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An Ghníomhaireacht um Chaomhnú Comhshaoil

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Contaminant Movement and Attenuation along Pathways from the Land Surface to Aquatic Receptors – A Review

STRIVE

Environmental Protection Agency Programme

2007-2013

SSTI Strategy for Science, Technology and Innovation

Comhshaol, Oidhreacht agus Rialtas Áitiúil
Environment, Heritage and Local Government

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EPA STRIVE Programme 2007–2013

Contaminant Movement and Attenuation along Pathways from the Land Surface to Aquatic Receptors – A Review

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STRIVE Report

Prepared for the Environmental Protection Agency

by

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The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

The Pathways Project aims to address the challenge of developing a better understanding of hydrological processes, water-borne contaminant fate and transport, and the subsequent impact of these contaminants on aquatic ecosystems in Irish River Basin Districts (RBDs). The project will develop a Catchment Management Tool (CMT) that may be employed by RBD management to ensure that good Water Framework Directive (WFD) status is achieved and/or maintained by 2015. CMT development requires the following project objectives to be addressed:

1. Identification of significant hydrological pathways within RBDs;
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 critical source areas contributing diffuse pollutants to groundwater, surface water and relevant ecological receptors; and
5. Development of a CMT employing data collected during the study in line with the requirements of the end-user.

The project literature report aims to provide an overview of current understanding and knowledge gaps in relation to diffuse contaminant flow and attenuation pathways and the assessment of the impact of these contaminants on aquatic receptors in rivers and streams.

The hydrological conceptual model proposed for the Pathways Project to act as the basis for further study is based on that developed by the Working Group on Groundwater and adopted in the recent Irish surface water and groundwater interactions study (RPS, 2008[1]). This model identifies five main pathways:

1. Overland flow;
2. Interflow;
3. Shallow groundwater flow;
4. Deep groundwater flow; and
5. Discrete fault/conduit flow.

In the Pathways Project, it is proposed to apply a range of physical and chemical hydrograph separation techniques, developed using high-resolution field data from selected study catchments and existing literature, to quantify flow along different pathways. Mathematical modelling of hydrograph responses using the integrated hydrological water quality data sets collected will shed further light on contaminant transport/attenuation and further strengthen confidence in CMT outputs.

Primary knowledge gaps in Ireland concerning pathway contributions to hydrological budgets include a proper understanding of contaminant transport and attenuation processes occurring in interflow, flow through drains, and overland flow at the field scale. The Pathways Project aims to add to knowledge of these issues. This report examines the current literature available on transport and attenuation of these contaminants and identifies knowledge gaps that focus research objectives.

Ultimately the impact of contaminants of concern on catchment aquatic biota must be assessed. Aquatic biota integrates the effects of prevailing physico–chemical conditions in freshwater habitats and is considered the receptor in the WFD. Currently, efforts to understand biological responses to various stressors are curtailed by the scarcity of reliable high-frequency integrated hydrological/water quality data.

1. RPS, 2008. *Further Characterisation Study: An Integrated Approach to Quantifying Groundwater and Surface Water Contributions of Stream Flow.* Report prepared for South Western River Basin District, Ireland. RPS, Dun Laoghaire, Ireland.

1 Introduction

1.1 Introduction to the Pathways Project

The Water Framework Directive (WFD) is considered one of the most comprehensive pieces of European Union (EU) water legislation promulgated to date. In contrast to previous EU directives, the WFD takes an integrated view of the water cycle and its components. Most notably groundwater and surface water can no longer be viewed as isolated entities, but must be considered as integral components in the overall water balance of a river basin (Kallis and Butler, 2001). Such an integrated approach requires increased emphasis on developing scientifically justifiable criteria to support decisions aimed at achieving integrated water management in River Basin Districts (RBDs) across the EU. In Ireland this has resulted in management issues being considered for a total of eight RBDs. Each RBD has been subsequently subdivided into individual water bodies to better address issues that influence quantitative and qualitative aspects of water management. In a significant departure from previous directives, the WFD requires water body classification to involve an assessment of ecological elements including hydromorphological and chemical conditions (Irvine et al*.,* 2002). This classification process includes establishing the relationship between quantitative and qualitative catchment pressures and their impacts on aquatic ecosystems to determine whether a water body runs the risk of having poor WFD status, and thus requiring responsive action.

To carry out such risk assessments effectively requires a conceptual understanding of diffuse pollutant transport and attenuation processes occurring along hydrological and hydrogeological pathways that connect contaminant sources to surface water and groundwater receptors. This conceptual understanding will form a basis for the development of a catchment management tool (CMT) which will enable assessment of the risk of contaminant migration from diffuse sources to water bodies, and if necessary allow management practices to be implemented to ensure that good status is reached and maintained.

1.2 Project Background

In contrast to many other parts of the EU, the development of hydrological models and CMTs for Irish RBDs is particularly challenging given the highly heterogeneous geological conditions across the country that vary substantially over short distances. As a result, many RBDs may contain a range of highly heterogeneous aquifer types (Daly et al*.,* 2006) that are often overlain by subsoils and associated soils bearing little relation to the underlying rock. As a consequence, approaches to integrated water management developed in RBDs with more homogeneous conditions are often difficult to apply in Irish settings. Similarly, many of the processes reported from elsewhere deal with different climatic conditions, where associated geological processes have resulted in soil and subsoil types that differ significantly from the Irish context. These differences in climatic and geological conditions suggest that much hydrological research completed elsewhere may not be directly applicable to the Irish context and thus requires verification, and/or appropriate modification. Furthermore, research techniques and methods employed in many studies completed to date have tended to be discipline-specific. Conversely, cross-disciplinary approaches are more rarely applied, despite proven benefits (Stuart, 2000). Such approaches are necessary to achieve the aims of the WFD.

