part of this research, in conjunction with a fellow *Pathways Project* student (Eva Mockler), and a retired land drainage expert from Teagasc (Tim Gleeson). The purpose of the maps was two-fold: to inform the pathways separations in the hydrological modelling in the catchment management tool; and to apportion pathway nutrient transport factors in the catchment characterization tool. The maps were tested in three of the four study catchments and have been used in the first version of the catchment management support tools. However, they are considered to be a work in progress that will evolve with further development of the catchment management support tools. A full description of the maps, the development process and the testing that has been carried out, highlighting the contributions of this researcher, is provided in Appendix 2. A brief summary is included here.

8.8.2 Presence/absence map

The presence/absence map predicts the areas of Ireland where there are likely to be land drains. A decision tree was used to develop to guide a set of GIS rules or algorithms to highlight the drained areas, based around number of assumptions relating to soil drainage, slope and land use. The presence/absence map predicted that the total area of land drained in Ireland was 44% of agricultural land, or 29.4% of the Republic of Ireland, which compares very favourably with previous published estimates based on representative land surveys (Bruton and Convery, 1982).

It is acknowledged that the map presents the lands that are likely to be drained, rather than actually drained, so a land drain efficiency factor has been introduced for the purposes of the hydrological modelling to allow for overestimates, uncertainties and blockages. On the basis of the catchment results, validation exercises and the hydrological modelling, the efficiency factor is currently set at 0.8, which means that 80% of the land area needing to be drained is likely to be drained effectively. Ongoing research may revise this estimate in the future.

8.8.3 Land drainage problem map

This research has found that the type of land drainage problem, i.e. the hydro(geo)logical pathways that deliver the water that needs to be drained, has a significant bearing on nutrient delivery from land drains. Three categories of drainage with specific implications for nutrient management have been identified based on this research, and are presented on the land drainage problem map:

(i) *Surface water drainage* due to poor infiltration in poorly drained soils and subsoils. An example of this occurs in the soil and subsoil land drains in the Mattock catchment, where SRP can be high with rainfall events, but nitrate is typically low except where nutrient loads are increased (Section 8.3.2).

(ii) *Transition zone drainage* which is often high in nitrate, and occasionally high in phosphorus. Examples of this occur in the Gortinlieve catchment in the transition zone boreholes (Section 5.3.4) and in the Mattock in the transition zone supported land drains (Sections 8.3.2) and ditches (Section 8.4.3).

(iii) *Groundwater drainage*, where nutrient concentrations depend on the hydrogeological regime. In Regionally Important aquifers, drainage is high in nitrate but low in phosphorus. This is because in these environments, deeper bedrock groundwater pathways dominate, and phosphorus infiltrating through the overlying permeable soils and subsoils is often attenuated (unless the depth to rock is very shallow), yet nitrate does infiltrate. An example of this type was found in the upper Nuenna catchment (Section 5.4.3.3). In poorly productive aquifers, drainage will be low in nitrate and phosphorus because in these environments, groundwater is confined under the low permeability tills and much of the nitrate that does infiltrate is attenuated. These are of course generalizations; there will be exceptions where rock is at or near surface and therefore there is no effective protective soil/subsoil cover, where there are point sources of contamination, and where the soil and subsoil parent material is not the underlying bedrock due to glacial carryover.

The land drainage problem map (Figure A2.4) has been generated for Ireland and tested in three of the four study catchments. Preliminary results are encouraging but further testing and validation is required. The map has immediate application in the *Pathways* catchment management support tools, and more widely from a nutrient management perspective as Ireland moves forward to meet its Food Harvest 2020 objectives. The methodology will likely also be of interest in other countries where similar mapping and nutrient management issues arise.

9 Discussion and conclusions

9.1 Introduction

Management of pollution from diffuse agricultural and small point sources remains a significant challenge worldwide. Targeting the most hydrologically sensitive, highest-risk areas within a catchment for nutrient management purposes, i.e. the CSAs (Haygarth et al., 2005, Heathwaite et al., 2005), is an efficient means of prioritizing resources to achieve good environmental outcomes (Doody et al., 2012, Daly, 2013). Understanding and quantifying the contribution of each hydro(geo)logical pathway to the receptors of interest, in terms of flow and nutrient transport, is an important part of identifying CSAs.

A generic four-pathway flow model had previously been identified by the Irish Groundwater Working Group (Daly and Hunter Williams, referenced in RPS (2008)) as being appropriate for Ireland; this model incorporated overland flow, interflow, shallow groundwater and deep groundwater (Section 1.4). In glaciated catchments, such as those in Ireland and much of Europe, the diverse soils and subsoils ensure that the interflow pathway plays a significant role in water and contaminant transport processes, but its role is poorly understood, particularly in low-lying agricultural catchments (Kennedy et al., 2012, Klaus and McDonnell, 2013).

The overall aim of this research was to develop an improved conceptual understanding of the near-surface pathways in the delivery of flow and nutrients to streams in these types of catchments. The research outcomes have contributed to a larger project, the *Pathways Project*, which has developed a suite of national catchment management support tools that identify the CSAs and will be used by regulatory and resource management agencies as part of implementation of the Water Framework Directive (Archbold et al., 2014).

9.2 Research philosophy

The underlying philosophy in this research was to apply a range of research techniques and methods at different scales (Blume et al., 2009, Hrachowitz et al., 2013), within a conceptual model framework, as a means of limiting the dependence on any one particular method and therefore reducing the levels of uncertainty. An integrated approach that recognized that nutrient transfer processes are part of a dynamic flow pathway continuum was considered important for a robust understanding of catchment nutrient transport.

Field investigations were carried out in four study catchments, Gortinlieve, Glen Burn, Mattock and Nuenna, ranging in size from 5 to 36 km^2. Conceptual models were developed to provide a four-dimensional hydro(geo)logical framework for understanding catchment dynamics. A programme of background and event water quality sampling was carried out in each catchment to gain insight into the pathways transporting flow and nutrients to streams. Chemical hydrograph separation methods quantified the proportion of flow through each pathway, and the results were integrated with results from physical hydrograph separation methods, NAM hydrological modelling, and other methods to achieve a deeper understanding.

A field-scale soil moisture dynamics study was carried out in one of the study catchments, the Mattock, to investigate the soil water conditions under which interflow occurred. This evidence was used to refine the conceptual model and corroborate the quantitative estimates from the chemical hydrograph separation methods. A programme of field sampling within the near-surface pathways was also conducted, which provided supporting evidence as well as insights into nutrient transfer. This approach had the advantage of gaining process understanding at the field scale, while reducing the limitations regarding representivity and scaling up that are inherent in conducting field-scale studies by incorporating catchment-scale methods.

The Mattock catchment is underlain by poorly productive aquifers, low permeability subsoils and poorly drained soils, and was selected for the intensive study as these types of catchment conditions comprise over 70% of the land area in Ireland. Similar hydrogeological regimes were present in two of the other study catchments, which was useful for comparative purposes; the fourth catchment was underlain by a karst aquifer with free-draining soils and subsoils, which provided suitable contrast. This integrated approach has helped to broaden the findings so that a conceptual understanding of the near-surface pathways could be developed that had applicability at the national scale for inclusion in the national models.

Five research objectives were outlined in Chapter 1 which are considered in turn in the following sections. The first objective, to provide a critique of the existing conceptual model on the basis of the research findings, and the last objective, to develop an improved conceptual model for the near-surface pathways, are combined towards the end of this discussion in Section 9.6.

9.3 Quantification of pathways contributions to streams

9.3.1 Introduction

Quantifying the contribution of each pathway to the stream in the three poorly drained catchments was a central aspect of this research, and the *Pathways Project* in general, so that the flow and contaminants could be realistically apportioned in the hydrological model underpinning

the catchment management support tools. Similar chemical hydrograph separations were not carried out in the Nuenna catchment as the contribution of the interflow pathway was estimated to be negligible because the soils and subsoils are so permeable, and their chemistry is indistinguishable from groundwater in the underlying bedrock, both being of strong $CaCO_3$ type (Section 5.4).

9.3.2 Chemical hydrograph separations

The chemical hydrograph separations (Section 6.2) showed that at low flows, the interflow pathway was the dominant pathway contributing to the stream in the Mattock catchment (60%) with the remainder coming from bedrock groundwater. Interflow was also dominant in the Glen Burn catchment in summer (96%), but in the winter months, the water tables were higher in the inter-drumlin areas and shallow groundwater was dominant in the stream (92%). In Gortinlieve, the transition zone was the dominant contributing pathway at low flows (55–70%), except in the lower catchment in the groundwater discharge area in wetter antecedent conditions, when water tables were high and the proportion of groundwater increased.

During the events, the overland flow pathway contributed the largest proportion of flow overall in the Mattock catchment (33–52%), followed closely by interflow (39–50%); the groundwater pathway contributed least (10–28%). Overland flow was highest in peak flows following drier antecedent conditions but interflow became increasingly more dominant in event peaks with increasingly wet antecedent soil moisture conditions.

During the summer event in the Glen Burn catchment, interflow provided the highest proportion of flow as water tables were low. During the winter event, however, although the initial peak was overland flow, interflow became dominant as the catchment wetted up. In this catchment, the depth to the low permeability bedrock is shallow in the inter-drumlin areas and water from the soils and subsoils is delivered very effectively to the stream via the artificial drainage network.

In Gortinlieve, the transition zone delivered a very high proportion of stream flow during the high-intensity rainfall event (up to 77%) due to rapidly changed heads with the influx of rainfall, but a more typical pattern otherwise emerged of higher overland flow in the upper steeper part of the catchment, and similar transition zone/overland flow contributions (45–50%) in the lower catchment.

In summary, these results highlight that the interflow component in the poorly drained catchments was typically high in baseflow conditions, and became increasingly greater than overland flow during rainfall events as the soils became more saturated. This finding, which is

counter-intuitive, was supported by the soil water dynamics, and the sampling in the land drains and ditches in the Mattock, and it is consistent with recent research by Kennedy et al. (2012) who found that as the catchment became wetter, pools of subsurface soil water and groundwater were the dominant sources of streamflow. They suggested that a more quantitative understanding of soil water and groundwater transport via tile drains would be an important step forward. This research provides such quantification and sheds new light on the importance of the interflow pathway in these types of catchments underlain by poorly productive aquifers, at all flow levels. It improves on previous Irish estimates, for example, Mellander et al. (2012) reported that just 2–15% of flow was delivered via the interflow pathway in four Irish catchments ranging from poorly drained to well drained.

9.3.3 Integration of the chemistry with the NAM modelling

Integration of the results from the chemical hydrograph separation with those from the NAM modelling presented four important findings that provided further insights into the conceptual model (Section 6.5). First, at low flows in winter in the Mattock, the NAM model predicted that the proportion of slow flow 'groundwater' in the stream was approximately only half of that estimated using the chemistry. This indicated that water with a groundwater chemical signature reached the stream more quickly than simulated by the NAM model. This is likely to be because, in the field, the drainage network delivered water with a bedrock groundwater signature to the streams from the upper parts of the catchment more rapidly than would otherwise have been possible in their absence.

Second, the NAM model predicted that the slowest 'groundwater' response pathway was the largest contributor to flow in the summer months in the Mattock, but based on the chemistry, this slow flow component was actually made up of a combination of groundwater and interflow in the ratio of 2:3. This was likely to be because the land drains continued to drain the soils and subsoils during the baseflow period. This finding was supported by the soil moisture dynamics and the sampling in the land drains and it provides an improved understanding of the concept of baseflow in catchments underlain by poorly productive aquifers.

Third, at low flows in the Gortinlieve catchment, the 'interflow' pathway contribution predicted from the NAM model was well matched proportionally with the transition zone component based on the chemistry. This suggests that the transition zone behaved more like interflow than groundwater in terms of its response time to the stream. Further discussion on the transition zone is provided in Section 9.6.4.

Fourth, in high flows in all three catchments, the NAM predicted the vast majority of flow in the river to be derived from the quickest response pathway, nominally 'overland flow', but the chemistry indicated that much of this water was actually derived from the interflow pathway, or the transition zone pathway in the case of Gortinlieve. This highlights that the land drains responded very quickly during events, such that this water was being accounted for with the overland flow pathway in the model.

In summary, the integration of the NAM modelling results with the chemistry showed the importance of artificial drainage system in transferring groundwater and interflow to the stream with quicker response times than would otherwise be expected. As outlined by Ogunkoya and Jenkins (1993), chemical hydrograph separation approaches provide insights into the source of the water, but not the delivery pathways. Integrating the results from the chemical hydrograph separation methods with the NAM modelling results, in the context of the conceptual models, provided an improved comprehensive understanding of the pathway dynamics in each catchment during events. These findings contributed to the conceptualization of flow for modelling purposes in the catchment management support tools, as outlined in Section 9.8.

9.4 Insights from the soil moisture dynamics

The soil moisture dynamics study was carried out in the Mattock catchment and proved useful for providing process understanding to conceptualize interflow, and to support the quantification of the interflow pathway from the chemical hydrograph separation approach. In general, it was found that the tension and hydraulic head data were more useful than the soil moisture content for distinguishing the different pathway responses, because the low permeability soils and subsoils were frequently fully saturated, or returned to saturated conditions very quickly with the onset of rain.

9.4.1 Evidence for interflow

This research has found that there is evidence from the soil water dynamics to confirm the findings from the chemical hydrograph separation approach that interflow is an important pathway for the delivery of flow in the Mattock catchment (Section 7.5.1). Rapid changes in soil moisture content, and a large range in soil moisture content at zero tension, suggested that there was preferential flow in the upper soils and underlying SILT/CLAY layer. Slow drainage occurred through evapotranspiration and seepage through the matrix, whereas there was rapid drainage through macropores, preferential flowpaths and the land drains. The dual flow mechanism has been observed previously in other research (Seiler et al., 2002).

The hydraulic head data indicated that the deeper underlying CLAY layer was an effective barrier to downward percolation and that the upper soils and SILT/CLAY acted as a single hydraulic unit, which supported lateral interflow above the low permeability barrier, in a similar mechanism to that found in other studies (Ahuja and Ross, 1983). Results provided evidence for interflow at depths of up to 75 cm, which is greater than that found in other Irish literature (Burke et al., 1974a, Tunney et al., 2000, Diamond and Sills, 2001), but this study suggests that interflow is highly dependent on the drainage system and the depth at which it has been installed. The permanent water table was present in a permeable sandy SILT or SAND/GRAVEL layer under the CLAY.

9.4.2 Comparison with chemical hydrograph separation data

The proportion of interflow in stream flow at low flows predicted by the chemical hydrograph separation method (60%) was consistent with estimates of interflow based on calculations of the soil drainage using the soil moisture characteristics, as well as field observations of land drain flows (Section 7.3). During the events, the time-series matric potential data provided explanatory information to support the chemical hydrograph separation estimates (Section 7.4). For example, the chemistry predicted that the first peak flow in the first of two intensively monitored events in June 2012 was predominantly overland flow, whereas the first peak flow in the second event was dominated by interflow. This was contrary to the results from the NAM modelling, which had suggested that very high proportions of the stream flow were derived from overland flow in both events. The matric potential data indicated that the soils were unsaturated at depth during the first event, which supported the interpretation from the chemistry that the majority of the stream flow was running off the catchment without significant interaction with the soils. During the second event, there was an upward hydraulic gradient from the deeper soils, suggesting that significant interflow discharge was likely. These data were further supported by measurements of land drain flows during the events.

This event analysis highlights the importance of combining methods as outlined by (Blume et al., 2009). For example, had the results from the NAM modelling been used on their own to determine the pathway contributions for the June events, without the chemistry and/or the soil matric potential data, as has been the case in previous studies (refer to Table 3.3), the prediction of the proportion of overland flow would have been too high, and could have led to an overestimation of the phosphorus load in the stream, because the transport of phosphorus is usually linked to the overland flow pathway in catchment contaminant transfer models (Wade et al., 2002).

9.4.3 Landscape position

The soil water dynamics data also highlighted that there were different flow generation processes operating in different landscape positions during the events, which when combined with the near-surface pathways sampling results, was found to have implications for nutrient transfer (Section 7.5). For example, the soils at all levels in the most down gradient cluster in the soil monitoring transect were almost permanently saturated, which was surprising given that the site had been purposely selected to be outside the likely extent of the riparian zone. These soils are important areas for overland flow generation, while delivering a consistent but important background component of interflow. The permanently saturated conditions suggest the nitrate content in the interflow derived from this landscape position will be low. However, these areas are important critical source areas for the management of nutrients applied at the surface, particularly phosphorus. This will be an important consideration when assessing the necessary extent of buffer zones, for example, to protect the stream from phosphorus runoff (Dahlke et al., 2012, Doody et al., 2012). These findings are likely to be replicated in other catchments.

Site 2, which was upgradient of Site 1, showed the greatest variability in soil moisture contents and hydraulic heads, which highlighted both the effects of the soil drainage and the location of the site upgradient of the permanently saturated areas. The soil moisture dynamics at this site corresponded best with the predictions from the chemical hydrogaph separation, highlighting that the artificially drained soils were most important for interflow generation at the event scale. This site was less important for overland flow, and would therefore appear at first glance to be less sensitive to phosphorus losses. However, the land drain sampling indicated the importance of the first flush effect and how sometimes high levels of phosphorus were washed through the soils into the drainage system in the early stages of an event. These areas therefore also require management of excess phosphorus application.

At Site 4, near the catchment divide, the head responses in the soils and subsoils were slower than further downgradient, suggesting a slower release of interflow during the recession periods. This was supported by flow measurements in land drains in these areas.

In summary, the soil moisture dynamics research provided direct, hillslope-scale, process evidence for interflow, as it occurred in different parts of the hydrogeological landscape, which was related to measured drainage through land drains, and catchment-scale estimates of interflow from the hydrograph separations. This research therefore bridged the important scale gap (Hrachowitz et al., 2013) and was consistent with a recommendation by Kirchner (2006) that designing new data networks, field observations, and field experiments, with explicit recognition

of the spatial and temporal heterogeneity of hydrologic processes was a promising direction forward.

9.5 The role of artificial drainage

A suite of eight land drains and ten ditches around the Mattock catchment were sampled regularly as part of this research, to determine the spatial and temporal variability in chemistry and nutrient concentrations in the drainage system. Flows were measured regularly in five of the land drains (Section 8.2).

Land drain flows varied over five orders of magnitude from 0 to 0.8 l/s. It was found that land drains continued to flow under unsaturated conditions, corroborating the evidence from the soil dynamics study that flow through macropores was important. The chemistry of both the land drains and the ditches highlighted that the origin of all drainage waters could be assigned to one of four different hydrogeological drainage regimes: soils, subsoils, transition zone or groundwater. The drainage regimes were found to have a significant bearing on nutrient transport (Section 8.3).

Drains and ditches collected nitrate from stores that were perched above lower permeability layers in the landscape (Section 8.7.1). Nitrate stores were found to be highest in the drains draining the transition zone in the groundwater recharge areas, where conditions were unfavourable for denitrification. Nitrate stores were also found to be high where there were high loads, such as from small point sources (e.g. domestic wastewater treatment plant, areas highly trafficked by animals) above a soil or subsoil low permeability barrier to flow. Nitrate was otherwise generally low in the soils and subsoils and in the groundwater due to low infiltration and/or attenuation.

Soluble phosphorus was high in all land drains and ditches on occasion, although the mechanisms of its delivery were different to nitrate. There was evidence that phosphorus was washed through the soils and subsoils from the surface into the drainage system via preferential flow paths and that the supply became exhausted as the event progressed. This was in contrast to nitrate loads, which increased with increasing land drain flow. Phosphorus was also delivered from small point sources directly into ditches, or the transition zone where the depth to rock was shallow. Phosphorus was low, however, where the drainage intercepted rising groundwater. A first flush effect for both phosphorus and nitrate was seen in land drains following dry periods.

These findings highlight that the drainage networks contributed significantly to the flow and nutrient transport processes in the catchment. The increasing nitrate loads as land drain flow increased and the high proportion of interflow in the stream during high flows, as highlighted by

the pathways separations methods, indicate that interflow provided a significant contribution to the overall load in the stream. This is consistent with other research in the literature that suggests that the artificial drainage network can be a significant source of nutrients (Haygarth et al., 1998, Tesoriero et al., 2009, Rozemeijer et al., 2010, Cuadra and Vidon, 2011). However, this research has provided new evidence that the origin of the drainage water, specifically its hydrogeological setting, has a significant bearing on the dynamics of nutrient transfers in drainage waters at the catchment scale. First attempts have also been made to generate a national map that summarizes these relationships, which will be useful for the purposes of delineating CSAs. Initial results are encouraging but further testing is required (See Appendix 2).

9.6 Improved conceptual model for the near-surface pathways

The literature review and the review of the available catchment data highlighted that further research was needed to better conceptualize the near-surface pathways, i.e. interflow, artificial drainage, and the transition zone where the depth to bedrock was shallow. These pathways are especially important in Ireland as much of the country is underlain by less than 3 m of soils and subsoils, however the research also has application in similar environments elsewhere.

In the Nuenna karst catchment, there were few land drains present (except in the limited upland areas on the Namurian shales) and any that were observed were for the purpose of relieving high groundwater levels, as evidenced by their hydrochemistry, which was the same as the groundwater. Interflow as a direct pathway to the stream was thus not considered to be a significant pathway as soil and subsoil water recharged first into bedrock before it was transported laterally into the stream (Section 5.4).

The improved conceptual model for the transport of nitrate and soluble phosphorus in the near-surface pathways in catchments underlain by poorly productive aquifers is summarized in the following paragraphs and illustrated in Figure 9.1. As identified in Chapter 2, the near-surface pathways are only one part of a continuum of flow components that make up the stream hydrograph, and it was a principle in this research that were addressed in the context of all the other pathways. A brief summary of the findings in relation to the overland flow and shallow and deep groundwater pathways is therefore provided for completeness.