Recent years have witnessed the development and compilation of spatially variable, yet relevant, data sets derived from a diverse range of environmental/ geoscientific disciplines reflecting the variability of environmental conditions across Ireland. Many of these data sets display considerable potential in shedding further light on pollutant behaviour in the hydrological cycle. Integration of relevant aspects of these data sets into a CMT can assist considerably in determining appropriate measures to be undertaken to maintain or improve hydrological conditions in RBDs to meet WFD objectives.

The proposed programme of work aims to integrate the results of relevant existing studies with those to be completed during the lifetime of this project. Integration of these diverse sources of information into a multidisciplinary framework will enhance current understanding of Irish hydrological processes and determine how contaminants derived from diverse diffuse sources may be transported and, where relevant, attenuated before they might ultimately impact receptors.

With this aim in mind the Pathways Project intends to develop a CMT that may be employed by RBD management to ensure that appropriate measures may be taken to achieve and/or retain good WFD status. Achieving this aim requires the following project objectives to be addressed:

1. Identification of significant hydrological pathways within RBDs;

2. Quantification of flows along the identified hydrological pathways;

3. Identification of significant 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 critical source areas (CSAs) for diffuse pollutants reaching groundwater, surface water and relevant ecological receptors; and

5. Development of a CMT suited to Irish conditions and in line with the requirements of the end-user.

These objectives will be met with the ultimate view of satisfying the requirements of WFD legislation and associated daughter directives. This will require an awareness of current and developing legislation that may have immediate relevance to water management in Irish RBDs.

1.3 The WFD and Legislative Drivers

On 22 December 2000, the European Union (EU) passed the WFD, which was transposed into Irish Legislation by the European Communities (Water Policy) Regulations 2003 (Statutory Instrument 722) on 22 December 2003. Previous European water legislation focused on specific parts of the water environment, e.g. groundwater or surface water. As such, legislation considered each of these parts as a separate entity, despite their interconnection in the hydrological cycle. Abstractions from one water body were often implicitly regarded as isolated and thus not affecting another. Moreover, water quality legislation focused primarily on protecting human health, whereas the impacts on hydrologically dependent ecosystems were often of secondary importance.

Building on existing legislation, the WFD introduced additional, broader ecological objectives designed to protect and, where necessary, restore aquatic ecosystems, while continuing to require protection of public health. EU-wide objectives for integrated water management based on RBD administrative units aim to maintain the ‘high status’ of waters where it exists, preventing any deterioration in the existing status of waters, and achieving at least ‘good status’ in relation to all waters by 2015 (ERBD, 2008b).

The overall objective of the WFD is to bring about the effective co-ordination of water environment policy and regulation across Europe in order to:

- Protect and enhance the status of aquatic ecosystems;

- Promote sustainable water use based on long-term protection of available water resources;

- Provide for sufficient supply of good quality surface water and groundwater as needed for sustainable, balanced and equitable water use;

- Provide for enhanced protection and improvement of the aquatic environment by reducing/phasing out of discharges, emissions and losses of priority substances;

- Contribute to mitigating the effects of floods and droughts;

- Protect territorial and marine waters; and

- Establish a register of ‘protected areas’, e.g. areas designated for protection of habitats or species (ERBD, 2008b).

Since promulgation, the WFD was supplemented with the Groundwater Directive (Directive 2006/118/EC) and the Priority Substances Directive (Directive 2008/105/EC).

The Groundwater Directive is designed to prevent and combat groundwater pollution and makes provisions including:

- Criteria for assessing chemical status of groundwater;
- Criteria for identifying significant and sustained upward trends in groundwater pollution levels, and for defining starting points for reversing these trends; and
- Preventing and limiting indirect discharges of pollutants into groundwater (Europa, 2009: http://ec.europa.eu/environment/water/waterframework/groundwater.html).

The WFD has established a list of priority substances that are toxic, persistent pollutants that accumulate in living organisms and in the wider environment. The EU has identified that substances need to be eliminated from circulation/use most urgently to protect the wider environment from their impacts. These include organohalogens, organophosphorus, cadmium and mercury and derived compounds. The Priority Substances Directive introduces environmental quality standards for priority substances and also requires concentrations of priority substances in sediment and/or biota to be analysed and then minimised (Europa, 2009: http://ec.europa.eu/environment/water/waterframework/groundwater.html).

1.4 Irish RBDs

In line with the European Communities (Water Policy) Regulations 2003 (Statutory Instrument 722), eight RBDs have been established in Ireland. Seven RBDs occur, at least in part, in the Republic of Ireland, including the North Western, Neagh Bann and Shannon cross-border (international) RBDs; the North Eastern RBD is wholly internal to Northern Ireland as shown in Fig. 1.1 (DoEHLG, 2005).

WFD Regulations require co-ordination of actions by all relevant public authorities for water quality management in RBDs, their characterisation, the establishment of environmental objectives, and the development of programmes of measures and River

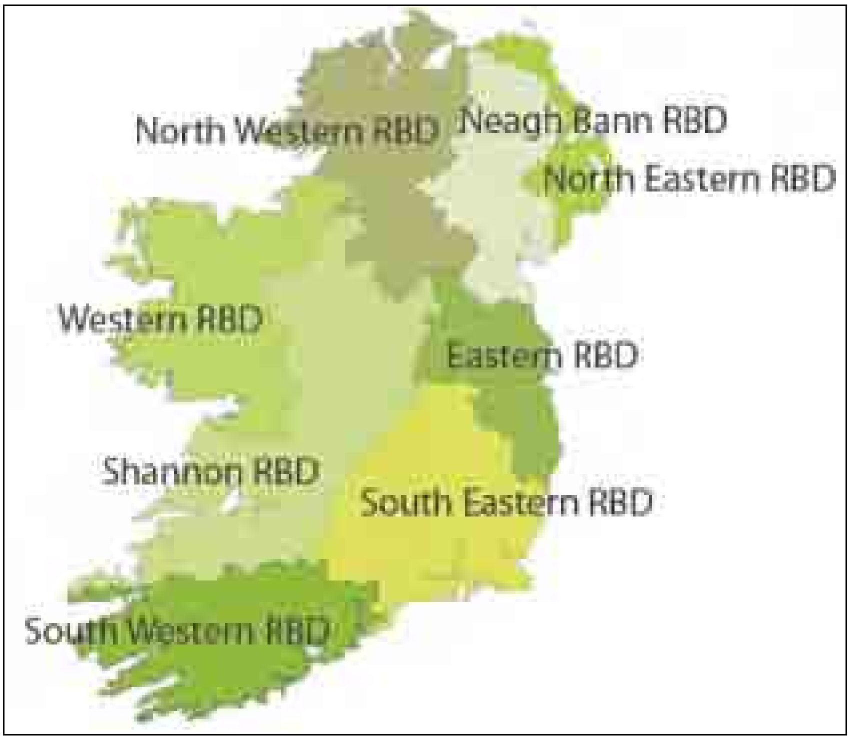

Figure 1.1. River Basin Districts on the island of Ireland (ERBD, 2008b).

Basin Management Plans (RBMPs). The Environmental Protection Agency (EPA) is identified as the competent authority for co-ordinating and reporting this activity nationally, while the local authorities work jointly within their designated RBD to produce the RBMP and programmes of measures under the leadership of the RBD co-ordinating authority (ERBD, 2008b). In order to implement the WFD, a number of key tasks must be completed in accordance with Table 1.1.

On the RBD level, each RBD manager is responsible for the following (DoEHLG, 2005):

- Defining what is meant by 'good' status by setting environmental quality objectives for surface waters and groundwaters;
- Identifying in detail the characteristics of the RBD, including the environmental impact of human activity;
- Assessing the present water quality in the RBD;
- Undertaking an analysis of the significant water quality management issues;
- Identifying the pollution control measures required to achieve the environmental objectives;
- Consulting with interested parties about the pollution control measures, the costs involved and the benefits arising; and
- Implementing the agreed control measures, monitoring the improvements in water quality and reviewing progress and revising water management plans to achieve the quality objectives.

1.5 RBMPs

Relevant local authorities, acting jointly, within each RBD are charged with the responsibility of making the RBMP for their district and for water quality protection, as described in the legislation. Draft RBD plans underwent a period of public consultation prior to adoption at the end of December 2009. The finalised programme of measures must be applied to ensure those water bodies identified as below 'good' status will be restored to at least 'good' status by 2015. The programme of measures has also been designed to ensure that those areas already designated 'good' status or above will be protected and the status retained. Any remaining issues or new problems will be tackled in two further 6-year plans scheduled for 2015–2021 and 2021–2027.

The RBMPs assessed the status of water bodies by implementation of monitoring programmes and identification of areas requiring improvement. The

Table 1.1. Implementation of the Water Framework Directive as scheduled in Irish legislation (modified from ERBD, 2008b).

Key date	Current and future key tasks
2008	• Prepare and publish draft River Basin Management Plans (RBMPs) for consultation. • Each River Basin District to publish a draft programme of measures for consultation
2009	• Establish environmental objectives and final programme of measures and develop RBMPs for their implementation • RBMPs to be finalised and published
2010	• Water pricing policies to be put in place that take into account the principle of 'cost recovery' for water services
2012	• Programme of measures to be fully implemented • Interim progress report to be prepared on the implementation of the programme of measures
2015	• Meet environmental objectives of first RBMP • Adopt the second RBMP
2021/2027	• New RBMP to be completed

WFD stipulates mandatory measures and the RBD plans have identified actions under these measures, setting out existing and new plans and programmes to ensure full and effective implementation. Each plan has assessed the effectiveness of the mandatory measures in meeting objectives and has identified cases where supplementary measures are required to improve the status of water bodies. In these cases, supplementary measures have been assessed to determine whether the combination of measures can meet the objectives of each RBD. Each RBMP outlines the objectives and specifies where extended timescales or lower objectives will be necessary. This process results in a tailored action plan for each RBD which puts forward a detailed suite of measures setting out what, where, and when actions are needed and who is responsible for ensuring that the actions are undertaken and completed. Once each RBMP has been adopted and implemented, each local authority will be responsible for the administration of the RBMP for those water bodies and terrestrial ecosystems that lie within its own territory; local authorities are ultimately accountable to the EPA (ERBD, 2008b).

1.6 CMT Objectives for RBD Management

Each RBD must ensure that the prescribed programme of measures can achieve the required objectives, that is overall good status by 2015. A CMT will be developed to assess the impacts of pressures from CSAs, identify the likely pathway(s) and attenuation factors based on mathematical models. This will permit the assessment of the likely impact of land use on catchment water quality and aquatic biota.