9.6.1 Overland flow

The overland flow pathway was considered in this research, and in the *Pathways Project*, to comprise flow on the land surface to depths of 20 mm (Archbold et al., 2010). This research found through the pathways sampling, however, that overland flow had a range of different chemistries,

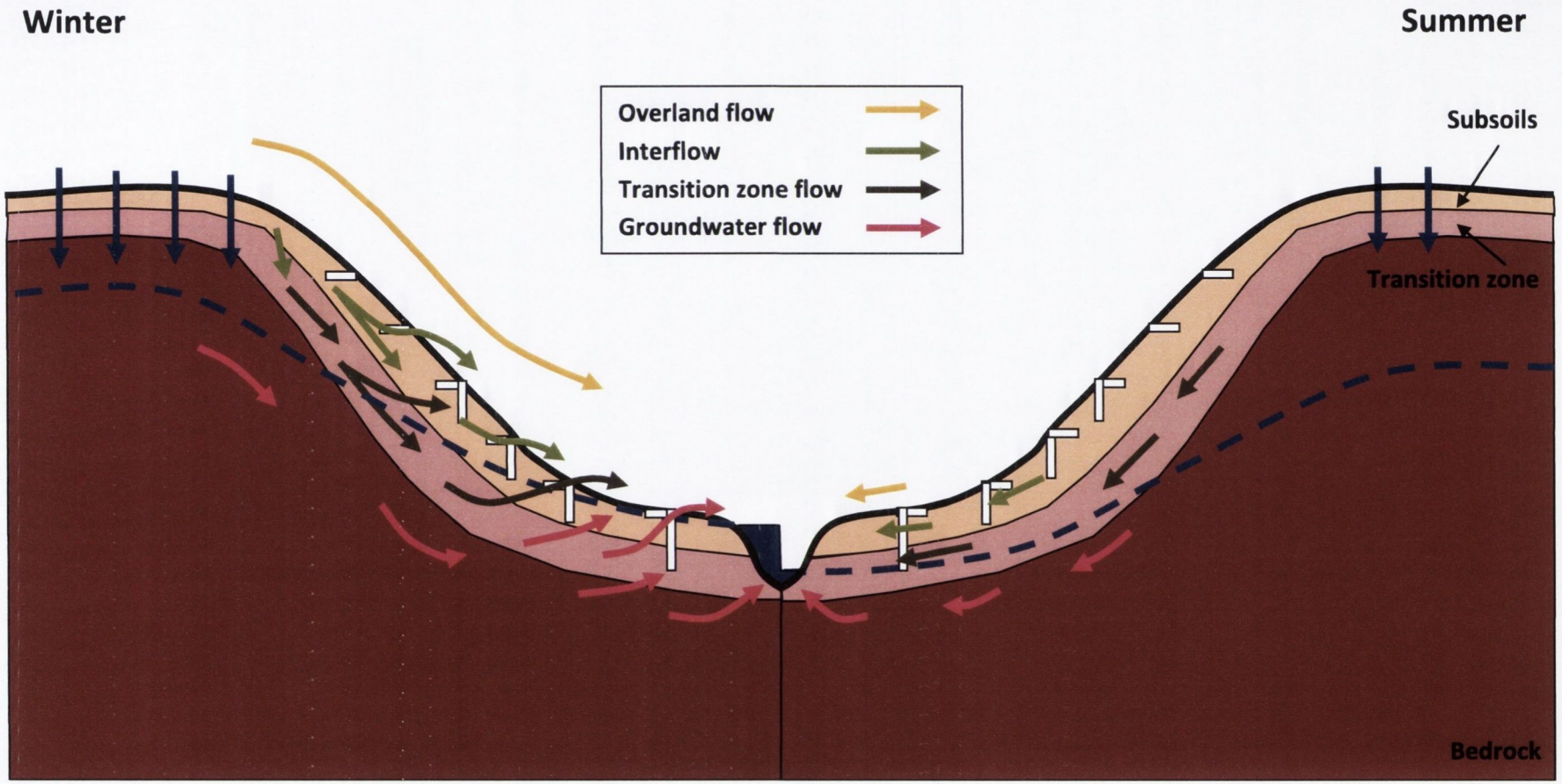

Figure 9.1. Conceptual model for winter (left) and summer (right) flow in the near-surface pathways in catchments underlain by poorly productive aquifers. Blue arrow, rainfall; broken blue line, water table; horizontal white rectangles, land drains; vertical white rectangles, ditches. Colour of flow arrows identify the source of the water, e.g. pink arrows flowing at the surface in winter indicate that water with a groundwater signature can be delivered via overland flow. Drains and ditches can be a significant delivery pathway for water with an interflow, transition zone and/or groundwater signature, as represented where the arrows intersect the white rectangles. Flow in the transition zone can have a subsoil/interflow, transition zone or groundwater signature. Arrows at the surface indicate overland flow. Length and numbers of pathway arrows indicate relative importance of flow.

highlighting that, in some parts of all the catchments, it had originated from the subsurface and was often return flow or rejected recharge from the soils, subsoils or bedrock. Integration of the results from the chemical hydrograph separation methods with the NAM modelling highlighted that the return flow mechanism provided a means for water with a subsurface origin to reach the river with a quickflow response that was more typically associated with overland flow. Overland flow with a hydrochemistry similar to that of groundwater was also observed in the Nuenna catchment, which emphasizes the role of groundwater flooding in karst catchments (Hughes et al., 2011).

These findings have implications for catchment modelling: from a hydrological modelling perspective, the pathway response times derived from the NAM are of greater interest for model calibration purposes; whereas from a nutrient transport perspective, the origin is more important because nitrate and phosphate tend to accumulate in different geological layers. It was identified therefore, that for nutrient modelling purposes in the catchment management support tools, it was important that overland flow was distinguished on the basis of its origin and chemistry, rather than just its response time.

9.6.2 Interflow, stream flow and catchment dynamics

During summer baseflow conditions, when water tables were low, the majority of flow in the streams was derived from the soils and subsoils, and was delivered to the stream via the drainage network, preferential flowpaths and the slower flow soil matrix. Under these conditions, the concentrations of nutrients from diffuse sources were relatively low, but the influence of small point sources was significant in places.

During summer rainfall events, once the soils became fully saturated, which happened relatively quickly based on the matric potential data, the hydraulic heads increased sufficiently to increase the flow in the land drains. The land drains delivered nitrate from stores in the subsurface overlying lower permeability horizons, which increased with increasing land drain flow. This caused corresponding increases in loads in the stream, which were relatively high because of the high proportion of interflow contributing to the total flow, as determined by the chemical hydrograph separation. The concentration of nitrate in the stream was diluted in high flow due to dilution of the interflow with overland flow, although the loads delivered via the land drains continued to increase.

Phosphorus was initially washed into the land drain system from the surface via macropores and preferential flowpaths until the sources of the loads began to be depleted. By this stage, the soils

were becoming saturated leading to saturation excess overland flow, and a greater emphasis on the overland flow pathway for the delivery of phosphorus.

During winter baseflow conditions, when water tables increased, so too did the proportion of shallow groundwater and transition zone water. The interflow contribution remained high however, with continued high nitrate loads. During winter events, nitrate sources in the upper soils began to be depleted, as happened in the upper catchment area of the Mattock, but there was no equivalent depletion in the stores at the bedrock-subsoils boundary. Higher loads from small point sources contributing nutrients to the transition zone may have been a factor. Phosphorus loads increased due to the generation of overland flow.

9.6.3 Artificial drainage

The interflow pathway contributions are heavily influenced by the artificial land drainage network and in reality are only likely to be significant in hydrological events where there is a land drain (or the transition zone) present to speed up the lateral transport processes. Where the drainage network is present, the interflow contributions have been found to be relatively large. The land drains may drain the soils and subsoils, as in the Mattock catchment, or may drain the transition zone as in the case of Gortinlieve and Glen Burn. Where land drainage is absent, as in parts of the Gortinlieve catchment, the soils and subsoils quickly fill to capacity and water is discharged as return flow.

Sampling in the land drains highlighted that there was a first flush effect for both nitrate and SRP in interflow with the onset of rain: nitrate being delivered from stores above low permeability horizons and SRP being washed in through macropores. Flushing effects for nitrate in the subsurface have been widely observed, but few studies have tried to explain the hydrological dynamics of the phenomenon at the hillslope and catchment scale (Ocampo et al., 2006).

As described in Section 2.4, it is widely reported from other countries that field drains are important for the delivery of nutrients to streams, but there is little in the literature to describe the processes or to link hillslope-scale findings with catchment-scale impacts, such as have been achieved in this research. This research has provided a mechanistic explanation for the increased nitrate in ditches and seeps that were reported in Mellander et al. (2012), and suggests that the impacts of low permeability clayey layers are often more widespread in poorly productive catchments than reported by Melland et al. (2012b). The findings highlight that the common understanding that the dilution of nitrate in streams at high flows is because it is delivered via a groundwater pathway (Soulsby et al., 2003a, Tesoriero et al., 2009) is not always appropriate in poorly drained catchments. It is acknowledged, however, that differences in the use of the term

groundwater between scientists of different disciplines, e.g. water below the permanent water table versus temporary perched saturated areas in the subsurface, may also be a factor (Barthel, 2014).

This study has also newly identified that the hydrogeological setting into which the drainage has been developed is a major driver for drain nutrient dynamics, and may be a useful predictor for drain management in the future. The role of field drainage in the delivery of nutrients will be an important consideration in the coming years as Ireland seeks to meet its Food Harvest 2020 objectives by bringing more marginal land into production through further development of agricultural drainage (Ibrahim et al., 2013, Tuohy et al., 2013).

9.6.4 Transition zone

It was highlighted in the literature review (Section 2.5) that there was little information available about the role of the transition zone, as it is defined in Ireland. With the exception of alluvial deposits, the transition zone has been identified as the most permeable geological horizon in the subsurface in catchments underlain by poorly productive bedrock aquifers (Comte et al., 2012). The transition zone was found to operate differently in two different hydrogeological scenarios in these catchments. In groundwater recharge zones, water in the transition zone was perched, and its chemistry and hydrological response time was more similar to interflow than bedrock groundwater. The underlying competent bedrock acted as a barrier to the downward infiltration of flow and nutrients ensuring that it was an important lateral transport pathway. The transition zone contained nitrate and SRP where it was overlain by thin soils and subsoils; elsewhere nitrate was more important. If the fill and spill flow mechanism (Tromp-van Meerveld and McDonnell, 2006) is applicable in Ireland, it is likely that it will occur in this scenario. Further research would be required to confirm.

In contrast, in groundwater discharge zones in stream valleys where there were upward hydraulic gradients from the bedrock, the transition zone was better connected hydraulically to the shallow groundwater, and the differentiation between them, in terms of their contribution to the stream, was less important. In these environments, the signature of the transition zone flowpath was the same as the shallow groundwater and in essence, the transition zone was simply a discharge pathway for the deeper bedrock groundwater. In the poorly productive aquifers, groundwater in this type of transition zone was typically lower in nutrients than that in the transition zone in the groundwater recharge zones, which is likely to be because of the lower transmissivity in the bedrock in the first instance, which limited the infiltration of flow and nutrients and potentially provided opportunity for attenuation.

Although the transition zone may not be universally present in all catchments in the formal sense as a relatively high transmissivity layer (as in the lower Mattock and Glen Burn catchments), it still marks an important permeability boundary between the subsoils and the bedrock that presents a barrier to downward infiltration and acts as a store for nutrients. In these cases, return flow is likely to develop when rock is close to the surface and the subsoils are fully saturated; these environments are also typically suited for the installation of artificial drainage networks, as was found in the Glen Burn, which in turn deliver the nutrient stores (and waters with the transition zone chemical signature) to the stream. A partial, barrier-type transition zone was also identified in the Nuenna karst catchment, but due to the high permeability of the underlying karst bedrock, it was not laterally continuous and therefore did not act as a significant delivery pathway to the stream (Section 5.4).

9.6.5 Shallow and deep groundwater

The shallow and deep groundwater pathways were less of a focus in this research although were considered as part of the development of the conceptual models and in the hydrograph separation techniques. These pathways were largely researched by another *Pathways Project* colleague (Alison Orr) and a discussion of her findings, which is also reported in the final project report (Deakin et al., 2014), is provided here for completeness.

In practice, in the catchments underlain by poorly productive aquifers, the shallow and deep groundwater pathways were found to operate mainly as a single interconnected hydraulic unit that had slightly lower transmissivities with depth, but with similar chemical signatures and nutrient concentrations (Orr, 2014). Although this is important from a groundwater resource or groundwater receptor perspective, it was found to be less of a factor in the delivery of nutrients to streams. Interactions with the stream depended on there being a connection via a fault or other major geological structure. In the karst catchment, the deep groundwater was very similar chemically to the water discharging at the springs, which in turn supplied the vast majority of water to the stream (Deakin et al., 2014).

This suggests that the bedrock structure may play a greater role in deep groundwater pathway functioning than the depth, when the stream is the receptor of interest. The *Pathways Project* did not include a catchment underlain by a locally important aquifer, however, and it is anticipated that the shallow groundwater pathway is likely to be more significant in these environments.

9.7 Pathways modelling framework

This research has provided new insights into the near-surface pathways, and has informed the pathways hydrological and contaminant modelling at the core of the *Pathways Project* catchment

management support tools. The modelling must by necessity be a simplification of the conditions found in the field, and must represent what is in reality, a hydro(geo)logical pathway continuum. The degree of complexity that can be incorporated is therefore limited, but yet it must be fit for purpose to adequately separate the pathways for the purposes of modelling the dominant contaminant transport mechanisms, to enable the resource management efforts to be focussed on areas of greatest impact. The following section summarizes very briefly how these research outcomes have influenced the modelling. Although the author contributed to the conceptualization in the work described, ultimately the methods used in the modelling were determined by *Pathways Project* colleagues developing the models, so only a brief summary is presented for completeness to highlight the relevance of this research.

9.7.1 Flow modelling

The overland flow pathway was modelled in a water balance framework as predominantly a soil moisture excess hydrological process. The interflow pathway was subdivided in the model into a slower flow contribution from the soil and subsoil matrix, and a quicker flow component from the soils and subsoils via the drainage network. The contribution from the bedrock groundwater was modelled as two separate pathways, with the deep groundwater having a slower response than the shallow groundwater.

In practice in the poorly productive aquifers, the different bedrock groundwater response times identified through the hydrological modelling may actually represent quicker flow from the larger hydraulically active fractures and the upper few metres of bedrock (the transition zone), versus much slower flow through the smaller diffuse fractures, rather than a differentiation based on depth. A similar differentiation arises in the karst catchment where the two pathway response times are likely to be governed by a quicker component via the conduits and a slower component via the diffuse fracture network. However, from the perspective of the stream, the spatial orientation of the slower and faster transport networks in the bedrock is less important in the model than the fact that they are present and that they contribute flow and contaminants to the stream at different rates than the rest of the bedrock.

Modelling the transition zone was a little more complex given the two subtypes that have been indentified in this research. In groundwater discharge zones, the transition zone was found to be essentially part of the quicker bedrock groundwater flow component, and it was therefore recommended that it be incorporated with the shallow groundwater pathway. In the groundwater recharge zones, the transition zone was found to comprise water that had infiltrated from the soils and subsoils, and therefore more closely resembled interflow. The higher hydraulic conductivity within the transition zone layer suggested it was best included with the quicker flow

drainage network within interflow. This was not ideal as the response time in the drainage network is likely to be quicker than in the transition zone, but nevertheless, the transition zone horizon is often targeted in poorly productive aquifer settings for drainage purposes, and therefore this approach was considered adequate as a first approximation.

9.7.2 Contaminant modelling

In catchments underlain by poorly productive aquifers and low permeability soils and subsoils, it was recommended that nitrate transport be modelled with the quicker component of interflow, i.e. incorporating the drain flow and transition zone pathways, and with the shallow groundwater pathway where the rock is close to the surface. It is probable that in the catchments underlain by the locally important aquifers, nitrate in shallow groundwater is also important. It was also recommended that phosphate be modelled as being delivered primarily via overland flow, with a contribution from the shallow groundwater where rock is close to the surface, and in field drains elsewhere.

In catchments underlain by more permeable bedrock aquifers, soils and subsoils, nitrate is more frequently delivered via the shallow and deep groundwater pathways, as the interflow pathway is typically less significant. In these catchments, phosphate can be present in shallow groundwater where rock is close to the surface, and in overland flow on saturated soils in groundwater discharge areas. It can also be present in deeper groundwater in karst areas where there is direct recharge of phosphate-rich surface waters via swallow holes or other point recharge locations.

9.8 Novel aspects of this research

9.8.1 Development of the concepts of near-surface pathways

This research has provided new insights into the role of the interflow, artificial drainage and transition zone pathways, and has further developed the generic conceptual model previously in use in Ireland. The research has been carried out in representative catchments with relatively low agricultural intensity rather than in controlled hydrologically isolated plots, which is often the norm, so that direct relationships could be made with catchment stream flows and the results would be representative of the wider conditions in the field. Although this research has been carried out in four catchments on the island of Ireland, this improved understanding will also be applicable in other countries with comparably complex geology, rich glacial history and temperate climates, such as the United Kingdom and other parts of western Europe.

9.8.2 Integration of several different methods

The application of several different techniques in this research, at several scales and in different catchments, has provided a comprehensive improved understanding of the nature of the interflow pathway, as well as its role in nutrient transport. This was consistent with the recommendations from several studies that different methods should be combined (Haygarth et al., 2005, Doody et al., 2012, Beven and Germann, 2013, Bracken et al., 2013), especially hydrograph separation methods (Burns, 2002), although it is rare that it is carried out in practice (McGlynn et al., 2002). To the best of the author's knowledge, with the exception of one study carried out in a very different type of hydrogeological regime — in a steep-sided, non-glaciated, forested catchment in New Zealand (McDonnell et al., 1991) — corroboration of results of pathways separations using soil moisture dynamics has not featured in the literature. Similarly, no reports of research integrating pathways separations derived from hydrological modelling with the results of the chemical hydrograph separations were found. The integration of all three methods, as well as the direct sampling in the near-surface pathways, has integrated field-scale process understanding with catchment-scale generalizations to provide a robust understanding of the near-surface pathway dynamics in these types of hydrogeological settings that has not been achieved before.

9.8.3 Modification of the chemical hydrograph separation approach

A new modification of the EMMA approach (Christophersen et al., 1990) was developed for use in this research that recognized the differences in data availability in the study catchments. The approach was a conceptual model-based, stream-focussed approach, which was used in the catchments where the end member sampling data were limited. The approach took the stream chemistry as the starting point and used the available end member samples, in the context of the conceptual model, to try to explain what was happening at different points in the hydrograph, rather than initially determining the end members independently based on spot samples from the catchment, as is the more traditional approach. This approach was found to be robust, although depended on a strong conceptual model being developed.

9.8.4 Use of the flow duration curve for pathways identification

Although flow duration curves (FDCs) have been widely used to infer different pathway contributions using various indices (Smakhtin, 2001), no previous studies were found that had identified the different pathways using the changes in slopes of the curve on a long-linear plot, and subsequently verified them using independent field methods, as was demonstrated here for the Glen Burn and Mattock catchments. The separated FDCs were subsequently used successfully

to support the generation of annual estimates for the chemical hydrograph separations for comparing with modelled outputs.

9.8.5 Use of the conceptual model as a framework for catchment management

The development and use of catchment conceptual models[12] that consider a full hydro(geo)logical profile has been a fundamental part of this research in all catchments. The models have helped to provide a consistent framework, within and between catchments, and for relating results from one method to those of another. It is argued on the basis of this research that, as the hydrological and hydrogeological regimes are part of the same continuum, it is no longer adequate to consider catchment hydrological and processes and nutrient management approaches from the traditional top-down perspective; rather a bottom-up approach incorporating the full geological profile from the deep bedrock upwards is the only justifiable approach.

The development of conceptual models is fundamental in groundwater studies (Freeze and Cherry, 1979), but they are not commonly reported in the catchment science and hydrology literature. Hydrological studies often tend to be carried out in isolation, which, it is acknowledged, leads to limitations in their outcomes (McGlynn et al., 2002). Allen et al. (2014), for example, suggested that groundwater conceptual models should inform the design of effective programmes of measures in catchments where the baseflow index (BFI) is >0.5, because of the greater influence of groundwater in the travel times of pollutants from source to receptor. It is contested here, however, that the subsurface flowpaths are also important where the BFI is <0.5. For example, the interaction of shallow groundwater and the near-surface pathways in the inter-drumlin areas in the Glen Burn catchment is a primary driver in stream nutrient dynamics; and the different processes in the transition zone in the Gortinlieve catchment in groundwater recharge areas, versus groundwater discharge areas, are a critical factor in nitrate transfer because of the transmissivity, residence times and attenuation potential in the bedrock in the different settings.

A new approach to defining the landscape that is analogous to the use of the conceptual model in this research has been recently proposed by Zehe et al. (2014). They suggested that different parts of the landscape operate in functionally similar ways because they have been exposed to similar flows of energy, water and nutrients in the past and present, and have likely therefore adapted in the same self-organizing manner. The authors argue that if 'type sites' from each major landscape unit, or elementary functional units (EFU), are examined in detail, it should be possible to predict the overall catchment functioning. However, although factors such as

[12] It is important to recall here that the term conceptual model has been used in this research in the hydrogeological sense, i.e. a simple three-dimensional understanding of how a catchment functions, rather than the hydrological definition used by Beven (1993), i.e. a lumped hydrological model. The differences in the definitions are further discussed in Barthel (2014).

radiation, bedrock topography and geology are included, the EFUs are differentiated mainly on the basis of their soils and vegetation communities.

It is suggested here that the EFUs could be improved by placing the deeper three-dimensional (or four-dimensional) hydrogeological framework used in this research more at the core of their approach. This is because the soils and vegetation communities are fundamentally established on the basis of the underlying bedrock and its hydrogeological regime. However, it is acknowledged that the incorporation of vegetation and climate aspects is potentially a very useful addition to the development of conceptual hydrogeological models.

In a similar vein, in another recent paper, Schulte et al. (2014) described the concept of functional land management (FLM), in which they consider land use and soils as the driving factors in a framework for balancing ecosystem services with the sustainable intensification of agriculture. They highlight, for example, that some soils have further capacity for denitrification and are therefore suitable for agricultural intensification, while other soils may be better suited to improving biodiversity values. It is suggested here that their approach could also be improved by integrating a deeper conceptualization of the hydrogeology, because it is the pathways that deliver the nutrients in the soils to the streams that are the critical factor, not necessarily the soils alone. For example, denitrification can also take place in the bedrock, and soils that are considered to be favourable for denitrification in a lower landscape position in a groundwater discharge zone, may not attenuate to the same degree in an upper landscape position in a groundwater recharge zone.

A commitment to a deeper integration of the full hydrogeological profile in catchment studies, in a conceptual model framework, would go a long way towards addressing the problem identified recently by Barthel (2014) that groundwater and surface water disciplines are still not truly integrated. Until such time as that is addressed, it is the conclusion of this researcher that significant further breakthroughs in catchment science will not be achieved.

9.9 Recommendations for further research

Ten recommendations for further work are proposed which are described below.

1. Policy solutions for management of artificial drainage

This research has identified that land drains and ditches are an important pathway for the contribution of flow and nutrients to streams. Artificial drainage is however, an intrinsic part of the farming landscape to the extent that in some areas, grant schemes have been made available in the past to farmers to develop drainage networks to make farms more productive (Bruton and

Convery, 1982). Development of new drainage systems is highly likely in Ireland in the coming years with the lifting of the dairy quota and the Food Harvest 2020 objectives (Ibrahim et al, 2013). Further research is required to look at practical ways of managing nutrient losses via artificial drainage schemes. Edge of field wetlands for example, have been shown to be effective in reducing phosphorus loss from drains and ditches in the United Kingdom (Ockenden et al, 2012). The use of permeable reactive interceptors in drains for reducing nitrate losses, which have added benefits in relation to reduction of greenhouse gas losses, are also currently being trialled in a major Irish study (Fenton et al, 2014).

However the issue is complex. A recent Irish study in two contrasting catchments found that ditches were typically over-engineered which, it was suggested, was likely to lead to a reduction in nutrient transfer (Shore et al, 2014). Removal of fine sediment from the ditches was also considered in that study to be a useful nutrient reduction strategy, as well as the somewhat contradictory strategy of maintaining vegetation to encourage nutrient uptake. Ditches are also considered to provide important ecosystems habitats in agricultural landscapes (Herzon and Helenius, 2008). In any event, effective solutions will need to be acceptable to farmers and will need to be developed in such a way that farm productivity is not compromised. New research programmes should therefore incorporate both scientific and stakeholder engagement components.

2. Locally Important aquifer

This research has provided insights into how the near-surface pathways operate in catchments underlain by poorly productive aquifers where significant intermixing occurs, and in permeable karst settings where their role is limited. To complete the understanding, further research should be carried out in a catchment underlain by a locally important aquifer, with moderate to low permeability subsoils, which would represent an intermediate type hydro(geo)logical flow regime. It is anticipated that in these types of catchments, the shallow groundwater pathway may be more important than in the catchments underlain by poorly productive rocks, there may be less intermixing in the near surface, longer residence times, and therefore greater opportunity for nutrient attenuation. Such a catchment was not included initially in this research because there was none that had been previously instrumented with the appropriate borehole monitoring infrastructure.

3. Residence times and nutrient lag times

Previous reports in the literature have suggested that nutrient residence and transfer times in the landscape may be significant, and that the lag time between when a management measure is implemented and when positive effects may be recognized, may exceed current WFD

expectations (Schulte et al., 2010, Fenton et al., 2011, Ward et al., 2013). However, this research has found preliminary evidence that the residence times in the near-surface pathways in poorly drained catchments may be relatively short; for example, phosphorus was quickly washed through the soils and subsoil land drains as the events progressed. This has been corroborated by a recent trial in Austria to determine whether monitoring water quality in land drains could be an appropriate means of achieving a more rapid and representative indication of the effectiveness of programmes of measures (Gabriel et al., 2013). This may also be a useful approach to consider in the poorly drained catchments in Ireland.

Future work should consider the issue of lag times for nitrate and phosphate in the near-surface pathways in Irish catchments in different hydrogeological settings. This would provide evidence to support realistic expectations for when ecological benefits might be achieved in response to management measures in the Irish context. It could also be used to develop a set of recommendations for use of the drainage network as part of catchment-scale monitoring programmes where measures have been, or are to be, implemented.

4. Temporal variability in end members

Preliminary work on assessing the temporal variability of the end members in the mixing model for the Mattock catchment in particular, has been carried out as part of this research. Further field research and data analysis would be useful to try to develop a robust statistical means of incorporating the natural temporal variability in the end members into the mixing analysis approach. This may provide more dynamic pathways separations that could potentially be used to provide further insight into the first flush effect.

5. Transition zone dynamics

Further investigation into the hydrological role of the transition zone in stream flow generation would be beneficial to support the conceptual model, both in the study catchments already studied, but also perhaps in some of the other EPA poorly productive aquifer monitoring sites where the borehole infrastructure has already been installed (i.e. the Ryewater, New Village, Glencastle and Dripsey catchments). Higher resolution water balance and chemistry data should be collected in the transition zone and in the river to contrast with the available continuous groundwater level data.

6. Delivery mechanisms for impacts of small point sources

The monitoring data for the ditches, land drains and boreholes in the transition zone in the Mattock and Gortinlieve catchments all indicated that the transition zone is an important nutrient storage and transport pathway in catchments underlain by poorly productive aquifers. The

question remains, however, as to the relative impacts of small point sources versus diffuse sources on water in this zone, which is an important consideration from a nutrient management perspective. Further collaborative work with an ongoing project in Trinity College Dublin to look at the impacts of wastewater treatment systems on rivers and wells would be beneficial to consider the importance of the transition zone and/or the artificial drainage networks as possible pathways and delivery mechanisms.

7. Hyporheic zone

In the three poorly productive catchments, the alluvial deposits near the stream channels are important sources of nitrogen. Whether or not that nitrogen is delivered to the stream through the alluvium (as opposed to through artificial drainage) depends on complex biogeochemical interactions and nutrient cycling in the hyporheic zone (Zarnetske et al., 2011). The hyporheic zone was not considered as part of this study, but future research into its dynamics in the four study catchments, particularly its role in controlling attenuation processes in Irish conditions, would be a useful addition to the existing *Pathways Project* body of knowledge. It would be interesting to determine, for instance, whether the importance of the land drains for the delivery of nitrate in the poorly drained catchments outweighs the influence of the hyporheic zone, because the latter is largely bypassed in high flows when the majority of the nitrate is transferred via the drainage network.

8. Land drain problem map

Further development of the land drain problems map is required to test the model hypotheses in other catchment settings (refer to Appendix 2).

9. Landscape management units

Future thought could be given to framing an alternative and more robust landscape management unit approach that combines the conceptual model approach used here with the additional vegetation, ecosystem and biodiversity factors raised by Zehe et al. (2014) and Schulte et al. (2014), as discussed in Section 9.8.5. These units would encompass all the elements of sustainable environmental management, and would be fully grounded in hydro(geo)logical, soil science, agricultural production and ecological disciplines. They could be used as a landscape management unit that encompasses all these values, and would serve as a 'one stop shop' for environmental management.

10. Other research

Recent research by Tayfur et al. (2014) found that significant improvement was made to their rainfall-runoff models by incorporating soil moisture information at depths of 10, 20 and 40 cm.

Further collaborative work could consider using the soil moisture and tension data for the Mattock to further constrain the catchment modelling tool.

The conceptual model for the Glen Burn drumlin catchment could be improved further by continuously monitoring the near-surface pathways in the inter-drumlin areas using shallow piezometers, soil moisture monitoring equipment and chemistry sampling. Drumlin landscapes are common in Ireland so this would be a useful extension to the current dataset.

Further exploration of the available soil moisture dynamics data may yield additional information on, for example, soil drainage characteristics at higher flows, the role of the capillary fringe and the groundwater ridging effect in Irish soils.

9.10 Concluding remarks

At the end of this thesis, it is appropriate to recall the Gillham-McDonnell public discourse referred to in Chapter 2 about their different perspectives on the role of the capillary fringe versus macropores in stream flow generation, which stemmed from their different experiences in different catchments. Although three of the four *Pathways Project* study catchments were selected in poorly drained catchments, such that they would be representative of catchments in Ireland, it has transpired that they are all spectacularly unique. As outlined by Hrachowitz et al. (2013), it is only by finding the common attributes, using different techniques across multiple scales, rather than dwelling on differences, that we can begin to generalize within catchments, which is the first step towards bringing the science into the political decision-making arena. It is hoped that this thesis has contributed to this first step by achieving a better understanding of the near-surface pathways and their role in nutrient transfer to streams, especially in catchments underlain by poorly productive aquifers. Yet it is clear that it has raised even more questions... and that there is much more work to do.

10 References

ABDUL, A. S. & GILLHAM, R. W. 1989. Field studies on the effects of the capillary fringe on streamflow generation. *Journal of Hydrology,* 112.

ADDISCOTT, T. M. 1996. Fertilizers and nitrate leaching in agricultural chemicals and the environment. *In:* HESTER, R. E. & HARRISON, R. M. (eds.) *Issues in Environmental Science and Technology.* Cambridge, UK: Royal Society of Chemistry.

ADDISCOTT, T. M., BROCKIE, D. & CATT, J. A. 2000. Phosphate losses through field drains in a heavy cultivated soil. *Journal of Environmental Quality,* 29, 522-532.

AHUJA, L. R. & ROSS, J. D. 1983. Effect of subsoil conductivity and thickness on interflow pathways, rates and source areas for chemicals in a sloping layered soil with seepage face. *Journal of Hydrology,* 64, 189-204.

ALLEN, D. J., DARLING, W. G., DAVIES, J., NEWELL, A. J., GOODDY, D. C. & COLLINS, A. L. 2014. Groundwater conceptual models: implications for evaluating diffuse pollution mitigation measures. *Quarterly Journal of Engineering Geology and Hydrogeology,* 47, 65-80.

ALLEN, R. G., PEREIRA, L. S., RAES, D. & SMITH, M. 1998. Crop evapotranspiration — guidelines for computing crop water requirements. *FAO Irrigation and Drainage Paper 56.* Rome.

ANDERSON, M. G. & BURT, T. P. 1980. Interpretation of recession flow. *Journal of Hydrology,* 46, 89-101.

ANDERSSON, H., BERGSTRÖM, L., DJODJIC, F., ULÉN, B. & KIRCHMANN, H. 2013. Topsoil and Subsoil Properties Influence Phosphorus Leaching from Four Agricultural Soils. *Journal of Environmental Quality,* 42, 455-463.

ANSELL, J. & WHARTON, F. 1992. *Risk: Analysis, Assessment and Management.,* Chichester, John Wiley & Sons.

APHA, WPCF & WEF 2005. *Standard methods for the examination of water and wastewater,* American Public Health Association, Water Pollution Control Federation and Water Environment Federation.

ARCHBOLD, M., BRUEN, M., DEAKIN, J., DESTA, M., FLYNN, R., KELLY-QUINN, M., MISSTEAR, B., MOCKLER, E., ORR, A., PACKHAM, I. & THOMPSON, J. J. D. 2014. The Pathways Project: synthesis report. Dublin: Environmental Protection Agency.

ARCHBOLD, M., BRUEN, M., DEAKIN, J., DOODY, D., FLYNN, R., KELLY-QUINN, M., MISSTEAR, B. & OFTERDINGER, U. 2010. Contaminant movement and attenuation along pathways from the land surface to aquatic receptors - a review. Strive Research Report 2007-WQ-CD-1-S1. Wexford, Ireland: Environmental Protection Agency.

ASLIBEKIAN, O. 1999. Regional assessment of groundwater recharge. *GSI Groundwater Newsletter,* 35, 8-11.

AUBERT, A. H., GASCUEL-ODOUX, C., GRUAU, G., AKKAL, N., FAUCHEUX, M., FAUVEL, Y., GRIMALDI, C., HAMON, Y., JAFFREZIC, A., LECOZ-BOUTNIK, M., MOLENAT, J., PETITJEAN, P., RUIZ, L. & MEROT, P. 2013. Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high frequency, multisolute 10 yr-long monitoring study. *Hydrology and Earth System Sciences,* 17, 1379-1391.

BACHMAIR, S. & WEILER, M. 2012. Hillslope characteristics as controls of subsurface flow variability. *Hydrol. Earth Syst. Sci.,* 16, 3699-3715.

BARNES, B. S. 1939. The structure of discharge-recession curves. *Transactions of the American Geophysical Union,* 20, 721-725.

BARTHEL, R. 2014. HESS Opinions "Integration of groundwater and surface water research: an interdisciplinary problem?". *Hydrology and Earth System Sciences Discussions,* 11, 2011-2044.

BAZEMORE, D. E., ESHLEMAN, K. N. & HOLLENBECK, K. J. 1994. The role of soilwater in stormflow generation in a forested headwater catchment: synthesis of natural tracer and hydrometric evidence. *Journal of Hydrology,* 162, 47-75.

BEARDMORE, N. 1851. *Manual of Hydrology,* London, Waterlow and Sons.

BEHRENDT, H., BACH, M., OPITZ, D. & PAGENKOPF, W. G. 2004. Maßgebliche anthropogene Einflüsse auf die Gewässerqualität. *In:* BECKER, H. & LAHMER, W. (eds.) *Wasser- und Nährstoffhaushalt in Elbegebiet und Möglichkeiten zur Stoffeintragsminderung. Konzepte zur nachhaltigen Entwicklung einer Flusslandschaft, Band 1.* Berlin: Weißensee Verlag.

BENSKIN, C., GRANT, F., JONCZYK, J., LLOYD, C. & OUTRAM, F. N. 2013. Investigating catchment storm responses across the national demonstration test catchments platform. Eden Demonstration Catchments Programme, UK.

BEVEN, K. 1993. Prophecy, reality and uncertainty in distributed hydrological modelling. *Advances in Water Resources,* 16, 41-51.

BEVEN, K. 2006a. A manifesto for the equifinality thesis. *Journal of Hydrology,* 320, 18-36.

BEVEN, K. J. 1989. Interflow. *In:* MOREL-SEYTOUX, H. J. (ed.) *Unsaturated Flow in Hydrologic Modeling.* Springer Netherlands.

BEVEN, K. J. 2006b. Streamflow generation processes. *In:* MCDONNELL, J. J. (ed.) *Benchmark papers in hydrology I.* UK: International Association of Hydrological Sciences.

BEVEN, K. J. & GERMANN, P. 2013. Macropores and water flow in soils revisited. *Water Resources Research,* 49, 3071-3092.

BILOTTA, G. S., BRAZIER, R. E. & HAYGARTH, P. M. 2008. Rethinking the Contribution of Drained and Undrained Grasslands to Sediment-Related Water Quality Problems. *Journal of Environmental Quality,* 37, 906-914.

BLONQUIST JR, J. M., JONES, S. B. & ROBINSON, D. A. 2006. Precise irrigation scheduling for turfgrass using a subsurface electromagnetic soil moisture sensor. *Agricultural Water Management,* 84, 153-165.

BLUME, T., ZEHE, E. & BRONSTERT, A. 2009. Use of soil moisture dynamics and patterns at different spatio-temporal scales for the investigation of subsurface flow processes. *Hydrology and Earth System Sciences,* 13, 1215-1234.

BOOLTINK, H. W. G. 1995. Field monitoring of nitrate leaching and water flow in a structured clay soil. *Agriculture, Ecosystems & Environment,* 52, 251-261.

BOORMAN, D., HOLLIS, J. M. & LILLY, A. 1995. Hydrology of soil types: a hydrologically based classification of the soils of the United Kingdom. Wallingford, UK: Institute of Hydrology.

BOWES, M. J., SMITH, J. T., JARVIE, H. P. & NEAL, C. 2008. Modelling of phosphorus inputs to rivers from diffuse and point sources. *Science of the Total Environment,* 395, 125-138.

BRACKEN, L. J., WAINWRIGHT, J., ALI, G. A., TETZLAFF, D., SMITH, M. W., REANEY, S. M. & ROY, A. G. 2013. Concepts of hydrological connectivity: Research approaches, pathways and future agendas. *Earth-Science Reviews,* 119, 17-34.

BRODIE, R. S. & HOSTETLER, S. 2005. A review of techniques for analysing baseflow from stream hydrographs. Canberra, Australia: Bureau of Rural Sciences.

BROOKS, R. H. & COREY, A. T. 1964. Hydraulic properties of porous media. Hydrology Paper 3. Fort Collins, CO: Colorado State University.

BRUTON, R. & CONVERY, F. J. 1982. *Land Drainage Policy in Ireland,* Dublin, ESRI.

BSI 1994. Soil Quality. Part 3: Chemical methods. *Determination of dry matter and water content on a mass basis by a gravimetric method (BS7755-3.1).* London, UK: British Standards Institution.

BURKE, W., MULQUEEN, J. & BUTLER, P. 1974a. Aspects of the hydrology of a gley on a drumlin. *Irish Journal of Agricultural Research,* 13, 215-229.

BURKE, W., MULQUEEN, J. & BUTLER, P. 1974b. Fertiliser losses in drainage water from a surface water gley. *Irish Journal of Agricultural Research,* 13, 203-214.

BURNS, D. A. 2002. Stormflow-hydrograph separation based on isotopes: the thrill is gone - what's next? *Hydrological Processes,* 16, 1515-1517.

BUSS, S. R., RIVETT, M. O., MORGAN, P. & BEMMENT, C. D. 2005. Attenuation of nitrate in the sub-surface environment. UK: Environment Agency.

BUTTLE, J. M. 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. *Progress in Physical Geography,* 18**,** 16-41.

BUTTLE, J. M. 2006. Isotope Hydrograph Separation of Runoff Sources. *Encyclopedia of Hydrological Sciences.* John Wiley & Sons, Ltd.

BYRNE, A. 2011. *River hydrograph analysis using chemical data.* BEng, Trinity College.

CARTWRIGHT, I., GILFEDDER, B. & HOFMANN, H. 2014. Contrasts between estimates of baseflow help discern multiple sources of water contributing to rivers. *Hydrology and Earth System Sciences,* 18**,** 15-30.

CAVAZZA, L., PATRUNO, A. & CIRILLO, E. 2007. Field capacity in soils with a yearly oscillating water table. *Biosystems Engineering,* 98**,** 364-370.

CHIN, D. A. 2006. *Water-Resources Engineering*, Pearson Prentice Hall.

CHRISMAN, B. & ZREDA, M. 2013. Quantifying mesoscale soil moisture with the cosmic-ray rover. *Hydrology and Earth System Sciences,* 17**,** 5097-5108.

CHRISTOPHERSEN, N., NEAL, C., HOOPER, R. P., VOGT, R. D. & ANDERSEN, S. 1990. Modelling streamwater chemistry as a mixture of soilwater end-members — A step towards second-generation acidification models. *Journal of Hydrology,* 116**,** 307-320.

CLABBY, K. J., BRADLEY, C., CRAIG, M., DALY, D., LUCEY, J., MCGARRIGLE, M., O'BOYLE, S., TIERNEY, D. & BOWMAN, J. 2008. Water quality in Ireland 2004-2006. Wexford: Environmental Protection Agency.

COMTE, J.-C., CASSIDY, R., NITSCHE, J., OFTERDINGER, U., PILATOVA, K. & FLYNN, R. 2012. The typology of Irish hard-rock aquifers based on an integrated hydrogeological and geophysical approach. *Hydrogeology Journal,* 20**,** 1569-1588.

COX, J. W., VARCOE, J., CHITTLEBOROUGH, D. J. & VAN LEEUWEN, J. 2005. Using gypsum to reduce phosphorus in runoff from subcatchments in south Australia. *Journal of Environmental Quality,* 34**,** 2118-2128.

CROCKFORD, L. 2009. *Conceptual model of the Mattock catchment.* MSc, Queens University Belfast.

CUADRA, P. E. & VIDON, P. 2011. Storm nitrogen dynamics in tile-drain flow in the US Midwest. *Biogeochemistry,* 104**,** 293-308.

CUENCA, R. & NOILHAN, J. 1991. Use of Soil Moisture Measurements in Hydrologic Balance Studies. *In:* SCHMUGGE, T. & ANDRÉ, J.-C. (eds.) *Land Surface Evaporation.* Springer New York.

CUTHBERT, M. O., MACKAY, R., TELLAM, J. H. & THATCHER, K. E. 2010. Combining unsaturated and saturated hydraulic observations to understand and estimate groundwater recharge through glacial till. *Journal of Hydrology,* 391**,** 263-276.

DAFF 2011. Food Harvest 2020 - a vision for Irish agri-food and fisheries. Dublin: Department of Agriculture, Fisheries and Food.