The CMT aims to be an easy-to-use package which allows the RBD technical personnel to investigate the effects of a range of land uses. This is the key to ensuring that models are used by stakeholders. To ensure that the CMT meets the expectations of the end-users, a series of workshops will be held and the CMT will be developed in line with feedback from the workshops. An end-users group will be identified. It will comprise those involved in river basin management, for example RBD managers, local authorities and the EPA.

Development of a CMT for the geological and hydrological conditions routinely encountered in Ireland poses particular challenges. Briefly, this will involve considering hydrological processes, and associated contaminant pathways in simple, relatively homogeneous catchments, to obtain an improved understanding of the relative importance of various contaminant pathways under conditions that are possible to characterise. Upscaling/Adapting to large more heterogeneous catchments will involve integrating findings from studies completed at a simpler level into a composite model incorporating contrasting hydrological conditions. The approach will be employed in a diverse range of settings with the aim of encompassing a wide variety of environmental conditions, routinely encountered in Irish RBDs.

To achieve the above will require a number of type catchments to be selected, which will act as a focus for further field-based data collection. These data will permit the current conceptual models of contaminant transport in Irish RBDs to be reappraised, and the relative significance of different pathways in delivering contaminants to receptors to be evaluated. Field data and other available information sources will be used to form and/or refine hydrochemical and hydrological numerical models, which form the basis of a generic CMT. The CMT will have a simple to use graphical user interface (GUI), enabling modification to suit conditions in specific RBDs in order to assist managers in achieving and maintaining good status by 2015.

1.7 Specific Aim and Objectives of the Literature Review

This literature review aims to review, assess and identify knowledge gaps in current understanding of hydrological flow in relation to diffuse contaminants, CSAs, and their associated impacts on aquatic ecosystems in Irish settings. It has been used to inform and constrain the study area selection process and subsequent fieldwork to ensure that relevant knowledge gaps are filled prior to modelling and CMT development.

Based on the above, the objectives of the report are to:

- Review and compile the findings of international and national studies to support assessment and modelling of hydrological and hydrogeological pathways in relation to overland flow, interflow, shallow, deep and conduit groundwater flow and identification of current knowledge gaps to provide focus for fieldwork;

- Review and compile relevant literature concerning the fate and transport of pathogens, pesticides, nitrogen and phosphorus, and sediments, with particular emphasis on ensuring that appropriate data are/will be available to support the proposed CMT; and

- Review and assess the suitability of ecological metrics currently used to assess the impact of contaminants of concern on aquatic biota.

2 Flow Pathways and River Hydrograph Separation

The terms overland flow, interflow and baseflow are often used to describe the components of a river flow hydrograph. These terms are explained in Section 2.1. In Section 2.2, physical methods of analysing the flow contributions to hydrographs are described, followed by the use of chemical methods for hydrograph separation in Section 2.3. The chapter concludes with a brief review of the application of models (ranging from simple rainfall–runoff relationships to complex distributed numerical models) in the investigation of flow pathways.

2.1 Introduction to Flow Pathways

In considering pathway contributions to river flow, a commonly applied model encompasses three pathways:

1. Overland flow;
2. Interflow; and
3. Baseflow

(e.g. Chin, 2006).

Overland flow is generally regarded as *sheet flow* occurring on the land surface (Shaw, 1994). It is sometimes termed *surface runoff* or *direct runoff* and produces a rapid response in a stream hydrograph. The classic, Hortonian, concept of overland flow is flow that occurs when the water input rate from a storm event exceeds the infiltration capacity of the soil, and when the rainfall duration exceeds the so-called time of ponding. This type of overland flow, usually referred to as *infiltration excess overland flow*, is now usually considered to be important mainly in arid areas, or in areas where soil permeability is low (Dingman, 2002). The more common type of overland flow in temperate climates is flow that results only after the soil becomes saturated; this is usually termed *saturation excess overland flow* (Nash et al., 2002).

The term *interflow* (also commonly referred to as *throughflow*) is described in the literature in different ways. Dingman (2002) points out that "*Many writers have referred to such flow, but have often been ambiguous as to its exact mechanism: it is sometimes described as unsaturated Darcian flow in the soil matrix, sometimes as pipe flow in macropores that largely bypass the unsaturated soil matrix, and sometimes as flow in saturated zones of very limited vertical extent caused by soil horizons that impede vertical infiltration*". In the context of river hydrograph analysis, Wilson (1990) notes that "*interflow refers to water travelling horizontally through the upper horizons of the soil, perhaps in artificial tile drain systems….*". Bedient et al. (2008) refer to interflow as *subsurface storm flow*. Bradbury and Rushton (1998) and Rushton (2003) use the term *delayed runoff* to describe infiltrating water that does not pass downwards through the subsoil to become recharge, but rather leaves the subsoil to enter streams or drainage ditches. They note that this delayed runoff is sometimes called interflow. Notwithstanding the variety of descriptions, the term interflow can be employed generally to describe any lateral subsurface flow that occurs between the ground surface and the water table (Dingman, 2002; Nash et al., 2002; Chin, 2006). As such, interflow can occur in both the topsoil and subsoil, and may include unsaturated matrix flow, bypass or macropore flow, saturated flow (from locally perched water tables) and possibly field drainage (the inclusion of field drains within interflow or overland flow for Irish conditions is considered in Section 3.6).