DAHLKE, H. E., EASTON, Z. M., LYON, S. W., TODD WALTER, M., DESTOUNI, G. & STEENHUIS, T. S. 2012. Dissecting the variable source area concept – Subsurface flow pathways and water mixing processes in a hillslope. *Journal of Hydrology,* 420-421**,** 125-141.

DALY, D. A Healthy Catchment Initiative for Ireland - Making Integrated Catchment Management Happen. Groundwater and Catchment Management. 33rd Annual Conference of the International Association of Hydrogeologists (Irish Group), 2013 Tullamore, Co. Offaly, Ireland. IAH (Irish Group).

DALY, E. P. 1994a. Groundwater resources of the Nore River Basin. Dublin, Ireland: Geological Survey of Ireland.

DALY, E. P. 1994b. Groundwater resources of the Nore River basin. Dublin: Geological Survey of Ireland.

DALY, K., JEFFREY, D. & TUNNEY, H. 2001. The effects of soil type on phosphorus sorption capacity and desorption dynamics in Irish grassland soil. *Soil Use and Management,* 17**,** 12-20.

DARCY, H. 1856. *Les fountaines publique de la ville de Dijon,* Paris, Dalmont.

DAVISON, P. S., WITHERS, P. J., LORD, E. I., BETSON, M. J. & STRÖMQVIST, J. 2008. PSYCHIC–A process-based model of phosphorus and sediment mobilisation and delivery within agricultural catchments. Part 1: Model description and parameterisation. *Journal of Hydrology,* 350**,** 290-302.

DEAKIN, J. 1994. *Groundwater protection in Co. Limerick.* MSc Research MSc (Research), Trinity College.

DEAKIN, J., ARCHBOLD, M., ORR, A., O'BRIEN, R., MAHER, P., THOMPSON, J. J. D., COCCHIGLIA, L., KELLY-QUINN, M., MISSTEAR, B., OFTERDINGER, U. & FLYNN, R. 2014. Field investigations and catchment conceptual models. *Pathways Project* final report, Vol. 1. *Strive report.* Environmental Protection Agency.

DEAKIN, J., MISSTEAR, B., ARCHBOLD, M. & FLYNN, R. 2013. Hydrogeological Pathways in Two Contrasting Catchments - Implications for Management. *Groundwater and Catchment Management. 33rd Annual Conference of the International Association of Hydrogeologists (Irish Group).* Tullamore, Co. Offaly, Ireland: IAH (Irish Group).

DEAKIN, J., MISSTEAR, B., MURPHY, A., DOWLING, M. & FLYNN, R. 2010. Investigating water flow and contaminant pathways to rivers using chemical hydrograph separation. *National Hydrology Conference.* Althlone, Co. Westmeath: ICP/ICID.

DEVLIN, M. 2012. *Soil moisture assessment in an agricultural catchment, Mount Stewart, Ards Peninsula, Co. Down.* MSc, Queens University Belfast.

DI, H. J. & CAMERON, K. C. 2002. Nitrate leaching in temperate agroecosystems: sources, factors and mitigating strategies. *Nutrient Cycling in Agroecosystems,* 64**,** 237-256.

DIAMOND, J. & SHANLEY, T. 1998. Infiltration rate assessment of some major soils. End of Project Report. ARMIS 4102. Wexford: Teagasc, Johnstown Castle.

DIAMOND, J. & SILLS, P. 2001. Soil water regimes. End of Project Report. ARMIS 4479. Wexford: Teagasc, Johnstown Castle.

DILLON, T. 2010. *Quantifying flow in the Nuenna catchment.* MSc, Trinity College Dublin.

DINGMAN, S. L. 2002. *Physical Hydrology,* Prentice Hall.

DOELG, EPA & GSI 1999. Groundwater Protection Schemes. Dublin, Ireland: Department of Environment and Local Government, Environmental Protection Agency and the Geological Survey of Ireland.

DOMAGALSKI, J. L. & JOHNSON, H. M. 2012. Phosphorus and groundwater: establishing links between agricultural use and transport to streams. *In:* STUDY, A. C. T. (ed.) *Fact sheet 2012-3004.* CA, USA: USGS.

DOODY, D. G., ARCHBOLD, M., FOY, R. H. & FLYNN, R. 2012. Approaches to the implementation of the Water Framework Directive: Targeting mitigation measures at critical source areas of diffuse phosphorus in Irish catchments. *Journal of Environmental Management,* 93**,** 225-234.

DOODY, D. G., HIGGINS, A., MATTHEWS, D., FOY, R. H., PILATOVA, K., DUFFY, O. & WATSON, C. J. 2010. Overland flow initiation from a drumlin grassland hillslope. *Soil Use and Management,* 26**,** 286-298.

DOWLING, D. 2009. *Chemical hydrograph analysis.* BEng, Trinity College.

DRISCOLL, F. G. 1986. *Groundwater and Wells,* St. Paul, Minnesota, Johnson Filtration Systems Inc.

DUNNE, T. & BLACK, R. D. 1970. Partial area contributions to storm runoff in a small New England watershed. *Water Resources Research,* 6**,** 1296-1311.

DURAND, P. & TORRES, J. L. J. 1996. Solute transfer in agricultural catchments: the interest and limits of mixing models. *Journal of Hydrology,* 181**,** 1-22.

EC 2000. EU Water Framework Directive. *2000/60/EC.* European Union: Official Journal of the European Communities.

EC 2009. Environmental objectives (surface water) regulations. *S.I. No. 272 of 2009.* Ireland.

EC 2010. Environmental objectives (Groundwater) regulations. *S.I. 9 of 2010.* Ireland.

EDWARDS, A. C., WATSON, H. A. & COOK, Y. E. M. 2012. Source strengths, transport pathways and delivery mechanisms of nutrients, suspended solids and coliforms within a small agricultural headwater catchment. *Science of the Total Environment,* 434**,** 123-129.

EDWARDS, A. C. & WITHERS, P. J. A. 2008. Transport and delivery of suspended solids, nitrogen and phosphorus from various sources to freshwaters in the UK. *Journal of Hydrology,* 350, 144-153.

ELSER, J. J., BRACKEN, M. E. S., CLELAND, E. E., GRUNER, D. S., HARPOLE, W. S., HILLEBRAND, H., NGAI, J. T., SEABLOOM, E. W., SHURIN, J. B. & SMITH, J. E. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters,* 10, 1135-1142.

EPA 2005. Collon waste water discharge licence application, Attachment F1: receiving water, discharge requirements and environmental considerations, Louth County Council.

EPA 2009. Code of Practice. Waste water treatment and disposal systems serving single houses. Wexford, Ireland: Environmental Protection Agency.

EPA 2010. Water Quality in Ireland 2007-2009. *In:* MCGARRIGLE, M. L., LUCEY, J. & O'CINNEIDE, M. (eds.). Wexford, Ireland: Environmental Protection Agency.

EPA 2012. Ireland's Environment 2012 - An Assessment. *In:* LEHANE, M. & O'LEARY, B. (eds.). Wexford, Ireland: Environmental Protection Agency.

EPA 2013. Integrated Water Quality Report 2012 - South East Ireland. *In:* BOWDEN, C. (ed.). Wexford: Environmental Protection Agency.

ESHLEMAN, K. N., POLLARD, J. S. & O'BRIEN, A. K. 1993. Determination of contributing areas for saturation overland flow from chemical hydrograph separations. *Water Resources Research,* 29, 3577-3587.

FENTON, O., COXON, C. E., HARIA, A. H., HORAN, B., HUMPHREYS, J., JOHNSTON, P., MURPHY, P., NECPALOVA, M., PREMROV, A. & RICHARDS, K. 2009a. Variations in travel time for N loading to groundwaters in four case studies in Ireland: implications for policy makers and regulators. *Tearmann: Irish Journal of Agricultural Research,* 7, 129-142.

FENTON, O., RICHARDS, K. G., KIRWAN, L., KHALIL, M. I. & HEALY, M. G. 2009b. Factors affecting nitrate distribution in shallow groundwater under a beef farm in south eastern Ireland. *Journal of Environmental Management,* 90, 3135-46.

FENTON, O., SCHULTE, R. P. O., JORDAN, P., LALOR, S. T. J. & RICHARDS, K. G. 2011. Time lag: a methodology for the estimation of vertical and horizontal travel and flushing timescales to nitrate threshold concentrations in Irish aquifers. *Environmental Science & Policy,* 14, 419-431.

FENTON, O., HEALY, M. G., BRENNAN, F., JAHANGIR, M. M. R., LANIGAN, G. J., RICHARDS, K. G. & IBRAHIM, T. G. 2014. Permeable reactive interceptors: blocking diffuse nutrient and greenhouse gases losses in key areas of the farming landscape. *The Journal of Agricultural Science,* 1-11 (in press).

FINCH, T. F., GARDINER, M. J., COMEY, A. & RADFORD, T. 1983. Soils of County Meath. *Soil Survey Bulletin No. 37.* Dublin, Ireland: An Foras Taluntais.

FINN, J. 2012. *The investigation of point sources and diffuse inputs of two rivers underlain by poorly productive aquifers.* MSc MSc, Queens University Belfast.

FITZSIMONS, V., DALY, D. & DEAKIN, J. 2003. GSI guidelines for assessment and mapping of groundwater vulnerability to contamination. Dublin: Geological Survey of Ireland.

FITZSIMONS, V., DALY, D., WRIGHT, G. & HUNTER-WILLIAMS, T. Rock type versus fractures - current understanding of Irish aquifers. Groundwater in Ireland, 25th anniversary conference, 2005 Tullamore, Co. Offaly. IAH (Irish Group).

FITZSIMONS, V. & MISSTEAR, B. D. R. 2006. Estimating groundwater recharge through tills: a sensitivity analysis of soil moisture budgets and till properties in Ireland. *Hydrogeology Journal,* 14, 548-561.

FLURY, M., FLÜHLER, H., JURY, W. A. & LEUENBERGER, J. 1994. Susceptibility of soils to preferential flow of water: A field study. *Water Resources Research,* 30, 1945-1954.

FORD, D. & WILLIAMS, P. 1989. *Karst Geomorphology and Hydrology,* Cambridge, UK, Chapman and Hall.

FREER, J., MCDONNELL, J. J., BEVEN, K. J., PETERS, N. E., BURNS, D. A., HOOPER, R. P., AULENBACH, B. & KENDALL, C. 2002. The role of bedrock topography on subsurface storm flow. *Water Resources Research,* 38, 1269.

FREEZE, R. A. & CHERRY, J. A. 1979. *Groundwater,* Engelwood Cliffs, NJ, Prentice Hall.

GABRIEL, O., BRIELMANN, H., HUMMER, F., LINDINGER, H., GRATH, J. & SCHILLING, C. 2013. Tile drainage monitoring – a useful instrument to assess the effectiveness of agricultural measures to reduce nitrate emissions to surface waters? *In:* FRATERS, D. & KOVAR, K. (eds.) *Land Use and Water Quality: Reducing Effects of Agriculture.* The Hague.

GABRIELLI, C. P., MCDONNELL, J. J. & JARVIS, W. T. 2012. The role of bedrock groundwater in rainfall–runoff response at hillslope and catchment scales. *Journal of Hydrology,* 450–451, 117-133.

GALVIN, L. F. 1966. Land drainage survey. *Irish Journal of Agricultural Research,* 5, 79-88.

GALVIN, L. F. 1969. Land drainage survey II. *Irish Journal of Agricultural Research,* 8, 1-18.

GALVIN, L. F. 1971. Land drainage survey III: maps of Ireland showing the general distribution of drainage problems and of drainage schemes. *Irish Journal of Agricultural Research,* 10, 213-221.

GALVIN, L. F. 1983. The drainage of impermeable soils in high rainfall areas *Irish Journal of Agricultural Research,* 22, 161-187.

GÄRDENÄS, A. I., ŠIMŮNEK, J., JARVIS, N. & VAN GENUCHTEN, M. T. 2006. Two-dimensional modelling of preferential water flow and pesticide transport from a tile-drained field. *Journal of Hydrology,* 329, 647-660.

GARRETT, C. G., VULAVA, V. M., CALLAHAN, T. J. & JONES, M. L. 2012. Groundwater-surface water interactions in a lowland watershed: source contribution to stream flow. *Hydrological Processes,* 26, 3195-3206.

GENEREUX, D. 1998. Quantifying uncertainty in tracer-based hydrograph separations. *Water Resources Research,* 34, 915-919.

GERMANN, P. & BEVEN, K. 1981. Water flow in soil macropores I. An experimental approach. *Journal of Soil Science,* 32, 1-13.

GHEBREMICHAEL, L. T., VEITH, T. L. & HAMLETT, J. M. 2013. Integrated watershed- and farm-scale modeling framework for targeting critical source areas while maintaining farm economic viability. *Journal of Environmental Management,* 114, 381-394.

GILL, L. W., O'LUANAIGH, N., JOHNSTON, P. M., MISSTEAR, B. D. R. & O'SUILLEABHAIN, C. 2009. Nutrient loading on subsoils from on-site wastewater effluent, comparing septic tank and secondary treatment systems. *Water Research,* 43, 2739-2749.

GILLHAM, R. W. 1984. The capillary fringe and its effect on water table response. *Journal of Hydrology,* 67, 307-324.

GILLHAM, R. W. & JAYATILAKA, C. J. 1998. Response to comment by Jeffrey J. McDonnell and James M. Buttle on 'A deterministic-empirical model of the effect of the capillary fringe on near-stream area runoff. 1. Description of the model' (Journal of Hydrology 184 (1996) 299-315). *Journal of Hydrology,* 207, 286-289.

GLEESON, T. 1992. Runoff risk of Irish soils. *In:* SHERWOOD, M. (ed.) *Weather, Soils and Pollution from Agriculture.* Dublin: Agmet.

GLEESON, T. 1996. Runoff risks of Irish soils. *In:* COLLINS, J. F. & CUMMINS, T. (eds.) *Agroclimatic Atlas of Ireland.* Dublin: Agmet.

GRANGER, S. J., BOL, R., ANTHONY, S., OWENS, P. N., WHITE, S. M. & HAYGARTH, P. M. 2010. Chapter 3 - Towards a holistic classification of diffuse agricultural water pollution from intensively managed grasslands on heavy soils. *In:* DONALD, L. S. (ed.) *Advances in Agronomy.* Academic Press.

GREGORY, C. 2012. *Assessing spatial variations in river discharge / flood risk from a stream in north Co. Down.* MEng MEng, Queens University Belfast.

GROVES, P. 2010. Collon Public Water Supply Scheme - Groundwater Source Protection Zones. Geological Survey of Ireland.

GVOZDIĆ, V., BRANA, J., MALATESTI, N. & ROLAND, D. 2012. Principal component analysis of surface water quality data of the River Drava in eastern Croatia (24 year survey). *Journal of Hydroinformatics,* 14, 1051-1060.

HAHN, C. 2012. *Phosphorus losses from grassland dominated catchments: modeling and experimental validation.* Doctor of Sciences Doctor of Sciences, ETH Zurich.

HAISE, H. R., HAAS, H. J. & JENSEN, L. R. 1955. Soil moisture studies of some great plains soils: II. Field capacity as related to 1/3-atmosphere percentage, and "minimum point" as related to 15- and 26-atmosphere percentages. *Soil Science Society of America Journal,* 19, 20-25.

HAMMOND, R. F. & GLEESON, T. 2003. Soil series and pollution risk to water. *In:* HAMMOND, R. F. & BRENNAN, L. E. (eds.) *Soils of Co. Offaly. Soil Survey Bulletin No. 43.* Dublin: Teagasc.

HARIA, A. & SHAND, P. 2004. Evidence for deep sub-surface flow routing in forested upland Wales: implications for contaminant transport and stream flow generation. *Hydrology and Earth System Sciences,* 8, 334-344.

HARIA, A. H. & SHAND, P. 2006. Near-stream soil water–groundwater coupling in the headwaters of the Afon Hafren, Wales: Implications for surface water quality. *Journal of Hydrology,* 331, 567-579.

HARIA, A. H., SHAND, P., SOULSBY, C. & NOORDUIJN, S. 2013. Spatial delineation of groundwater–surface water interactions through intensive in-stream profiling. *Hydrological Processes,* 27, 628-634.

HARR, R. D. 1977. Water flux in soil and subsoil on a steep forested slope. *Journal of Hydrology,* 33, 37-58.

HARROD, T. R. & THEURER, F. D. 2002. Sediment. *In:* HAYGARTH, P. M. & JARVIS, S. C. (eds.) *Agriculture, hydrology and water quality.* UK: CAB International.

HATCH, D. J., JARVIS, S. C., ROOK, A. J. & BRISTOW, A. W. 1997. Ionic contents of leachate from grassland soils: a comparison between ceramic suction cup samples and drainage. *Soil Use and Management,* 13, 68-74.

HAYGARTH, P. M., CONDRON, L. M., HEATHWAITE, A. L., TURNER, B. L. & HARRIS, G. P. 2005. The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Science of the Total Environment,* 344, 5-14.

HAYGARTH, P. M., HEATHWAITE, A. L., JARVIS, S. C. & HARROD, T. R. 2000. Hydrological factors for phosphorus transfer from agricultural soils. *Advances in Agronomy,* 69, 153-178

HAYGARTH, P. M., HEPWORTH, L. & JARVIS, S. C. 1998. Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland. *European Journal of Soil Science,* 49, 65-72.

HEATHWAITE, A. L. & DILS, R. M. 2000. Characterising phosphorus loss in surface and subsurface hydrological pathways. *Science of the Total Environment,* 251–252, 523-538.

HEATHWAITE, A. L. & JOHNES, P. J. 1996. Contribution of nitrogen species and phosphorus fractions to stream water quality in agricultural catchments. *Hydrological Processes,* 10, 971-973.

HEATHWAITE, A. L., QUINN, P. F. & HEWETT, C. J. M. 2005. Modelling and managing critical source areas of diffuse pollution from agricultural land using flow connectivity simulation. *Journal of Hydrology,* 304, 446-461.

HECKRATH, G., BROOKES, P. C., POULTON, P. R. & GOULDING, K. W. T. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. *Journal of Environmental Quality,* 24, 904-910.

HERZON, I. & HELENIUS, J. 2008. Agricultural drainage ditches, their biological importance and functioning. *Biological Conservation,* 141, 1171-1183.

HEWLETT, J. D. & HIBBERT, A. R. Factors affecting the response of small watersheds to precipitation in humid areas. *In:* SOPPER, W. E. & LULL, H. W., eds. International Symposium on Forest Hydrology, 1967. Pergamon, Oxford, 275-290.

HILL, A. R., KEMP, W. A., BUTTLE, J. M. & GOODYEAR, D. 1999. Nitrogen chemistry of subsurface storm runoff on forested Canadian Shield hillslopes. *Water Resources Research,* 35, 811-821.

HILLEL, D. 1982. *Introduction to Soil Physics,* London, UK, Academic Press.

HINO, M., ODAKA, Y., NADAOKA, K. & SATO, A. 1988. Effect of initial soil moisture content on the vertical infiltration process — A guide to the problem of runoff-ratio and loss. *Journal of Hydrology,* 102, 267-284.

HIRT, U., MEYER, B. C. & HAMMANN, T. 2005. Proportions of subsurface drainages in large areas — methodological study in the Middle Mulde catchment (Germany). *Journal of Plant Nutrition and Soil Science,* 168, 375-385.

HOLMAN, I. P., WHELAN, M. J., HOWDEN, N. J. K., BELLAMY, P. H., WILLBY, N. J., RIVAS-CASADO, M. & MCCONVEY, P. 2008. Phosphorus in groundwater — an overlooked contributor to eutrophication? *Hydrological Processes,* 22, 5121-5127.

HOLZ, G. K. 2010. Sources and processes of contaminant loss from an intensively grazed catchment inferred from patterns in discharge and concentration of thirteen analytes using high intensity sampling. *Journal of Hydrology,* 383, 194-208.

HOODA, P. S., RENDELL, A. R. & EDWARDS, A. C. 2000. Relating soil phosphorus indices to potential phosphorus release to water. *Journal of Environmental Quality,* 29, 1166-1171.

HOOPER, R. P., CHRISTOPHERSEN, N. & PETERS, N. E. 1990. Modelling streamwater chemistry as a mixture of soilwater end-members — An application to the Panola Mountain catchment, Georgia, U.S.A. *Journal of Hydrology,* 116, 321-343.

HOOPER, R. P. & SHOEMAKER, C. A. 1986. A comparison of chemical and isotopic hydrograph separation. *Water Resources Research,* 22, 1444-1454.

HORAN, B., SHALLOO, L. & PATTON, D. 2012. What stocking rate for my farm? Maximising milk production from pasture. *Dairy Conference.* Teagasc.

HORTON, R. E. 1933. The role of infiltration in the hydrologic cycle. *Transactions of the American Geophysical Union,* 14, 446-460.

HRACHOWITZ, M., SAVENIJE, H. H. G., BLÖSCHL, G., MCDONNELL, J. J., SIVAPALAN, M., POMEROY, J. W., ARHEIMER, B., BLUME, T., CLARK, M. P., EHRET, U., FENICIA, F., FREER, J. E., GELFAN, A., GUPTA, H. V., HUGHES, D. A., HUT, R. W., MONTANARI, A., PANDE, S., TETZLAFF, D., TROCH, P. A., UHLENBROOK, S., WAGENER, T., WINSEMIUS, H. C., WOODS, R. A., ZEHE, E. & CUDENNEC, C. 2013. A decade of Predictions in Ungauged Basins (PUB) — a review. *Hydrological Sciences Journal,* 58, 1198-1255.

HUANG, C., GASCUEL-ODOUX, C. & CROS-CAYOT, S. 2002. Hillslope topographic and hydrologic effects on overland flow and erosion. *Catena,* 46, 177-188.

HUGENSCHMIDT, C., INGWERSEN, J., SANGCHAN, W., SUKVANACHAIKUL, Y., DUFFNER, A., UHLENBROOK, S. & STRECK, T. 2014. A three-component hydrograph separation based on geochemical tracers in a tropical mountainous headwater catchment in northern Thailand. *Hydrology and Earth System Sciences,* 18, 525-537.

HUGHES, A. G., VOUNAKI, T., PEACH, D. W., IRESON, A. M., JACKSON, C. R., BUTLER, A. P., BLOOMFIELD, J. P., FINCH, J. & WHEATER, H. S. 2011. Flood risk from groundwater: examples from a Chalk catchment in southern England. *Journal of Flood Risk Management,* 4, 143-155.

HUMPHREYS, J., CASEY, I. A., DARMODY, P., O'CONNELL, K., FENTON, O. & WATSON, C. J. 2008. Quantities of mineral N in soil and concentrations of nitrate-N in groundwater in four grassland-based systems of dairy production on a clay-loam soil in a moist temperate climate. *Grass and Forage Science,* 63, 481-494.

HUMPHREYS, J., TUNNEY, H. & DUGGAN, P. 1999. Soil analysis and comparison of soil phosphorus tests for the Bellsgrove catchment, Cavan. ARMIS 4366. Johnstown Castle, Wexford: Teagasc.

HUNTER WILLIAMS, N. H., MISSTEAR, B. D. R., DALY, D. & LEE, M. 2013. Development of a national groundwater recharge map for the Republic of Ireland. *Quarterly Journal of Engineering Geology and Hydrogeology,* 46, 493-506.

HUPET, F. & VANCLOOSTER, M. 2002. Intraseasonal dynamics of soil moisture variability within a small agricultural maize cropped field. *Journal of Hydrology,* 261, 86-101.

HYLAND, C., KETTERINGS, Q., DEWING, D., STOCKIN, K., CZYMMEK, K., ALBRECHT, G. & GEOHRING, L. 2005. Phosphorus basics - the phosphorus cycle. *Agronomy Fact Sheet Series.* New York: Nutrient Management Spear Program, Cornell University.

HYNDS, P. D., MISSTEAR, B. D. & GILL, L. W. 2012. Investigation of water consumption patterns among Irish adults for waterborne quantitative microbial risk assessment (QMRA). *Journal of Water & Health,* 10, 453-464.

IBRAHIM, T. G., FENTON, O., RICHARDS, K. G., FEALY, R. M. & HEALY, M. G. 2013. Spatial and temporal variations of nutrient loads in overland flow and subsurface drainage from a marginal land site in southeast Ireland. *Biology and Environment: Proceedings of the Royal Irish Academy,* In press.

JAHANGIR, M. M. R., KHALIL, M. I., JOHNSTON, P., CARDENAS, L. M., HATCH, D. J., BUTLER, M., BARRETT, M., O'FLAHERTY, V. & RICHARDS, K. G. 2012. Denitrification potential in subsoils: A mechanism to reduce nitrate leaching to groundwater. *Agriculture, Ecosystems & Environment,* 147, 13-23.

JARVIE, H. P., HAYGARTH, P. M., NEAL, C., BUTLER, P., SMITH, B., NADEN, P. S., A., J., NEAL, M., WICKHAM, H., ARMSTRONG, L., HARMAN, S. & PALMER-FELGATE, E. J. 2008. Stream water chemistry and quality along an upland–lowland rural land-use continuum, south west England. *Journal of Hydrology,* 350, 215-131.

JARVIE, H. P., NEAL, C. & WITHERS, P. J. A. 2006. Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? *Science of the Total Environment,* 360, 246-253.

JAYATILAKA, C. J. & GILLHAM, R. W. 1996. A deterministic-empirical model of the effect of the capillary fringe on near-stream area runoff. 1. Description of the model. *Journal of Hydrology,* 184.

JIN, L., ANDREWS, D. M., HOLMES, G. H., LIN, H. & BRANTLEY, S. L. 2011. Opening the 'black box': water chemistry reveals hydrological controls on weathering in the Susquehanna Shale Hills Critical Zone Observatory. *Vadose Zone Journal,* 10, 928-942.

JOERIN, C., BEVEN, K. J., IORGULESCU, I. & MUSY, A. 2002. Uncertainty in hydrograph separations based on geochemical mixing models. *Journal of Hydrology,* 255, 90-106.

JONES, J. P., SUDICKY, E. A., BROOKFIELD, A. E. & PARK, Y.–J. 2006. An assessment of the tracer-based approach to quantifying groundwater contributions to streamflow. *Water Resources Research,* 42, WO2407.

JORDAN, C. 1989. The effect of fertiliser type and application rate on denitrification losses from cut grassland in Northern Ireland. *Fertilizer research,* 19, 45-55.

JORDAN, P., MELLAND, A. R., MELLANDER, P. E., SHORTLE, G. & WALL, D. 2012. The seasonality of phosphorus transfers from land to water: implications for trophic impacts and policy evaluation. *Science of the Total Environment,* 434, 101-109.

JORDAN, P., MENARY, W., DALY, K., KIELY, G., MORGAN, G., BYRNE, P. & MOLES, R. 2005. Patterns and processes of phosphorus transfer from Irish grassland soils to rivers—integration of laboratory and catchment studies. *Journal of Hydrology,* 304, 20-34.

KANE, D. 2009. *Hydrograph separation using end member mixing models in the Oona Water river catchment.* PhD, University of Ulster.

KENNEDY, C. D., BATAILLE, C., LIU, Z., ALE, S., VANDEVELDE, J., ROSWELL, C. R., BOWLING, L. C. & BOWEN, G. J. 2012. Dynamics of nitrate and chloride during storm events in agricultural catchments with different subsurface drainage intensity (Indiana, USA). *Journal of Hydrology,* 466–467, 1-10.

KENNEDY, E. 2010. *An analysis of evapotranspiration calculations in south east Ireland.* MSc, Trinity College.

KEREBEL, A., CASSIDY, R., JORDAN, P. & HOLDEN, N. M. 2013. Soil moisture deficit as a predictor of the trend in soil water status of grass fields. *Soil Use and Management,* 29, 419-431.

KIRBY, C., NEWSON, M. D. & GILMAN, K. 1991. Plynlimon research: the first two decades. Wallingford, UK: Institute of Hydrology.

KIRCHNER, J. W. 2006. Getting the right answers for the right reasons: Linking measurements, analyses, and models to advance the science of hydrology. *Water Resources Research,* 42, W03S04.

KIRCHNER, J. W., FENG, X., NEAL, C. & ROBSON, A. J. 2004. The fine structure of water quality dynamics: the (high frequency) wave of the future. *Hydrological Processes,* 18.

KLAUS, J. & MCDONNELL, J. J. 2013. Hydrograph separation using stable isotopes: Review and evaluation. *Journal of Hydrology,* 505, 47-64.

KNIGHT, J. H. 1992. Sensitivity of time domain reflectometry measurements to lateral variations in soil water content. *Water Resources Research,* 28, 2345-2352.

KRÖGER, R., HOLLAND, M. M., MOORE, M. T. & COOPER, C. M. 2007. Hydrological variability and agricultural drainage ditch inorganic nitrogen reduction capacity. *Journal of Environmental Quality,* 36, 1646-1652.

KURZ, I., COXON, C. E., TUNNEY, H. & RYAN, D. 2005a. Effects of grassland management practices and environmental conditions on nutrient concentrations in overland flow. *Journal of Hydrology,* 304, 35-50.

KURZ, I., O'REILLY, C. D. & TUNNEY, H. 2006. Impact of cattle on soil physical properties and nutrient concentrations in overland flow from pasture in Ireland. *Agriculture, Ecosystems & Environment,* 113, 378-390.

KURZ, I., TUNNEY, H. & COXON, C. E. 2005b. The impact of agricultural management practices on nutrient losses to water: data on the effects of soil drainage characteristics. *Water Science & Technology,* 51, 73-81.

LA SALA, A. M. 1967. New approaches to water resources investigations in upstate New York. *Ground Water,* 5, 6-11.

LADOUCHE, B., PROBST, A., VIVILLE, D., IDIR, S., BAQUE, D., LOUBET, M., PROBST, J.-L. & BARIAC, T. 2001. Hydrograph separation using isotopic, chemical and hydrographic approaches (Strengbach catchment, France). *Journal of Hydrology,* 242, 255-274.

LAPWORTH, D. J., BARAN, N., STUART, M. E. & WARD, R. S. 2012. Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. *Environmental Pollution,* 163, 287-303.

LAWLER, D. M., PETTS, G. E., FOSTER, I. D. L. & HARPER, S. 2006. Turbidity dynamics during spring storm events in an urban headwater river system: the Upper Tame, West Midlands, UK. *Science of the Total Environment,* 360, 109-126.

LEE, M. 1999. *Surface indicators and land use as secondary indicators of groundwater recharge and vulnerability.* MSc Research, Trinity College.

LEHMAN, O. R. & AHUJA, L. R. 1985. Interflow of water and tracer chemical on sloping field plots with exposed seepage faces. *Journal of Hydrology,* 76, 307-317.

LIANG, W.-L. & UCHIDA, T. 2013. Effects of topography and soil depth on saturated-zone dynamics in steep hillslopes explored using the three-dimensional Richards' equation. *Journal of Hydrology*.

LOGUE, J. J. 1971. Rain intensity: Amount / frequency relationships in Ireland. Dublin, Ireland: Meteorological Service of Ireland.

LORD, E. I. & SHEPHERD, M. A. 1993. Developments in the use of porous ceramic cups for measuring nitrate leaching. *Journal of Soil Science,* 44, 435-449.

LUTHIN, J. N. 1957. *Drainage of Agricultural Lands,* Wisconsin, US, American Society of Agronomy.

MAAS, R. P., SMOLEN, M. D. & DRESSING, S. A. 1985. Selecting critical areas for nonpoint-source pollution control. *Journal of Soil and Water Conservation,* 40, 68-71.

MACCARTHAIGH, M. 1994. Summary details of water balances in Glyde, Dee, Finn and Blackwater (Monaghan) catchments for the period Dec 1975 - Nov 1977. Wexford: Environmental Protection Agency.

MACCARTHAIGH, M. 2011. A preliminary assessment of the flooding which occurred on 24 October 2011 in selected catchments on the east coast, based on data collected at the EPA-LA hydrometric stations. Dublin: Environmental Protection Agency.

MACKIN, F. 2011. *Developing a conceptual understanding of sediment dynamics in an agricultural catchment in Co. Donegal.* MSc, Queens University Belfast.

MAINSTONE, C. P. & PARR, W. 2002. Phosphorus in rivers — ecology and management. *Science of the Total Environment,* 282–283, 25-47.

MARTINEZ-SULLER, L., PROVOLO, G., BRENNAN, D., HOWLIN, T., CARTON, O., LALOR, S. T. J. & RICHARDS, K. 2010. A note on the estimation of nutrient value of cattle slurry using easily determined physical and chemical parameters. *Irish Journal of Agricultural and Food Research,* 49, 93-47.

MCALEER, E. 2011. *The effect of land use on stream nitrogen dynamics in a large agricultural watershed dominated by baseflow.* MSc, Queens University Belfast.

MCDONNELL, J. J. 1990. A rationale for old water discharge through macropores in a steep, humid catchment. *Water Resources Research,* 26, 2821-2832.

MCDONNELL, J. J. & BUTTLE, J. M. 1998. Comment on 'A deterministic-empirical model of the effect of the capillary fringe on near-stream area runoff. 1. Description of the model' by Jayatilaka, C.J. and Gillham, R.W. (Journal of Hydrology 184 (1996) 299-315). *Journal of Hydrology,* 207, 280-285.

MCDONNELL, J. J., OWENS, I. F. & STEWART, M. K. 1991. A case study of shallow flowpaths in a steep zero order basin: a physical-chemical-isotopic analysis *Water Resources Bulletin,* 27, 679-685.

MCDOWELL, R. W. & SHARPLEY, A. N. 2002. The effect of antecedent moisture conditions on sediment and phosphorus loss during overland flow: Mahantango Creek catchment, Pennsylvania, USA. *Hydrological Processes,* 16, 3037-3050.

MCGLYNN, B. L., MCDONNELL, J. J. & BRAMMER, D. D. 2002. A review of the evolving perceptual model of hillslope flowpaths at the Maimai catchments, New Zealand. *Journal of Hydrology,* 257, 1-26.

MCISAAC, G. F. & HU, X. 2004. Net N input and riverine N export from Illinois agricultural watersheds with and without extensive tile drainage. *Biogeochemistry,* 70, 253-273.

MELLAND, A., MELLANDER, P.-E., MURPHY, P., WALL, D., MECHAN, S., SHINE, O., SHORTLE, G. & JORDAN, P. Catchment monitoring technologies to identify critical source areas and times for nitrate transfer to streams. EGU General Assembly Conference Abstracts, 2012a. 9918.

MELLAND, A. R., MC CASKILL, M. R., WHITE, R. E. & CHAPMAN, D. F. 2008. Loss of phosphorus and nitrogen in runoff and subsurface drainage from high and low input pastures grazed by sheep in southern Australia. *Soil Research,* 46, 161-172.

MELLAND, A. R., MELLANDER, P. E., MURPHY, P. N. C., WALL, D. P., MECHAN, S., SHINE, O., SHORTLE, G. & JORDAN, P. 2012b. Stream water quality in intensive cereal cropping catchments with regulated nutrient management. *Environmental Science & Policy,* 24, 58-70.

MELLANDER, P.-E., JORDAN, P., MELLAND, A. R., MURPHY, P. N. C., WALL, D. P., MECHAN, S., MEEHAN, R., KELLY, C., SHINE, O. & SHORTLE, G. 2013. Quantification of phosphorus transport from a karstic agricultural watershed to emerging spring water. *Environmental Science & Technology,* 47, 6111-6119.

MELLANDER, P.-E., MELLAND, A. R., JORDAN, P., WALL, D. P., MURPHY, P. N. C. & SHORTLE, G. 2012. Quantifying nutrient transfer pathways in agricultural catchments using high temporal resolution data. *Environmental Science & Policy,* 24, 44-57.

MEREDITH, S. 2010. *Groundwater vulnerability mapping - Glen Burn Catchment, Ards peninsula, Co. Down.* MSc Environmental Engineering MSc Environmental Engineering, Queens University.

MILLY, P. C. D. 1987. Estimation of Brooks-Corey Parameters from water retention data. *Water Resources Research,* 23, 1085-1089.

MISSELBROOK, T. H., PAIN, B. F., STONE, A. C. & SCHOLEFIELD, D. 1995. Nutrient run-off following application of livestock wastes to grassland. *Environmental Pollution,* 88, 51-56.

MISSTEAR, B. & BROWN, L. 2008. Water Framework Directive: recharge and groundwater vulnerability. Final report. Wexford: Environmental Protection Agency.

MISSTEAR, B. & FITZSIMONS, V. 2007. Estimating groundwater recharge in fractured bedrock aquifers in Ireland. *In:* KRASNY, J. & SHARP, J. (eds.) *Groundwater in Fractured Rocks.* London: Special publication of the International Association of Hydrogeologists.

MISSTEAR, B. D. R., BROWN, L. & DALY, D. 2009. A methodology for making initial estimates of groundwater recharge from groundwater vulnerability mapping. *Hydrogeology Journal,* 17, 275-285.

MOCKLER, E., PACKHAM, I. & BRUEN, M. 2013a. Pathways catchment management tool - Investigating critical source areas with hydro(geo)logical knowledge. *Groundwater and Catchment Management. 33rd Annual Conference of the International Association of Hydrogeologists (Irish Group).* Tullamore, Co. Offaly, Ireland.

MOCKLER, E., PACKHAM, I. & BRUEN, M. 2013b. Pulling it altogether: information from FSU and EPA datasets in parameterising hydrology in the pathways catchment management tool. *National Hydrology Conference.* Tullamore, Co. Offaly: ICP/ICID.

MOE, H., CRAIG, M. & DALY, D. 2010. Groundwater works programme: poorly productive aquifer summary report. Wexford: Environmental Protection Agency.

MULQUEEN, J. 1971. Mole drain failure due to drawing moles downhill. *Irish Journal of Agricultural Research,* 10, 241-244.

MULQUEEN, J. 1998. Depth spacing and length of mole drains with application to afforestation. *Irish Journal of Agricultural and Food Research,* 37, 39-49.

MURPHY, A. 2010. *River hydrograph analysis using chemical data.* BEng, Trinity College.

MURPHY, J. & RILEY, J. P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta,* 27, 31-36.

MURPHY, S., BHREATHNACH, N., O'FLAHERTY, V., JORDAN, P. & WUERTZ, S. Microbial source tracking and transfer hydrodynamics in rural catchments. EGU General Assembly Conference Abstracts, 2013. 8491.

MUSY, A., SOUTTER, M. & PERROCHET, P. 1989. Evaluation of the hydrological response of a drainage network. *In:* MOREL-SEYTOUX, H. J. (ed.) *Unsaturated Flow in Hydrologic Modeling.* Springer Netherlands.

NASH, D., HALLIWELL, D. & COX, J. 2002. Hydrological mobilisation of pollutants at the field/slope scale. *In:* HAYGARTH, P. M. & JARVIS, S. C. (eds.) *Agriculture, Hydrology and Water Quality.* UK: CAB International.

NASH, D., HANNAH, M. & HALLIWELL, D. 2000. Factors affecting phosphorus export from a pasture-based grazing system. *Journal of Environmental Quality,* 29, 1160-1166.

NASR, A. & BRUEN, M. 2013. Derivation of a fuzzy national phosphorus export model using 84 Irish catchments. *Science of the Total Environment,* 443, 539-48.

NATHAN, R. J. & MACMAHON, T. A. 1990. Evaluation of automated techniques for baseflow and recession analysis. *Water Resources Research,* 26, 1465-1473.

NAZ, B. S., ALE, S. & BOWLING, L. C. 2009. Detecting subsurface drainage systems and estimating drain spacing in intensively managed agricultural landscapes. *Agricultural Water Management,* 96, 627-637.

NEAL, C., ROBSON, A. & SMITH, C. J. 1990. Acid neutralization capacity variations for the Hafren forest stream, mid-Wales: Inferences for hydrological processes. *Journal of Hydrology,* 121, 85-101.

NERC 1975. Flood Studies Report. London, UK: Natural Environment Research Council.

NI CHATHAIN, B., MOORKENS, E. & IRVINE, K. 2012. Management strategies for the Protection of High Status water bodies. Wexford: EPA.

NITSCHE, J. & FLYNN, R. 2011. Investigating hydraulically active fractures in a shallow meta-sedimentary bedrock aquifer using single well tracer testing, Mount Stewart, Northern Ireland. *Hydrostratigraphy of crystalline rock aquifers. NGWA focus conference on fractured rock and eastern groundwater regional issues.* Burlington, Vermont: National Groundwater Assocation.

NOVOTNY, V. 1999. Diffuse pollution from agriculture — A worldwide outlook. *Water Science and Technology,* 39, 1-13.

O'BRIEN, R. J. 2013. *Modelling of hydrological pathways in Irish catchments.* PhD PhD, Trinity College.

O'BRIEN, R. J., MISSTEAR, B. D., GILL, L. W., JOHNSTON, P. M. & FLYNN, R. 2014. Quantifying flows along hydrological pathways by applying a new filtering algorithm in conjunction with master recession curve analysis. *Hydrological Processes,* DOI:10.1002/hyp.10105.

O'NEILL, M. 2013. *Hydrochemical survey: investigation into spatial and temporal variations of point sources in a cultivated upland catchment watercourse.* BEng, Queens University Belfast.

O'REILLY, C. 2006. *Influence of hydrology on phosphorus transport from soil.* PhD PhD, UCD.

O'BRIEN, R. J., MISSTEAR, B. D., GILL, L. W., DEAKIN, J. L. & FLYNN, R. 2013. Developing an integrated hydrograph separation and lumped modelling approach to quantifying hydrological pathways in Irish river catchments. *Journal of Hydrology,* 486, 259-270.

OCAMPO, C. J., OLDHAM, C. E., SIVAPALAN, M. & TURNER, J. V. 2006. Hydrological versus biogeochemical controls on catchment nitrate export: a test of the flushing mechanism. *Hydrological Processes,* 20, 4269-4286.

OCKENDEN, M. C., DEASY, C., QUINTON, J. N., BAILEY, A. P., SURRIDGE, B. & STOATE, C. 2012. Evaluation of field wetlands for mitigation of diffuse pollution from agriculture: sediment retention, cost and effectiveness. *Environmental Science and Policy,* 24, 110-119.

OGUNKOYA, O. O. & JENKINS, A. 1993. Analysis of storm hydrograph and flow pathways using a three-component hydrograph separation model *Journal of Hydrology,* 142, 71-78.

ORR, A. 2014. *Hydrogeological influences on the fate and transport of nitrate in groundwater.* PhD, Queens University Belfast.

OUTRAM, F. N., LLOYD, C., JONCZYK, J., BENSKIN, C. M. H., GRANT, F., DORLING, S. R., STEELE, C. J., COLLINS, A. L., FREER, J., HAYGARTH, P. M., HISCOCK, K. M., JOHNES, P. J. & LOVETT, A. L. 2013. High-resolution monitoring of catchment nutrient response to the end of the 2011-2012 drought in England, captured by the demonstration test catchments. *Hydrology and Earth System Sciences Discussions,* 10, 15119-15165.

PATOINE, M., HÉBERT, S. & D'AUTEUIL-POTVIN, F. 2012. Water quality trends in the last decade for ten watersheds dominated by diffuse pollution in Québec (Canada). *Water Science & Technology,* 65, 1095-1101.