Overland flow and interflow together are sometimes referred to as *quickflow* (Chin, 2006), although some interflow pathways are clearly more rapid than others, and can have different impacts on water quality. In contrast to quickflow, the term *baseflow* is used to describe the 'slow flow' contribution to the river hydrograph from groundwater discharge. Dingman (2002) describes baseflow as "*water that enters* [the stream] *from persistent, slowly varying sources and maintains streamflow between water input events*". Chin (2006) states that baseflow is typically '(quasi-) independent' of the rainfall event and depends on the difference between the water table elevation in the aquifer and the water surface elevation in the stream.

The proportion of baseflow to total runoff is often referred to as the baseflow index (BFI) (Institute of Hydrology, 1980; Shaw, 1994). The BFI can be used to derive a recharge coefficient for an aquifer, which is the proportion of effective rainfall (total rainfall minus actual evapotranspiration (AE)) that becomes groundwater recharge (Fitzsimons and Misstear, 2006; Misstear and Brown, 2008; Misstear et al., 2009) – see Section 3.3.

2.2 River Hydrograph Analysis: Physical Methods

This section presents a brief review of physical methods for river hydrograph analysis; readers should refer to standard hydrology texts for further information on specific methods. Here, the focus is on those techniques commonly applied in Ireland; details of the Irish case studies are given in Chapter 3. A few of the assumptions underlying hydrograph analysis and how these are seldom met in practice will also be considered. The following review is based largely on Nathan and McMahon (1990), Brodie and Hostetler (2005), Misstear and Fitzsimons (2007), Misstear and Brown (2008) and RPS (2008).

The traditional methods of separating the overland flow, interflow and baseflow contributions to the river hydrograph were based on graphical analysis of the hydrograph recession. The basic relationship is:

$$Q_t = Q_0 \exp(-\alpha t) \qquad \text{Eqn 2.1}$$

where Q_t is the flow rate at time t, Q_0 is the initial flow rate and α is a constant. The term $\exp(-\alpha)$ is often referred to as the recession constant, k. One of the earliest graphical methods was proposed by Barnes (1939), in which the three components of flow (overland flow, interflow and baseflow) are distinguished on a semi-logarithmic plot of log Q versus t. Owing to the variability of hydrograph responses to different storm events (due, for example, to different antecedent moisture conditions), master recession curves (MRCs) can be constructed using data from several storm events in order to average out these variations. There are several means of preparing MRCs, including the matching strip method, the correlation method and the tabulation method (Nathan and McMahon, 1990; Sujono et al., 2004; Brodie and Hostetler, 2005). MRC analysis (using the matching strip and tabulation methods) was employed in the recent Irish study concerned with groundwater and surface water interactions to identify the baseflow (deep groundwater) contributions to river flow (RPS, 2008) (see Section 3.5).

In addition to recession analysis, there are many other graphical, analytical and automated approaches available for distinguishing the different flow components of a river flow hydrograph. Nathan and McMahon (1990) divide the approaches into two groups, depending on whether or not they take account of a delay in baseflow response to a storm event due to bank storage. The role of bank storage in reducing the groundwater contributions to river flow during the rising limb phase of a hydrograph is highlighted in Chen et al. (2006).

Automated baseflow separation techniques have the advantage that they can conveniently incorporate much longer periods of data than manual methods. The automated method developed by the Institute of Hydrology (Institute of Hydrology, 1980, 1989), now known as the Centre for Ecology and Hydrology, is one of the most common methods of baseflow analysis, and has been used in previous studies in Ireland (see Section 3.4). This method involves the identification of runoff minima at fixed time intervals and the selection of key ‘turning points’ from these minima. The length of this time interval is referred to as the ‘time base’ N (this is often set to 5 days), and represents the number of days after a peak in the hydrograph when runoff is assumed to cease. The number of days depends on catchment size.

The Boughton method is an analytical technique (Boughton, 1993, 1995; Chapman, 1999) in which the mathematical algorithm for calculating baseflow Q_b can be readily solved within a computer-based spreadsheet. The Boughton method originally incorporated only one parameter k, which is the recession constant during periods of no runoff (Boughton, 1993):

$$Q_b(i) = \frac{k}{2-k}Q(i-1) + \frac{1-k}{2-k}Q(i) \qquad \text{Eqn 2.2}$$

Boughton (Boughton, 1995) subsequently modified this equation to incorporate a second parameter *C*, which replaced 1 – *k*. This provides the algorithm with greater flexibility but makes it more subjective in its use by the operator:

$$Q_b(i) = \frac{k}{1+C}Q_b(i-1) + \frac{C}{1+C}Q(i) \quad \text{Eqn 2.3}$$

The Boughton method was applied in the recent EPA Science, Technology, Research and Innovation for the Environment (STRIVE) recharge and vulnerability project in Ireland, as described in Section 3.4.3.

The Institute of Hydrology and Boughton methods can be described as filtering separation methods (Brodie and Hostetler, 2005). Other examples include those based on the type of recursive digital filter used in signal analysis. These aim to separate out the low-frequency signal analogous to baseflow from the higher frequency signals analogous to overland flow and interflow. Although not based on hydrological principles, digital filtering techniques do provide rapid, objective and repeatable means of estimating the BFI (Nathan and McMahon, 1990).

In addition to techniques for separating the components of a river flow hydrograph, insights on flow pathway contributions can be gained from frequency analysis of river flows, including preparation of flow duration curves. These can be constructed using the entire flow record and show the percentage time that a particular flow is exceeded or equalled. Thus the *Q*90 flow is the flow that is equalled or exceeded 90% of the time. Although quantitative indices have been developed to indicate the contributions from groundwater storage, such as the *Q*90/*Q*50 ratio (Nathan and McMahon, 1990; Brodie and Hostetler, 2005), useful qualitative indications of the relative importance of baseflow contributions between different catchments can be gleaned from the shape of the flow duration curves: if the section of the flow duration curve below the median flow (*Q*50) has a shallow slope, this indicates a continuous baseflow contribution to the river, whereas a steep curve indicates comparatively smaller contributions from groundwater storage (Brodie and Hostetler, 2005).