PINDER, G. F. & JONES, J. F. 1969. Determination of the groundwater component of peak discharge from the chemistry of total runoff. *Water Resources Research,* 5, 438-445.

PREMROV, A., SCHULTE, R. P. O., COXON, C. E., HACKETT, R. & RICHARDS, K. G. 2010. Predicting soil moisture conditions for arable free draining soils in Ireland under spring cereal crop production. *Irish Journal of Agricultural and Food Research,* 49, 99-113.

QUIGLEY, M. 2012. *The impact of geological heterogeneity on flow rates in the Mattock catchment.* MSc, Queens University Belfast.

RABALAIS, N. N. 2002. Nitrogen in Aquatic Ecosystems. *AMBIO: A Journal of the Human Environment,* 31, 102-112.

RANALLI, A. J. & MACALADY, D. L. 2010. The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds – a review of the scientific literature. *Journal of Hydrology,* 389, 406-415.

RATH, M. & PEEL, S. 2005. Grassland in Ireland and the UK. *In:* MCGILLOWAY, D. A. (ed.) *Grassland: a gloabl resource.* The Netherlands: Wageningen Academic Publishers

RICHARDS, K., COXON, C. E. & RYAN, M. 2005. Unsaturated zone travel time to groundwater on a vulnerable site. *Irish Geography,* 38, 57-71.

ROBINS, N. S. & MISSTEAR, B. D. R. 2000. Groundwater in the Celtic regions. *In:* ROBINS, N. S. & MISSTEAR, B. D. R. (eds.) *Groundwater in the Celtic regions: studies in hard rock and Quaternary hydrogeology.* London: The Geological Society of London.

ROBINSON, D. A., BINLEY, A., CROOK, N., DAY-LEWIS, F. D., FERRÉ, T. P. A., GRAUCH, V. J. S., KNIGHT, R., KNOLL, M., LAKSHMI, V., MILLER, R., NYQUIST, J., PELLERIN, L., SINGHA, K. & SLATER, L. 2008. Advancing process-based watershed hydrological research using near-

surface geophysics: a vision for, and review of, electrical and magnetic geophysical methods. *Hydrological Processes,* 22, 3604-3635.

ROBINSON, M. 1990. Impact of improved land drainage on river flows. Wallingford, UK: Institute of Hydrology.

ROHAN, P. K. 1986. The Climate of Ireland. Dublin: The Stationary Office.

ROYER, T. V., DAVID, M. B. & GENTRY, L. E. 2006. Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: implications for reducing nutrient loading to the Mississippi River. *Environmental Science & Technology,* 40, 4126-4131.

ROZEMEIJER, J. C., VAN DER VELDE, Y., VAN GEER, F. C., BIERKENS, M. F. P. & BROERS, H. P. 2010. Direct measurements of the tile drain and groundwater flow route contributions to surface water contamination: From field-scale concentration patterns in groundwater to catchment-scale surface water quality. *Environmental Pollution,* 158, 3571-3579.

RPS 2008. Further characterisation study: an integrated approach to quantifying groundwater and surface water contributions of stream flow. Ireland: Southwestern River Basin District.

RUSHTON, K. R. & WARD, C. 1979. The estimation of groundwater recharge. *Journal of Hydrology,* 41, 345-361.

RYAN, M. Safe disposal of farmyard effluent. Environmental Impact Conference: Management, Treatment and Landspreading of Manures and Wastes, September 11-12 1991 Johnstown Castle, Wexford, Ireland. Teagasc.

RYAN, M., MCNAMARA, K., BROPHY, C., CONNOLLY, J., CARTON, O. T. & RICHARDS, K. 2005. Effect of agricultural practices in nitrate leaching. End of Project Report. RMIS 4973. Wexford: Teagasc Johnstown Castle Research Centre.

RYAN, M., NOONAN, D. & FANNING, A. 1998. Relative denitrification rates in surface and subsurface layers of a mineral soil. *Irish Journal of Agricultural and Food Research,* 37, 141-157.

SCANLON, B. R. 1985. A groundwater study of the Maine river basin, Co. Kerry. Report Series SR85/1. Dublin: Geological Survey of Ireland.

SCHILLING, K. E. & HELMERS, M. 2008. Tile drainage as karst: Conduit flow and diffuse flow in a tile-drained watershed. *Journal of Hydrology,* 349, 291-301.

SCHINDLER, D. W. 1977. Evolution of phosphorus limitation in lakes. *Science,* 195, 260-262.

SCHULTE, R. P. O., CREAMER, R. E., DONNELLAN, T., FARRELLY, N., FEALY, R., O'DONOGHUE, C. & O'HUALLACHAIN, D. 2014. Functional land management: A framework for managing soil-based ecosystem services for the sustainable intensification of agriculture. *Environmental Science & Policy,* 38, 45-58.

SCHULTE, R. P. O., DIAMOND, J., FINKELE, K., HOLDEN, N. M. & BRERETON, A. J. 2005. Predicting the soil moisture conditions of Irish grasslands. *Irish Journal of Agricultural and Food Research,* 44, 95-110.

SCHULTE, R. P. O., MELLAND, A. R., FENTON, O., HERLIHY, M., RICHARDS, K. & JORDAN, P. 2010. Modelling soil phosphorus decline: Expectations of Water Framework Directive policies. *Environmental Science & Policy,* 13, 472-484.

SCHULTE, R. P. O., RICHARDS, K., DALY, K., KURZ, I., MCDONALD, E. J. & HOLDEN, N. M. 2006. Agriculture, meteorology and water quality in Ireland: a regional evaluation of pressures and pathways of nutrient loss to water. *Biology and Environment: Proceedings of the Royal Irish Academy,* 106B, 117-133.

SEILER, K.-P., VON LOEWENSTERN, S. & SCHNEIDER, S. 2002. Matrix and by-pass flow in Quaternary and Tertiary sediments of agricultural areas in south Germany. *Geoderma,* 105, 299-306.

SEN, S., SRIVASTAVA, P., DANE, J. H., YOO, K. H. & SHAW, J. N. 2010. Spatial–temporal variability and hydrologic connectivity of runoff generation areas in a North Alabama pasture — implications for phosphorus transport. *Hydrological Processes,* 24, 342-356.

SHAHEDI, K. 2008. *Hillslope hydrological modelling: the role of bedrock geometry and hillslope-stream interaction.* PhD, Waegeningen University.

SHARPLEY, A., DANIEL, T. C., SIMS, J. T. & POTE, D. H. 1996. Determining environmentally sound soil phosphorus levels. *Journal of Soil and Water Conservation,* 51, 160-166.

SHARPLEY, A. & KLEINMAN, P. 2003. Effect of rainfall simulator and plot scale on overland flow and phosphorus transport. *Journal of Environmental Quality,* 32, 2172-2179.

SHAW, E. M. 1994. *Hydrology in Practice*, Routledge, Chapman & Hall, Incorporated.

SHAW, E. M., BEVEN, K., CHAPPELL, N. A. & LAMB, R. 2011. *Hydrology in Practice,* Great Britain, Spon Press.

SHENG, F., LIU, H., WANG, K., ZHANG, R. & TANG, Z. 2014. Investigation into preferential flow in natural unsaturated soils with field multiple-tracer infiltration experiments and the active region model. *Journal of Hydrology,* 508, 137-146.

SHORE, M., JORDAN, P., MELLANDER, P-E., KELLY-QUINN, M. & MELLAND, A.R. 2014. An agricultural drainage channel classification system for phosphorus management. *Agriculture, Ecosystems and Environment, (in press).*

SIDLE, R. C., NOGUCHI, S., TSUBOYAMA, Y. & LAURSEN, K. 2001. A conceptual model of preferential flow systems in forested hillslopes: evidence of self-organization. *Hydrological Processes,* 15, 1675-1692.

SIMS, J. T., SIMARD, R. R. & JOERN, B. C. 1998. Phosphorus loss in agricultural drainage: historical perspective and current research. *Journal of Environmental Quality,* 27, 277-293.

SKLASH, M. G. & FARVOLDEN, R. N. 1979. The role of groundwater in storm runoff. *Journal of Hydrology,* 43, 45-65.

SMAKHTIN, V. U. 2001. Low flow hydrology: a review. *Journal of Hydrology,* 240, 147-186.

SMITH, R. V., JORDAN, C. & ANNETT, J. A. 2005. A phosphorus budget for Northern Ireland: inputs to inland and coastal waters. *Journal of Hydrology,* 304, 193-202.

SMITH, V. H., TILMAN, G. D. & NEKOLA, J. C. 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution,* 100, 179-196.

SOULSBY, C. & DUNN, S. M. 2003. Towards integrating tracer studies in conceptual rainfall-runoff models: recent insights from a sub-arctic catchment in the Cairngorm Mountains, Scotland. *Hydrological Processes,* 17, 403-416.

SOULSBY, C., PETRY, J., BREWER, M. J., DUNN, S., OTT, B. & MALCOLM, I. A. 2003a. Identifying and assessing uncertainty in hydrological pathways: a novel approach to end member mixing in a Scottish agricultural catchment. *Journal of Hydrology,* 274, 109-128.

SOULSBY, C., RODGERS, P., SMART, R., DAWSON, J. & DUNN, S. 2003b. A tracer-based assessment of hydrological pathways at different spatial scales in a mesoscale Scottish catchment. *Hydrological Processes,* 17, 759-777.

SOULSBY, C., TETZLAFF, D., RODGERS, P., DUNN, S. & WALDRON, S. 2006. Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: An initial evaluation. *Journal of Hydrology,* 325, 197-221.

SRINIVASAN, M. S. & MCDOWELL, R. W. 2009. Identifying critical source areas for water quality: 1. Mapping and validating transport areas in three headwater catchments in Otago, New Zealand. *Journal of Hydrology,* 379, 54-67.

STAMM, C., FLÜHLER, H., GÄCHTER, R., LEUENBERGER, J. & WUNDERLI, H. 1998. Preferential transport of phosphorus in drained grassland soils. *Journal of Environmental Quality,* 27, 515-522.

STENITZER, E. 1993. Monitoring soil moisture regimes of field crops with gypsum blocks. *Theoretical and Applied Climatology,* 48, 159-165.

STEWART, M. K., MEHLHORN, J. & ELLIOT, S. 2007. Hydrometric and natural tracer (oxygen-18, silica, tritium and sulphur hexafluoride) evidence for a dominant groundwater contribution to Pukemanga Stream, New Zealand. *Hydrological Processes,* 21, 3340-3356.

STOCKWELL, B., LAYDEN, I., NICHOLLS, Z. & CARTER, J. 2012. Addressing rural diffuse pollution in peri-urban agricultural catchments using the FarmFLOW framework: a study in the Pumicestone catchment. *Australasian Journal of Environmental Management,* 19, 182-199.

STRAUSS, P., LEONE, A., RIPA, M. N., TURPIN, N., LESCOT, J. M. & LAPLANA, R. 2007. Using critical source areas for targeting cost-effective best management practices to mitigate phosphorus and sediment transfer at the watershed scale. *Soil Use and Management,* 23, 144-153.

SWARTZ, M., MISSTEAR, B. D. R., DALY, D. & FARRELL, E. R. 2003. Assessing subsoil permeability for groundwater vulnerability. *Quarterly Journal of Engineering Geology and Hydrogeology,* 36, 173-184.

TAYFUR, G., ZUCCO, G., BROCCA, L. & MORAMARCO, T. 2014. Coupling soil mositure and precipitation observations for predicting hourly runoff at small cachment scale. *Journal of Hydrology,* 510, 363-371.

TEDD, K. M., COXON, C. E., MISSTEAR, B. D., DALY, D., CRAIG, M., MANNIX, A. & WILLIAMS, N. H. 2014. An integrated pressure and pathway approach to the spatial analysis of groundwater nitrate: A case study from the southeast of Ireland. *Science of the Total Environment,* 476-477C, 460-476.

TESORIERO, A. J., DUFF, J. H. & WOLOCK, D. M. 2009. Identifying Pathways and Processes Affecting Nitrate and Orthophosphate Inputs to Streams in Agricultural Watersheds. *Journal of Environmental Quality,* 38, 1892-1900.

TETZLAFF, D., BREWER, M. J., MALCOLM, I. A. & SOULSBY, C. 2010. Storm flow and baseflow response to reduced acid deposition—using Bayesian compositional analysis in hydrograph separation with changing end members. *Hydrological Processes,* 24, 2300-2312.

TETZLAFF, D. & SOULSBY, C. 2008. Sources of baseflow in larger catchments – Using tracers to develop a holistic understanding of runoff generation. *Journal of Hydrology,* 359, 287-302.

TETZLAFF, D., SOULSBY, C., HRACHOWITZ, M. & SPEED, M. 2011. Relative influence of upland and lowland headwaters on the isotope hydrology and transit times of larger catchments. *Journal of Hydrology,* 400, 438-447.

THOMPSON, J., CASSIDY, R., DOODY, D. G. & FLYNN, R. 2014. Assessing suspended sediment dynamics in relation to ecological thresholds and sampling strategies in two Irish headwater catchments. *Science of the Total Environment,* 468–469, 345-357.

THOMPSON, J. J. D., DOODY, D. G., FLYNN, R. & WATSON, C. J. 2012. Dynamics of critical source areas: Does connectivity explain chemistry? *Science of the Total Environment,* 435–436, 499-508.

THOMSEN, I. K. & CHRISTENSEN, B. T. 1998. Cropping system and residue management effects on nitrate leaching and crop yields. *Agriculture, Ecosystems & Environment,* 68, 73-84.

TILLAPAUGH, J. A. 2009. *Tractor operator roll angle assessment and visual slope indicator effectiveness.* MSc, The Pennsylvania State University.

TIPPING, E., CORBISHLEY, H. T., KOPRIVNJAK, J.-F., LAPWORTH, D. J., MILLER, M. P., VINCENT, C. D. & HAMILTON-TAYLOR, J. 2009. Quantification of natural DOM from UV absorption at two wavelengths. *Environmental Chemistry,* 6, 472-476.

TROMP-VAN MEERVELD, H. J. & MCDONNELL, J. J. 2006. Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. *Water Resources Research,* 42, W02411.

TUNNEY, H., COULTER, B., DALY, K., KURZ, I., COXON, C. E., JEFFREY, D., MILLS, P., KIELY, G. & MORGAN, G. 2000. Quantification of phosphorus loss from soil to water. End of Project Report RMIS 4365. Johnstown Castle, Wexford, Ireland: Teagasc.

TUOHY, P., FENTON, O. & HUMPHREYS, J. 2012. Dig into the figures before breaking ground. *Today's Farm.*

TUOHY, P., FENTON, O., O'LOUGHLIN, J. & HUMPHREYS, J. 2013. Land drainage - a farmers practical guide to draining grassland in Ireland. *Moorepark 2013 Open Day.* Co. Cork: Moorepark Animal and Grassland Research and Innovation Centre, Teagasc.

UHLENBROOK, S. & HOEG, S. 2003. Quantifying uncertainty in tracer based hydrograph separations: a case study for two-, three- and five-component separations in a mountainous catchment. *Hydrological Processes,* 17, 431-453.

VAN DER HOVEN, S. J., SOLOMON, D. K. & MOLINE, G. R. 2002. Numerical simulation of unsaturated flow along preferential pathways: implications for the use of mass balance calculations for isotope storm hydrograph separation. *Journal of Hydrology,* 268, 214-233.

VAN GENUCHTEN, M. T. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal,* 44, 892-898.

VAN GRINSVEN, H. J., WARD, M. H., BENJAMIN, N. & DE KOK, T. M. 2006. Does the evidence about health risks associated with nitrate ingestion warrant an increase of the nitrate standard for drinking water? *Environmental Health,* 5, 26.

VAN VERSEVELD, W. J., MCDONNELL, J. J. & LAJTHA, K. 2009. The role of hillslope hydrology in controlling nutrient loss. *Journal of Hydrology,* 367, 177-187.

VEIHMEYER, F. J. & HENDRICKSON, A. H. 1949. Methods of measuring field capacity and permanent wilting percentage of soils. *Soil Science,* 68, 75-94.

VIDON, P. & CUADRA, P. E. 2010. Impact of precipitation characteristics on soil hydrology in tile-drained landscapes. *Hydrological Processes,* 24, 1821-1833.

WADE, A. J., WHITEHEAD, P. G. & BUTTERFIELD, D. 2002. The Integrated Catchments model of Phosphorus dynamics (INCA-P), a new approach for multiple source assessment in heterogeneous river systems: model structure and equations. *Hydrology and Earth System Sciences,* 6, 583-606.

WALL, D., JORDAN, P., MELLAND, A. R., MELLANDER, P. E., BUCKLEY, C., REANEY, S. M. & SHORTLE, G. 2011. Using the nutrient transfer continuum concept to evaluate the European Union Nitrates Directive National Action Programme. *Environmental Science & Policy,* 14, 664-674.

WALSH, P. 2011. *Investigation of point recharge, flow and nutrient levels in a lowland karst system in the southeast of Ireland.* MSc., Trinity College Dublin.

WANG, J. L. & YANG, Y. S. 2008. An approach to catchment-scale groundwater nitrate risk assessment from diffuse agricultural sources: a case study in the Upper Bann, Northern Ireland. *Hydrological Processes,* 22, 4274-4286.

WARD, R. S., WANG, L., STUART, M. E., BLOOMFIELD, J. P., GOODDY, D. C., LEWIS, M. A., MCKENZIE, A. A. & WILLIAMS, A. T. 2013. The UK 'nitrate time bomb'. *In:* FRATERS, D. & KOVAR, K. (eds.) *Land Use and Water Quality: Reducing Effects of Agriculture.* The Hague.

WASWA, G. W., CLULOW, A. D., FREESE, C., LE ROUX, P. A. L. & LORENTZ, S. A. 2013. Transient pressure waves in the vadose zone and the rapid water table response. *Vadose Zone Journal,* 12.

WATSON, C. J., JORDAN, C. & LENNOX, S. D. 2000a. Inorganic nitrogen in drainage water from grazed grassland in Northern Ireland. *Journal of Environmental Quality,* 29, 225-232.

WATSON, C. J., JORDAN, C. & LENNOX, S. D. 2000b. Organic nitrogen in drainage water from grassland in Northern Ireland. *Journal of Environmental Quality,* 29, 1233-1238.

WATSON, C. J. & MATTHEWS, D. I. 2008. A 10-year study of phosphorus balances and the impact of grazed grassland on total P redistribution within the soil profile. *European Journal of Soil Science,* 59, 1171-1176.

WATSON, C. J., SMITH, R. V. & MATTHEWS, D. I. 2007. Increase in phosphorus losses from grassland in response to Olsen-P accumulation. *J. Environ. Qual.,* 36, 1452-1460.

WEEKS, E. P. 2002. The Lisse effect revisited. *Ground Water,* 40, 652-656.

WEI, L., CHENG, X. & CAI, Y. 2013. Nutrient export via overland flow from a cultivated field of an Ultisol in southern China. *Hydrological Processes,* 27, 421-432.

WESTERN, A. W., BLÖSCHL, G. & GRAYSON, R. B. 1998. Geostatistical characterisation of soil moisture patterns in the Tarrawarra catchment. *Journal of Hydrology,* 205, 20-37.

WILCOCK, D. N. & ESSERY, C. I. 1984. Infiltration measurements in a small lowland catchment. *Journal of Hydrology,* 74, 191-204.

WILSON, C., COMTE, J.-C., CASSIDY, R., HEINTZ, L. & DICKSON, N. 2012. Geological investigation of the Mattock hard-rock catchment, Collon, Co. Louth, using a series of 2D surface electrical resistivity surveys. Groundwater Research Group, Queens University Belfast.

WILSON, C. J. & DIETRICH, W. E. 1987. The contribution of bedrock groundwater flow to storm runoff and high pore pressure development in hollows. *Symposium on Erosion and Sedimentation in the Pacific Rim.* Corvallis, Oregon: IAHS.

WILSON, E. M. 1990. *Engineering Hydrology. Fourth edition,* Macmillan Press.

WOODING, R. A. & CHAPMAN, T. G. 1966. Groundwater flow over a sloping impermeable layer: 1. Application of the Dupuit-Forchheimer assumption. *Journal of Geophysical Research,* 71, 2895-2902.

YANG, J. & CHU, X. 2013. Quantification of the spatio-temporal variations in hydrologic connectivity of small-scale topographic surfaces under various rainfall conditions. *Journal of Hydrology,* 505, 65-77.

ZARNETSKE, J. P., HAGGERTY, R., WONDZELL, S. M. & BAKER, M. A. 2011. Dynamics of nitrate production and removal as a function of residence time in the hyporheic zone. *Journal of Geophysical Research: Biogeosciences,* 116, G01025.

ZEHE, E., BECKER, R., BÁRDOSSY, A. & PLATE, E. 2005. Uncertainty of simulated catchment runoff response in the presence of threshold processes: role of initial soil moisture and precipitation. *Journal of Hydrology,* 315, 183-202.

ZEHE, E., EHRET, U., PFISTER, L., BLUME, T., SCHRÖDER, B., WESTHOFF, M., JACKISCH, C., SCHYMANSKI, S. J., WEILER, M., SCHULZ, K., ALLROGGEN, N., TRONICKE, J., DIETRICH, P., SCHERER, U., ECCARD, J., WULFMEYER, V. & KLEIDON, A. 2014. HESS Opinions: Functional units: a novel framework to explore the link between spatial organization and hydrological functioning of intermediate scale catchments. *Hydrology and Earth Systems Sciences Discussions,* 11, 3249-3313.