All the approaches for hydrograph analysis have significant limitations that are relevant to this Pathways Project. Recession curve analysis assumes a linear response, whereas parts of the flow system may behave in a non-linear manner; the distinction between baseflow and interflow is often arbitrary; bank storage effects often are not taken into account; analytical equations such as the Boughton two-parameter algorithm involve subjective decisions about the choice of values for the empirical constants; the digital filtering technique, in the words of Nathan and McMahon (1990) is "*just as arbitrary and as physically unrealistic as, say, the separation of baseflow based on a series of straight lines*"; indices based on frequency analysis do not necessarily correlate strongly with flow processes.

Halford and Mayer (2000) investigated some of the major assumptions underlying the use of hydrograph separation techniques for estimating groundwater discharge and recharge, including the assumptions that there is a direct relationship between the timing of groundwater and surface runoff peaks, and that bank storage effects are insignificant. They concluded that recession curve and other separation techniques, when used on their own, are "*poor tools for estimating groundwater discharge or recharge because the major assumptions of the methods are commonly and grossly violated*". Halford and Mayer went on to recommend that "*Multiple, alternative methods of estimating groundwater discharge and recharge should be used because of the uncertainty associated with any one technique*".

Eckhardt (2008) recently undertook a comparison of seven different baseflow separation methods for calculating BFIs in 65 catchments in North America. These included the Institute of Hydrology method and other automated methods (HYSEP and PART), which involve the connection of minimum points on a stream hydrograph, together with methods based on recursive digital filters (BFLOW and Eckhardt's own method). In his findings, the author notes that "*Since the true values of the baseflow index are unknown, it cannot be said which one of the methods gives the best estimate*". Although the author goes on to argue that his own algorithm appears to be "*hydrologically more plausible*" than the others, the study does serve to highlight the problem that there are usually inadequate data available to validate the results of hydrograph separation. Misstear and Fitzsimons (2007) attempted to address this problem, at least in part, in a study of a 'hybrid' sub-catchment in the Nore Basin, by calibrating the various empirical parameters included in automated separation techniques against well hydrographs (Section 3.4.2).

2.3 River Hydrograph Analysis: Chemical Methods

Analysis of river flow hydrograph data can be significantly enhanced by incorporating analyses of associated water chemistry data. Chemistry data involving natural chemical tracers can also be used to separate a chemical hydrograph to glean information about the contribution of flow along various pathways. Chemical mixing models can be created which can be used to identify up to five different flow components. Chemical methods have been widely applied abroad but have not been used in Ireland to any significant degree. In addition, the relationships between loadings of pollutants and streamflow duration can provide insights into the different flow regimes delivering contaminants to a stream, and hence the different flow pathways. Further detail on each of these approaches is provided in the following sections.

2.3.1 Natural chemical tracers and mixing models

The use of water chemistry and natural chemical tracers for hydrograph separation is a technique that has been employed for some time (e.g. LaSala, 1967; Pinder and Jones, 1969). The approach depends on the principle that as rainfall infiltrates through the landscape, solute concentration increases with increased residence time and contact with geological materials. Variations in solute concentrations in stream water over time, particularly during a storm event, can then be used to estimate the relative contributions of water with different residence times and therefore different hydrological flow paths through the system. A number of different flow components are typically identified — predominantly two or three, but occasionally up to five (Uhlenbrook and Hoeg, 2003). Two-component mixing models usually separate hydrographs into event or direct runoff and pre-event or subsurface waters, whilst three-component mixing models introduce a third soil water component that can be distinguished from the other two. This third component is typically loosely referred to as intermediate flow and can have a variety of definitions, the primary one being that it is different to overland flow and baseflow. Additional components, when used, typically include precipitation and/or more than one soil water or groundwater source.

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

$$Q_{tr}C_{tr} = Q_{dr}C_{dr} + Q_{gw}C_{gw} \qquad \text{Eqn 2.4}$$

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 streamflow components, as described in Ogunkoya and Jenkins (1993):

$$Q_{tr}C_{tr} = Q_1C_1 + Q_2C_2 + ...+ Q_mC_m \qquad \text{Eqn 2.5}$$

where the subscripts 1, 2, … *m* are the assumed components of the total runoff. The number of components to be distinguished dictates the number of tracers that need to be used: *n* tracers are needed to determine *n* + 1 streamflow components; or, in other words, where a streamflow hydrograph is to be separated into three streamflow components, two different tracers will be required, with the equation being solved for each.

Various statistical techniques are then applied to the data to generate quantitative estimates of the contributions of each of the end members to the flow and to estimate the degree of uncertainty in the results. Many methods typically rely on Monte Carlo analyses using generated data (e.g. Bazemore et al., 1994) or field data (Joerin et al., 1998, 2002), and/or other Bayesian statistical approaches (e.g. Soulsby et al., 2003a).

One particular formalised statistical technique for separating hydrographs using mixing models has been developed by Christophersen et al. (1990) and Hooper et al. (1990), and is known as End Member Mixing Analysis (EMMA). EMMA assumes that stream water is derived from a mixture of soil and/or groundwater solutions, known as end members, which form the boundaries of the possible stream water observations (Fig. 2.1). It is then possible to estimate the proportion of each of these soil-solution end members that constitutes a stream water observation (Hooper et al., 1990). This application has been widely used since its development in the early 1990s.