Appendix 1: Quality control issues with collection of the matric potential data

Significant quality control issues arose in the collection of the matric potential data, which are summarized in the following sections.

A1.1 Power supply

Power supply to the site was maintained with a 12 V heavy duty car battery and two solar panels (100 W and 40 W) with a trickle charger. During the winter months, when there was an additional drain on the system due to the cold weather, two car batteries were alternated and were fully charged on the domestic mains system in the intervening periods. The logger, battery and transducers were also insulated in an effort to reduce the impact. Despite these measures, and the significant and sustained efforts with the assistance of one of the Department's technicians to reconfigure the loggers, the power set up and the wiring to the transducers, it became apparent during the second winter that the power supply to the site was simply inadequate and there were often lengthy periods in the darker winter months when data were not being recorded.

A1.2 Logger reliability

The soil moisture data were logged using a separate older Campbell Scientific logger (CR23X) as there were not enough channels on the new, but cheaper Measurement Computing logger purchased for use with the tensiometers. However, it transpired that the CR23X was far more reliable and robust than the Measurement Computing datalogger. The Measurement Computing datalogger randomly switched to logging at 42-s intervals instead of every 15 min, which used up significant power resources and ultimately led to site power failures within a few days. These switches may have been related to minor dips or fluctuations in the power supply because they did not occur during the summer months when the solar panels were adequate to maintain high battery voltages. The CR23X was capable of a self restart after a power supply cut, whereas the Measurement Computing datalogger needed to be manually restarted. This resulted in significant periods when soil moisture data were recorded without corresponding matric potential data.

A1.3 Length of wiring

All tensiometers were wired to the same logger to facilitate synchronizing of the datasets. This required a 160-m length of cable to cover the extent of the site, only some of which was buried near the lower end at Site 1. Theoretical calculations of the impact of the cable length on the current suggested that it should have been minimal, but in practice, changing temperatures and the impact of wildlife chewing the cable appear to have had a significant effect. It was particularly challenging to maintain adequate power supply to Site 4, the uppermost site. When the power

dipped slightly below the optimum level, the transducers at Site 4 continued to record data that appeared plausible during the downloads on site. However, during the subsequent analysis when the calculated matric potential data were compared with the groundwater level, rainfall, soil moisture data and the catchment conceptual model, it became apparent that they were too low and fluctuated more than was probable in reality.

A1.4 Effective limits of the tensiometers

The tensiometers used in this study were relatively long (up to 96 inches or 2.44 m) so that soil moisture monitoring could be carried out at depth in the subsoils below the root zone, where they might be more usually installed. The equipment was also pre-purchased in set lengths with short and mid-sized extensions, on the basis of the findings in the trial pits. However, the configurations were modified slightly on the day of installation to take account of the drilling returns at each site, which resulted in some tensiometer assemblages being longer than optimal for their respective sites.

The longer the tensiometer, the greater the additional vacuum the water column creates in the tube, which means the practical limit of the tensiometer is also reduced. In the Jet Fill model of tensiometer used in this study, the manufacturer states that for every foot of tensiometer, there is 3 cbar of additional vacuum created; the effective limit of a 6-foot tensiometer is therefore reduced from 85 cbar to approximately 62–67 cbar. It was observed in the analysis of the data that when the effective limit was exceeded, the transducer continued to measure data that appeared reasonable at first glance, but again on analysis it became evident that they were unreliable.

The relatively low effective limit for the longer tensiometers was exceeded often, especially during the summer in 2013 when the matric potentials were high. When effective limits are exceeded, the manufacturer indicates that cavitation occurs, i.e. a small air bubble expands to a larger air bubble. The evidence from the data suggests that these bubbles interfered with the transducers and they continued to record unreliable data until they were purged at the next maintenance visit.

A1.5 Frequency of the maintenance scheduling

The monthly maintenance schedule, which was devised based on the first 6 months of the programme, was with hindsight, too infrequent. The spring and summer of 2012 were relatively wet and were not representative of the conditions that arose the following year. However, it is probable that with such low effective limits due to the long tensiometer lengths used in this study, even weekly visits may have been inadequate during the dry summer months.

Appendix 2: Development of a land drain map for Ireland

A2.1 Introduction

The results of this research have identified that artificial drainage plays an important role in the delivery of nutrients to Irish streams, yet the majority of the drainage schemes have been in place for many decades and there are no maps available indicating their locations. Similar findings and mapping problems have also arisen in other countries, e.g. Germany, mid-western United States and the United Kingdom, and there are several reports in the literature of attempts to predict and map their locations using GIS and remote sensing for water management purposes. For example, (Davison et al., 2008) used agricultural land-use data and the Hydrology Of Soil Types class to infer the presence of land drains for use with the PSYCHIC phosphorus and sediment model. Naz et al. (2009) used land cover, soil drainage class and surface slope to map land drains in Indiana, and study in Germany used soil and land-use mapping data, including soil type, soil water and substrate characteristics, hydromorphic characteristics and area of grassland (Hirt et al., 2005).

A2.2 Objectives

The first draft of a national land drain map has been developed as part of this research, in conjunction with a fellow *Pathways Project* student (Eva Mockler), and a retired land drainage expert from Teagasc (Tim Gleeson). The purpose of the map was two-fold: first to inform the pathways separations in the hydrological modelling in the catchment management tool, and second to apportion pathway nutrient transport factors in the catchment characterization tool. Thus, the map needed to be digital, to have applicability throughout Ireland, and to be based on GIS algorithms that used the readily available GIS layers. The relevant available layers included soil drainage (Teagasc), bedrock geology (GSI), aquifer classification (GSI), subsoil permeability (GSI), land use (Corine data), slope (OSI), and rainfall (Met Eireann).

The map was tested in three of the four study catchments (Section A2.6) and has been used in the first version of the catchment management support tools. It is considered to be a work in progress that will evolve with further development of the catchment management support tools. The next step is to publish it in the Irish literature with a view to seeking feedback and improvements from other researchers with detailed knowledge of land drains in other Irish catchments. In this respect, the map is considered to be in draft form at present.

The development of the map has been a joint effort. The role of this researcher in the process was to generate the technical assumptions and the decision tree based on the findings of this research, discussions with Tim Gleeson, and the literature; and to compare the results with field data and observations from the catchments. Mockler carried out the GIS processing and

hydrological model optimization, produced the maps and did the statistical analysis for the validation. Gleeson provided advice and expert opinion prior to the development of the map and has kindly agreed to critique the outcomes in additional selected catchments.

A2.3 Currently available relevant information

There are currently maps available in Ireland of arterial drainage improvement works that were carried out by the State in the 1900s on the main river channels. Although land drainage schemes were dependent on arterial drainage in certain catchments, and were supported by accompanying government-aided grant schemes, there was no general direct link found in this study between arterial drainage improvements and the area of land drains across the country (Mockler, *pers. comm.*).

Several estimates of the percentage of land needing drainage, or that had been drained, have been made by various authors on the basis of surveys over the years, which serve as a useful cross check on estimates derived through the current research. For example, a survey carried out under the *Land Drain Project*, a major Department of Agriculture scheme of field drainage and land reclamation in 1949, estimated that 44% of farmland, or 29% of the Republic of Ireland, required land drainage (Bruton and Convery, 1982). It was estimated by those authors that by 1980, 3 million acres (or 27% of farmland) had been developed by the *Land Drain Project*.

Another land drainage survey covering 490 km^2, or approximately 1% of farmland, was undertaken in the 1960s (July 1964 to June 1968) to gain an overall picture of drainage conditions and practices in Ireland (Galvin, 1966, Galvin, 1969, Galvin, 1971). The drainage schemes surveyed were mostly located in grassland (86.9%), with mineral subsoil (93.9%), in areas with low or moderate subsoil permeability (92%). Old broken drains were found on 43.2% of the area surveyed. Tile drains were used on 71% of the total acreage, open drains on 15% and stone drains on 11.7% (Galvin, 1969).

A third major drainage scheme, the Western Drainage Scheme, funded by the European Union, was to deliver a further 325,000 acres of drainage between 1979 and 1983, primarily in the wetter counties in the west of Ireland (Bruton and Convery, 1982). Land drainage in these counties had been developed more slowly because of their dependence on the associated arterial drainage works being completed first in order to make the schemes viable. There is no information available in the literature on whether these works were progressed.

Two relevant maps are currently available in paper form at a small scale (i.e. single A4 page) which have been used to inform the development of the map in this research. The first is a land

drainage problem map (Galvin, 1971), which was created from analysis of his survey data and the experiences of the field surveyors (Figure A2.1). The map identified 10 categories of drainage problems most frequently found across Ireland although it did not indicate areas that had actually been drained. The three main drainage problems encountered were seepage and springs occurring at the bottom of slopes overlying poorly draining bedrock (37.8%), impervious subsoils (31%) and high water tables (23.8%). The main drainage problems in areas of higher subsoil permeability were considered to be (i) groundwater flooding, (ii) hollows, (iii) high water table and (iv) seepage and springs.

A surface water runoff risk map was also developed by Gleeson (Gleeson, 1996, Gleeson, 1992), which divided the country into eight surface water runoff risk categories (with subcategories) that were based on rainfall, soil type, slope, geology and topography (Figure A2.2). This map also inherently considers the drainage problems, but there were inevitably some inconsistencies between the two maps at this scale.

A2.4 Drainage categories

This research has found, based on the catchments studied, that the pathways and the land drainage problem have a significant bearing on nutrient delivery from land drains. Three categories of drainage have therefore been identified that are relevant in diffuse nutrient transport in Irish catchments. The categories are based on the dominant hydro(geo)logical pathways, and are similar, but not identical, to those identified by Galvin and Gleeson:

(i) *Surface water drainage* due to poor infiltration in poorly drained soils and subsoils. An example of this occurs in the soil and subsoil land drains in the Mattock catchment, where SRP can be high with rainfall events, but nitrate is typically low except where nutrient loads are increased (Section 8.3.2). This category is similar to Gleeson's categories 2 and 3b (soils of low hydraulic conductivity) and Glavin's category 5 (impervious subsoil).

(ii) *Transition zone drainage* which is often high in nitrate, and occasionally high in phosphorus. Examples of this occur in the Gortinlieve catchment in the transition zone boreholes (Section 5.3.4) and in the Mattock in the transition zone supported land drains (Sections 8.3.2) and ditches (Section 8.4.3). This category is similar to Gleeson's categories 3a, 3c and 5, and Galvin's category 2 (seeps and springs at the bottom of slopes), but there is least agreement between their definitions in this category, particularly in the north east of the country.

Figure A2.1. Land drainage problem map modified from Galvin (1971). Red (1) = high water table; yellow (2) = seepage outbursts and springs at the bottom of slopes; blue (5) = impervious subsoil.

(iii) *Groundwater drainage*, where nutrient concentrations depend on the hydrogeological regime. In Regionally Important aquifers, drainage is high in nitrate but low in phosphorus. This is because in these environments, deeper bedrock groundwater pathways dominate, and phosphorus infiltrating through the overlying permeable soils and subsoils is often attenuated (unless the depth to rock is very shallow), yet nitrate does infiltrate. An example of this type was found in the upper Nuenna catchment

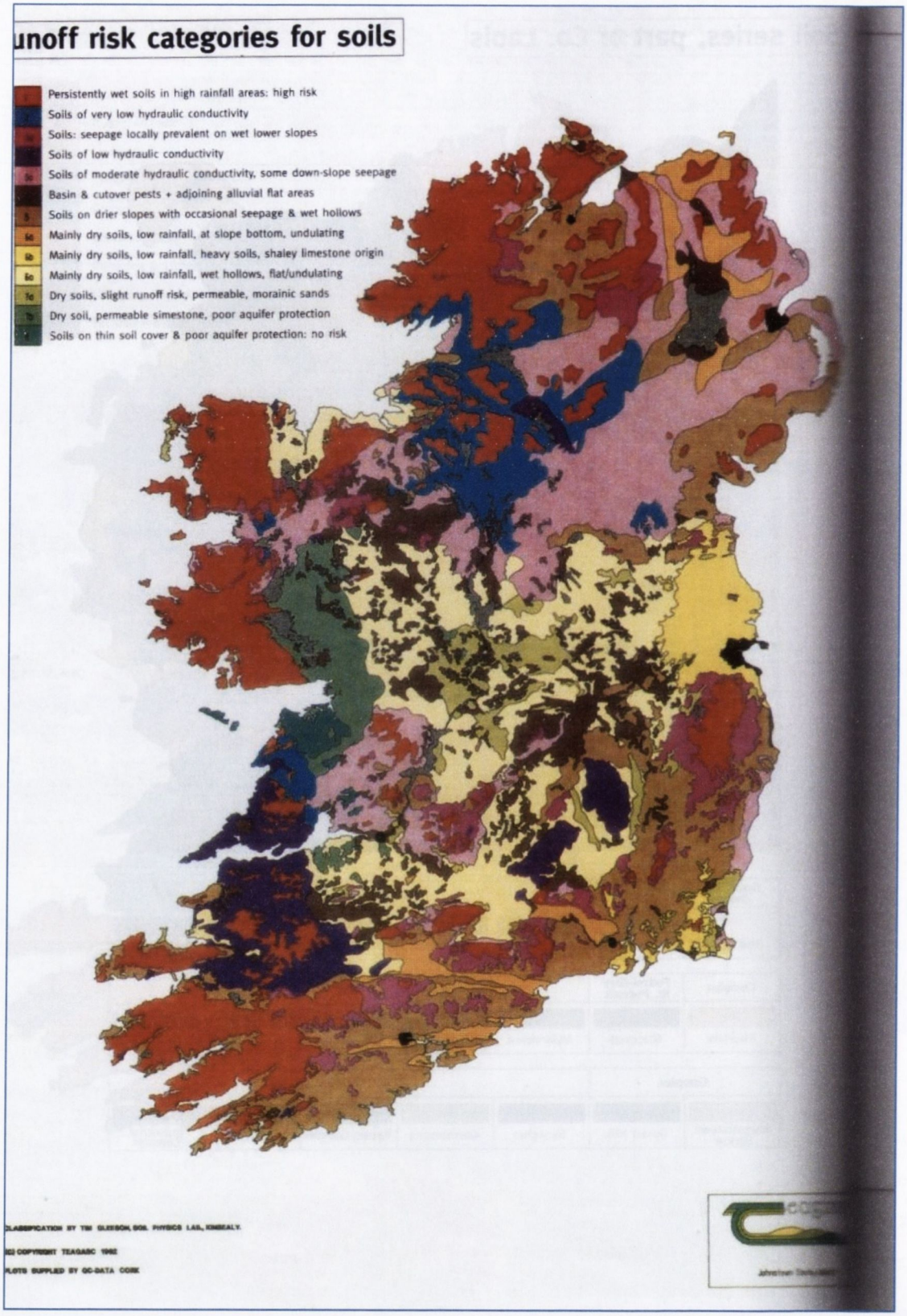

Figure A2.2. Runoff risk map developed by Gleeson (1992, 1996).

(Section 5.4.3.3). In poorly productive aquifers, it will be low in nitrate and phosphorus because in these environments, groundwater is confined under the low permeability tills and much of the nitrate that does infiltrate is attenuated. This category combines Galvin's high water table category, which applied in poorly productive aquifers, and Gleeson's categories 6, 7 and 8 (dry soils). These are of course generalizations; there will be exceptions where rock is at or near surface and therefore there is no effective protective soil/subsoil cover, where there are point sources of contamination, and where the soil and subsoil parent material is not the underlying bedrock due to glacial carryover.

A2.5 Assumptions and decision tree

The fundamental assumption that formed the basis of the GIS algorithms is that where agricultural soils are wet, farmers will have drained them to get the best out of their land, so long as it was worth their time and effort, and it was safe to do so. The factors that have driven the development of the map and the assumptions are described in the following sections.

Soil drainage

It is presumed that where agricultural soils are wet and poorly drained, artificial drainage has been developed. Where the soils are classified as well drained, it is presumed that there are no land drains present. It is likely that some land drains are not well maintained and may be currently ineffective, however, as there is no way of knowing where the poorly functioning land drains are, all poorly drained soils have been included. A separate land drain efficiency function has therefore been added to the water balance calculations in the hydrological modelling, which is discussed further in Section A2.7. The data source is the Teagasc soil mapping, which identifies wet/dry soil drainage in a manner similar to the UK HOST scheme (Boorman et al., 1995).

Land use

The first version of the map is restricted to predicting land drainage in agricultural areas. It is acknowledged that much of Ireland's forestry is also drained, but as there is less information available about it at present, and as the map is being produced primarily for use in agricultural areas, the land-use category is being restricted to agricultural at this time. All non-agricultural land as identified on the Corine maps is therefore excluded.

Altitude

Land above 300 m is considered to be upland in Ireland from an agricultural perspective (Rath and Peel, 2005). Temperatures are cooler, growing conditions are less favourable and the grazing conditions are classified as 'rough', which makes it less likely that a farmer has invested in land

drainage. Thus, all land above 300 m is considered to be not drained. Note: 96% of agriculture in Ireland is at altitudes <200 m OD based on the Corine data.

Slope

At slopes >12 degrees, tractor safety is a concern for operators (Tillapaugh, 2009) so it is less likely that drains have been installed in these areas. Experience from Ireland suggests that the safe limit is a slope of 1:5 (Gleeson, *pers. comm.*), which is a slope of approximately 11 degrees. A second slope threshold of 3 degrees is used to subdivide lands into those where there is little gradient and a high water table is likely and those where the gradient ensures that there are springs and seeps mainly at the bottom of the slopes. This threshold is based on categories used by (Hammond and Gleeson, 2003) to subdivide soil drainage classes in Co. Offaly.

Rainfall

Two rainfall classes were included to represent high and low rainfall. A relatively arbitrary threshold of 1200 mm/a was selected to differentiate the wetter conditions in the west from the drier conditions in the east based on long-term average data (Logue, 1971).

Parent materials

The soil parent material, including the bedrock and subsoils, is a dominant factor in determining the nature of the drainage problem. For the purpose of this assessment, the Geological Survey of Ireland's simplified rock units have been categorized into three groups with similar drainage characteristics based on their aquifer properties and shale content (Table A2.1). Group 1 rock units contain a high proportion of fine-grained shale, which gives rise to shale-rich soil parent materials, and consequently very low permeability soils. Group 2 rock units are dominated by interbedded sandstones and shales, such as the Ordovician and Silurian rocks, and although they also generate relatively low permeability subsoils and soils, the sand fraction ensures better drainage than the purer shales. Group 2 rocks also tend to have a well-developed transition zone between the subsoils and the top of the bedrock, which is often up to two orders of magnitude greater than the subsoils (Comte et al., 2012). As outlined in Chapter 5, the transition zone can transmit a significant quantity of subsurface flow and in the lower slopes in these areas, springs and seeps are common where the groundwater re-emerges at the break in slope. Group 3 rocks comprise the more permeable limestones in the low-lying plains in the midlands and in the south between the Old Red Sandstone hills, where if there are drainage problems, they are due to high water tables.

Table A2.1. Subdivision of the Geological Survey of Ireland's simplified rock units into three groups that give to rise to different types of catchment drainage. Group 1, surface water drainage; Group 2, transition zone drainage; Group 3, groundwater drainage.

Rock Unit	Description	Drainage Group
BV	Basalts and other Volcanic rocks	2
CM	Cambrian Metasediments	2
DKS	Devonian Kiltorcan-type Sandstones	3
DORS	Devonian Old Red Sandstones	2
DESSL	Dinantian (early) Sandstones, Shales and Limestones	2
DDL	Dinantian Dolomitized Limestones	3
DLIL	Dinantian Lower Impure Limestones	2
DMSSL	Dinantian Mixed Sandstones, Shales and Limestones	2
DMSC	Dinantian Mudstones and Sandstones (Cork Group)	2
DPBL	Dinantian Pure Bedded Limestones	3
DPUL	Dinantian Pure Unbedded Limestones	2
DS	Dinantian Sandstones	2
DSL	Dinantian Shales and Limestones	1
DUIL	Dinantian Upper Impure Limestones	2
GII	Granites and other Igneous Intrusive rocks	2
NSA	Namurian Sandstones	1
NSH	Namurian Shales	1
NU	Namurian Undifferentiated	1
OM	Ordovician Metasediments	2
OV	Ordovician Volcanics	2
PTMG	Permo-Triassic Mudstones and Gypsum	2
PTS	Permo-Triassic Sandstones	2
PM	Precambrian Marbles	2
PQGS	Precambrian Quartzites, Gneisses and Schists	2
SMV	Silurian Metasediments and Volcanics	2
WSA	Westphalian Sandstones	1
WSH	Westphalian Shales	1

On the basis of these assumptions, a decision tree was developed (Figure A2.3), from which the GIS algorithms were generated and a national map was produced (by Mockler). The map (Version 1) highlighting land drain presence and the type of land drainage problem is presented in Figure A2.4.

The new land drain map predicts that land drains cover an area of 20,680 km^2, or 44% of agricultural land, as identified using the Corine dataset. The results suggest that 57% of drained agricultural land has been drained because of high water tables, 28% of drainage is due to the presence of impermeable soils/subsoils, and 15% is related to the presence of seeps and springs on lower slopes. A breakdown of areal predictions by county indicates that Cavan and Leitrim have the highest percentage areas of land drained (66% and 51%), amounting to 84% and 89% of

those counties' agricultural land, respectively; Wicklow and Cork have the lowest percentage areas of predicted land drains (21% and 24%) in their respective agricultural areas.