2.3.1.1 Assumptions

There are a number of assumptions that are typically made in carrying out hydrological mixing analysis. These include the following:

- The tracer 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 (e.g. 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 streamflow components being analysed is small (e.g. two or three), the differences between potential components which are being amalgamated for the purposes of the analysis (e.g. vadose water and groundwater in two-component mixing) are insignificant (Sklash and Farvolden, 1979);
- The chemical or isotopic signatures of the streamflow components are distinguishable (Ladouche et al., 2001);
- Temporal and/or spatial variations in streamflow compositions are negligible or are accounted for in the model (Eshleman et al., 1993); and
- Specifically for EMMA, the signatures of the end members represent the extremes and that 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 likely to be difficult to satisfy in heterogeneous hydrogeological scenarios

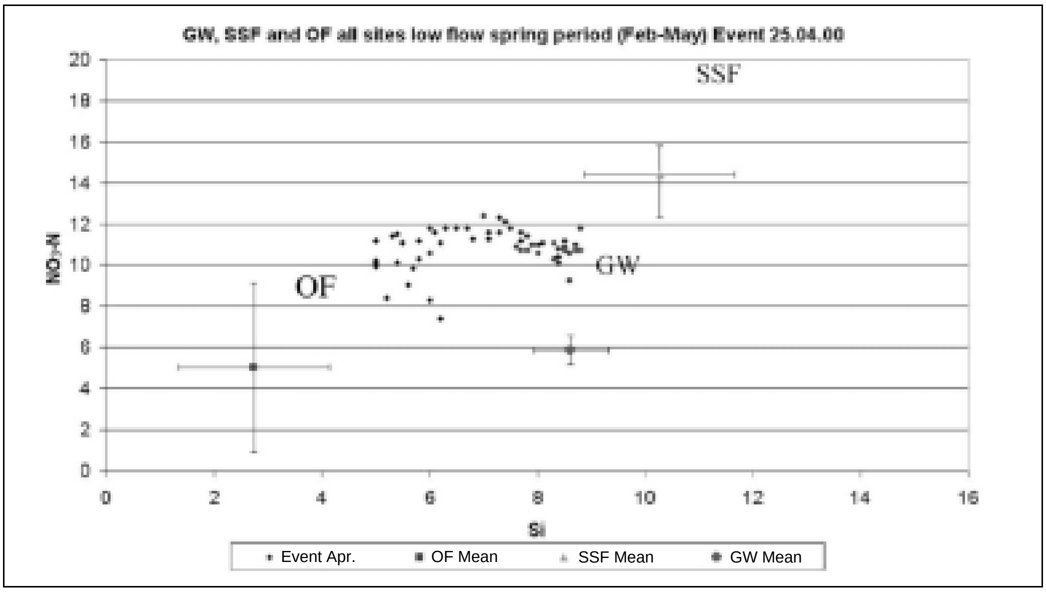

Figure 2.1. An example of a three-component hydrological mixing diagram for streamflow samples in an agricultural catchment in north-east Scotland using nitrate and silica as tracers. Three end members were identified: overland flow (OF), subsurface flow (SSF) and groundwater (GW) (after Soulsby et al., 2003a).

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. Soulsby et al. (2003a), for instance, used nitrate as a tracer and whilst they admit it is not completely conservative, they, and other authors (e.g. Durand and Torres, 1996), have found that 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 and attempts to mitigate them as far as possible are made (Genereux, 1998; Joerin et al., 2002; Soulsby et al., 2003a). Uncertainties are further discussed in Section 2.3.1.3.

2.3.1.2 Natural tracers

A range of different geochemical and isotopic tracers can be used for the analysis, depending on the hydrogeological characteristics of the catchment and the land uses within it. Silica has been widely used, for example by Soulsby and others in upland forested catchments in Scotland. Silica is a useful tracer because it is a weathering product of a range of geological materials from granite to limestone, and so would be expected to be fairly widespread in the landscape. It is generally assumed to be reasonably conservative in deeper subsurface systems, notwithstanding that it is an essential nutrient for many plants including some phytoplankton (diatoms) which can remove it from the water column, particularly during baseflow conditions in the summer months (Neal et al., 2005), or from wetland or swamp areas (Wels et al., 1991). Silica has also been found in new soil water that has had little residence time (Hooper and Shoemaker, 1986; Wels et al*.,* 1991) – thus potentially making it difficult to distinguish between soil water and groundwater in some situations.

Gran alkalinity has been used successfully by Soulsby and others in Scotland (Soulsby et al., 2003b, 2006, 2007), Jarvie and others in south-west England (Jarvie et al., 2008), and Neal and others in Wales (Neal et al., 2005). Gran alkalinity gives an approximation of the relative contributions of bicarbonate and organic acid to pH. While it can be influenced by land-use activities (e.g. high organic loading in manures), one of the advantages of using it as a tracer is its relationships with other very easily measured parameters. Jarvie and others (Jarvie et al., 2001), for example, modelled a continuous Gran alkalinity data set from fortnightly samples using continuous records of pH, conductivity and temperature.