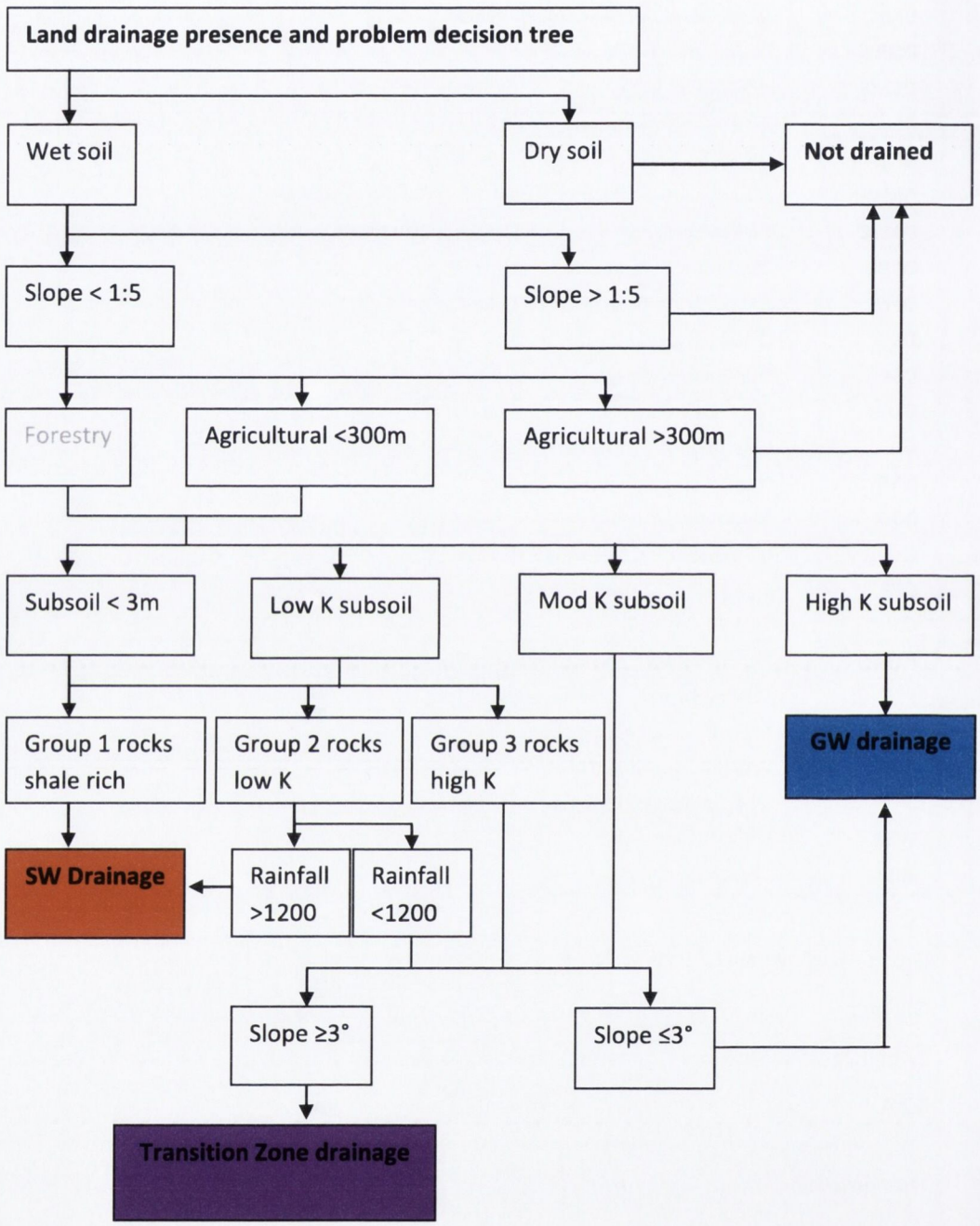

Figure A2.3. Decision tree to decide on the presence and type of land drainage. K = permeability; GW = groundwater; SW = surface water. Forestry is greyed out because it is not included in this first version of the map.

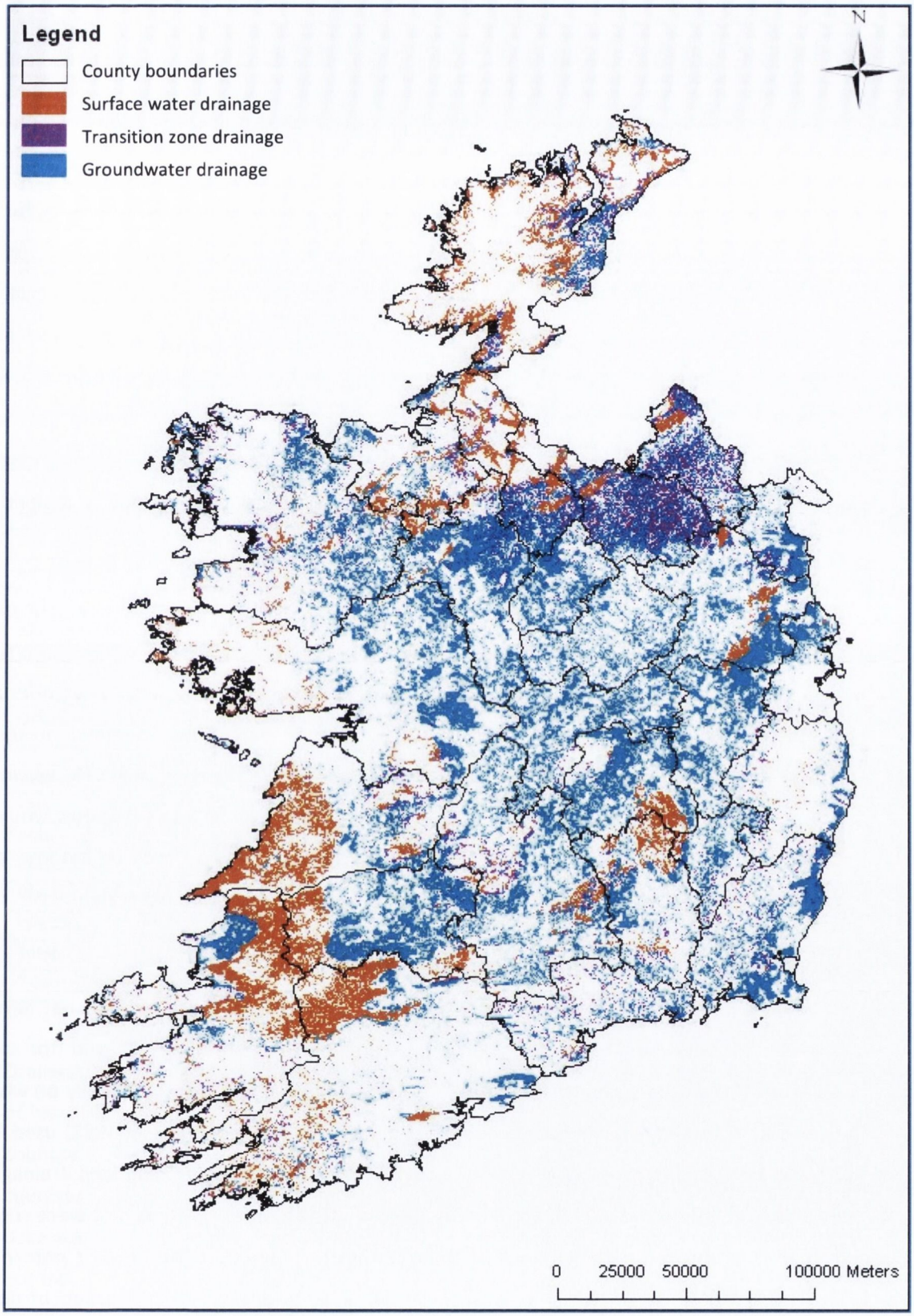

Figure A2.4. Land drain presence and drainage problem map (V1).

A2.6 Comparison of results with available data

The resulting map was compared with published and field data at national, county and catchment scales.

National scale

The current map predicts that the total area of land drained in Ireland is 44% of agricultural land, or 29.4% of the Republic of Ireland, which compares very favourably with the 1949 *Land Drain Project* estimates of land required to be drained (also 44% and 29%, respectively). This highlights that the methodology is, in the first instance, correctly identifying the proportion of lands that need to be drained on the basis of the starting assumption in the model that all lands that need to be drained, have been drained. The unusually high level of agreement between the results is considered to be because the geology has such a significant bearing on the drainage capacity of landscapes that it provides a clear and replicable basis for identifying poorly drained lands, despite more than six decades having elapsed between the two estimates.

Galvin (1969) reported national estimates of the percentage area of the dominant drainage problems: 37.8% seepage and springs occurring at the bottom of slopes, 31% impervious subsoils, and 23.8% high water tables. Although his drainage categories and the current categories are not identical, it is nevertheless useful to compare the results. The current estimates, in the same order, are 15% transition zone drainage; 28% surface water drainage and 57% groundwater drainage. Thus, although the impervious subsoils/surface water drainage categories would seem to be relatively consistent, it appears that the transition zone drainage may be too low, and the groundwater drainage too high. This was further reviewed at the catchment scale.

County scale

It is more difficult to compare different estimates of the actual areas of land that have been drained because they have been derived using different methodologies and for different purposes. Galvin and colleagues surveyed 1% of agricultural land and focussed only on what they termed the low and medium subsoil permeability areas. Bruton and Convery (1982) used Galvin's data as part of an economic analysis of the costs and benefits of government land drainage grant payment schemes. In that respect, they considered only drainage schemes that were supported by public funds, so it is highly probable that their figures underestimate the true percentage of lands drained. However, their figures are also likely to be offset by a proportion of publically funded drainage schemes that have now fallen into disrepair. Nevertheless, a comparison of the modelled and reported areas of land drains county by county is useful (Table A2.7).

Table A2.2. Comparison of predicted area of drained lands based on the current research and the area reported to be drained by Bruton and Convery (1982).

County	Agri Area (Corine)	Predicted Drained Area			Reported Drained Area (Bruton and Convery, 1982)		
	(km2)	(km2)	(% of County)	(% of Agri Land)	(km2)	Difference (%)	
Carlow	781	255	29%	33%	277.4	-9%	
Cavan	1520	1275	66%	84%	410.3	68%	*
Clare	2069	1164	34%	56%	351.9	70%	*
Cork	5733	1378	18%	24%	1102.8	20%	
Donegal	1843	1343	28%	73%	435	68%	*
Dublin	473	182	20%	38%	126	31%	
Galway	3331	1194	19%	36%	725	39%	*
Kerry	2243	1340	28%	60%	692.6	48%	*
Kildare	1380	580	34%	42%	520	10%	
Kilkenny	1857	609	29%	33%	437.4	28%	
Laois	1382	736	42%	53%	499.8	32%	
Leitrim	910	806	51%	89%	144.2	82%	*
Limerick	2289	1176	43%	51%	569	52%	
Longford	815	400	37%	49%	149.4	63%	*
Louth	704	268	33%	38%	132	51%	
Mayo	2369	1227	22%	52%	606.3	51%	*
Meath	2202	829	35%	38%	593.7	28%	
Monaghan	1183	716	55%	60%	288.4	60%	*
Offaly	1384	667	34%	48%	288.4	57%	
Roscommon	1815	1111	44%	61%	302.5	73%	*
Sligo	1129	504	27%	45%	162.4	68%	*
Tipperary	3511	1191	28%	34%	960.3	19%	
Waterford	1342	356	19%	27%	377.9	-6%	
Westmeath	1455	391	21%	27%	485.2	-24%	
Wexford	2143	751	32%	35%	703.5	6%	
Wicklow	1081	229	11%	21%	353.2	-54%	
Total	46945	20679	29%	44%	11694.4	43%	

*** Counties marked for Future Development in 1982**

Drained areas predicted by the current methodology are typically greater than the reported area of benefitting lands in 1980, with nearly double the total drained area estimated for the whole country. However, the greatest differences between predicted and reported values are for counties in the west and northwest of Ireland that were marked for future development in 1980 because they remained poorly drained and there is no evidence in the literature on whether or not this work was progressed.

Only four counties have a lower estimated area of drained land (Carlow, Waterford, Westmeath and Wicklow), all of which are dominated in the current estimates by groundwater drainage problems due to high water tables. This suggests that the current version of the map may be overpredicting high water tables.

Catchment scale

At the catchment scale, the results were compared with the drainage maps generated from the land-use surveys for the Mattock and Gortinlieve catchments, and field survey data (not shown) for the Nuenna catchment from McAleer (2011); the equivalent GIS layers are not available for Northern Ireland so direct comparison with the Glen Burn catchment was not possible.

The resulting maps compare favourably with the data and field observations in the Gortinlieve and Nuenna catchments, but less so in the Mattock. Comparison of the Gortinlieve catchment outputs is provided as an example in Figure A2.5. The results show that the predictions have performed well in the upper catchment area to the north where the altitude is high, the soils are peaty and the land is not farmed. In the lower catchment area, the predicted high water table is consistent with the finding in Chapter 5 that this a groundwater discharge zone. The new map has also correctly identified that seeps and springs are an issue in the mid-upper catchment. However, it appears that there may be an over-estimation in the percentage of the area actually drained when compared with the drainage survey. This is likely to be due to a number of reasons.

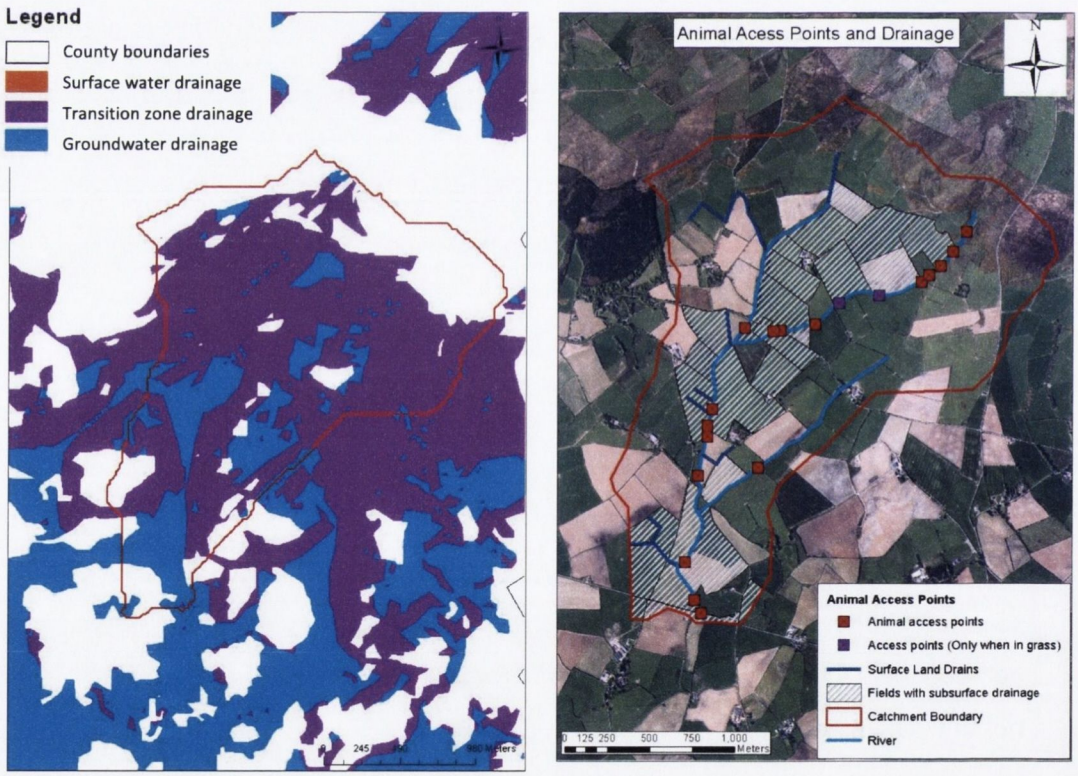

Figure A2.5. Comparison of the Gortinlieve predicted (left), and actual (right) lands drained.

First, the drainage survey may be incomplete because it is not clear from the student project whether all landholders were successfully contacted and confirmed that there was no drainage

present on their lands, or that the information was not, or could not be provided. A follow-up survey would be beneficial in this catchment. Second, from experience in the Mattock catchment, not all landholders are always precisely aware of the actual drainage on their farms because drains were often installed at least one, if not two generations previously, and the information has not been passed down. Nevertheless, the results do appear reasonable.

In the Mattock catchment (Figure A2.6), the predicted map has correctly identified the well-drained lands in the upper catchment areas and an area of gravels in the mid-catchment, and that transition zone drainage is important over the majority of the catchment. Similar issues arise with the reliability of the drainage map based on land-use surveys, but based on the conceptual model of the catchment and field observations, the extent of the predicted drained lands appears reasonable. However, the map appears to over-predict the groundwater drainage due to high water tables and no areas with surface water drainage have been identified but are known to be there from field observations. Further discussion is provided in the next section.

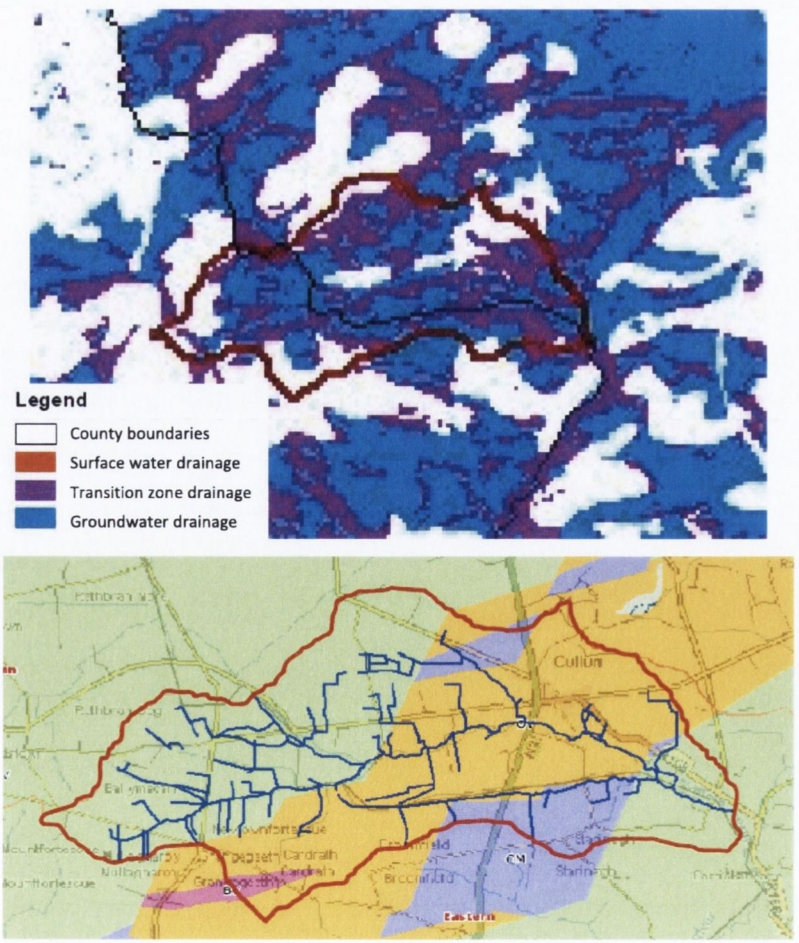

Figure A2.6. Comparison of the Mattock predicted (top), and actual (bottom) lands drained.

A2.7 Discussion

On the basis of the available information, the land drain map appears to be predicting well the total area of lands requiring drainage. Thus, if it is assumed that all lands that need to be drained have been drained, the map would appear reliable. However, this assumption is likely to overestimate the actual drainage in any given catchment, because even if all relevant lands have been drained, there will be blockages and inefficiencies that could affect the water balance. The approach nevertheless is conservative from a nutrient management perspective, because interflow has been found to be a key nutrient transport pathway, and it is therefore considered to be a reasonable starting point until further information becomes available.

To counterbalance the overestimate from a water balance perspective in the *Pathways* hydrological model, a land drain efficiency factor has been introduced to allow for overestimates, uncertainties and blockages. On the basis of the catchment results, validation exercises and the hydrological modelling, the efficiency factor is currently set at 0.8. Early indications from the modelling are that this may be a bit high and that 0.6 might be more appropriate, which would be more consistent with the 43% less drainage reported by Bruton and Convery (1982). It is hoped that this can be improved during the public review process. It may be appropriate, for instance, to apply the Bruton and Convery factors on a county by county basis.

Review of the land drainage problem categories in the catchments, and nationally, suggests that the current methodology may be overpredicting the proportion of groundwater drainage, particularly in the midlands where it is predicted to be the dominant issue. This may be due to the presence of poorly drained peat deposits overlying permeable limestones in low-lying areas, which although likely affected by high water tables, may not be drained due to inadequate gradients. The current map also appears to be underestimating the areas where surface water drainage is dominant in the Mattock catchment, although on a national basis it appears consistent with previous estimates. This is probably because the surface water drainage category in the model has been too tightly constrained to the very shaley bedrock lithologies and it therefore currently only represents the extreme end of the category. This will be reconsidered in the next version of the map. The transition zone drainage predictions appear to be reasonable in the study catchments but may be too low on a national scale. Further refinements should be possible when the maps are reviewed at catchment scale in other areas with Tim Gleeson, and if, and when feedback is received from other agricultural scientists.

In conclusion, it is considered that the map developed as part of this research has useful application in highlighting the areas where drains are likely to occur, and, with further refinement after comparing with other catchment data, the type of drainage problem that is likely to occur.

The type of drainage problem is important from a nutrient management perspective, whereas the total lands drained are of greater interest for hydrological modelling purposes. The map has immediate application in the *Pathways* catchment management support tools, and more widely from a nutrient management perspective as Ireland moves forward to meet its Food Harvest 2020 objectives. The methodology will likely also be of interest in other countries where similar mapping and nutrient management issues arise.