Stable isotopes are another widely used tracer, in particular $\delta^{18}O$, $\delta^{13}C$ from dissolved organic carbon (DOC) and deuterium ($\delta^{2}H$) (Wels et al., 1991; Pellerin et al*.,* 2008). Oxygen 18 (^{18}O) has been used in many hydrological studies to separate flows from different sources and identify recharge areas. One of its key characteristics is the evaporative isotopic signature which is more enriched with respect to ^{18}O. Hence, surface waters tend to show such signatures or water that has originated from irrigation for example (where significant evaporation may have occurred). Many studies also measure both $\delta^{18}O$ and $\delta^{2}H$ ratios at the same time – the difference from the so-called Global Meteoric Water Line (GMWL) can be used to indicate the history of the water (Clark and Fritz, 1997). ^{18}O appears to have been mainly used in the literature in areas where snow melt contributes to the storm flow as it is temperature dependent. Further research in the literature will be necessary to see whether the relatively narrow temperature gradient in Ireland may preclude using it successfully here. This topic is being investigated concurrently with the Pathways Project by Queen's University Belfast (QUB) researchers in an independent 3-year research programme which started in summer 2009.

DOC has also been used (Soulsby, 1992, 1995; Brown et al., 1999; Ladouche et al., 2001; Casper et al., 2003) as it distinguishes between waters that have had different degrees of contact with organic matter. It is generally assumed to be conservative but there are potential issues with impacts of solute flushing (Soulsby 1992, 1995; Ball and Trudgill, 1997; Ladouche et al., 2001). At some catchment scales, there may also be influences on tracer concentrations from different agricultural management practices. More recently, optical properties of DOC, such as fluorescence and ultraviolet (UV) absorbance characteristics, and particularly the spectral absorbance capacity at 254 nm (SAC^{254}), have been used as a surrogate for measuring DOC as they are quick, efficient and inexpensive (Bergamaschi et al., 2005; Hood et al., 2006; Izbicki et al., 2007; Zhang et al., 2007). SAC^{254}, together with silica, was used by Dellwyn Kane to separate hydrographs in the Oona Catchment in County Tyrone as part of his doctoral research conceptualising drumlin hydrology (Dellwyn Kane, University of Ulster, personal communication, 2009).

Other possible tracers of interest that have been widely used by researchers include electrical conductivity, pH, nitrate, total dissolved solids, chloride, calcium, magnesium, sodium, and potassium. There are various advantages and disadvantages in using each tracer, but tracer selection will ultimately be heavily dependent on the catchment characteristics. Specific catchment assessments need to be made prior to carrying out this sort of research to confirm that the tracers of interest can be considered to be conservative in the study area and can be used within the reasonable constraints of the methodological assumptions (Hooper and Shoemaker, 1986).

2.3.1.3 Uncertainty

There is a great deal of uncertainty involved in applying hydrochemical mixing models to quantify the contributions of different flow components to the streamflow. One of the biggest challenges is perhaps determining the spatial and temporal variabilities in the storm flow components, particularly in agricultural catchments, and incorporating those into the models (Pionke et al., 1993; Durand and Torres, 1996; Soulsby et al., 2003a). Broadly, uncertainties can be divided into conceptual model uncertainties and statistical uncertainties.

There are mitigating approaches that can be taken, however, to minimise the uncertainties. Many studies, for instance, apply the methodology in catchments with relatively uniform land use (typically forestry) and hydrogeological characteristics (Soulsby et al., 2003a), or use a large number of tracers (e.g. Pinder and Jones, 1969). Others use event-specific and scale-specific characterisations (e.g. Soulsby et al., 2003a) and select tracers that have large, i.e. orders of magnitude, variations in end member concentrations (Soulsby and Dunn, 2003). Reducing laboratory analytical errors and hydrological measurement errors is also important (Uhlenbrook and Hoeg, 2003), as is applying robust statistical techniques. Turner et al. (1990) recommended using a combined hydrometric/ hydrochemical approach for elucidating flow paths at the catchment scale.

One particular issue that has arisen recently in the literature is the need for higher temporal resolution in chemistry data than the traditional weekly or monthly grab samples to match the continuous flow records, and to sample over longer durations than just single flow events (Jarvie et al., 2001; Soulsby et al., 2003b, 2006; Kirchner et al., 2004). Whilst there are techniques available for making the best use of whatever data are available – Doctor and Alexander (2005), for example, devised and used a technique for extrapolation where there are long-term discharge records but relatively infrequent water quality sample data – this improved chemical resolution is expected to complete the hydrochemical picture of changes in flow over time and provide useful insights to greatly improve conceptual models (Kirchner et al., 2004). Soulsby et al. (2006) report that their future research in the Cairngorms will work towards improving the spatial and temporal resolution of measurements of tracer behaviour in the catchment using flow data at the gauging sites in conjunction with higher resolution water sampling in storm events.

2.3.1.4 Application of method

The early investigators used hydrochemical methods to show that, contrary to previous understanding, groundwater or old/pre-event water was a significant contributor to storm flow, releasing between one-quarter and more than three-quarters of peak flow events in some cases (Pinder and Jones 1969; Hooper and Shoemaker, 1986; Wels et al., 1991).

These techniques have also been shown to play an important role in quantifying hydrological flow. Sklash et al. (1986) used naturally occurring deuterium and the quickflow separation method of Hewlett and Hibbert (1967) to separate hydrographs for a catchment in New Zealand. The quickflow method is just one of many graphical and mathematical techniques available for drawing hydrograph separation lines. A line of constant slope is projected from the point of inflection on the rising limb of the hydrograph to its intersection with the recession limb. Everything above the line is considered to be quickflow, while that below is termed delayed flow. They found that this relatively arbitrary method overestimated the proportion of new water in the system by a factor of 7, thus showing that hydrochemical methods are a major step forward in the conceptualisation of hydrological pathways.

More recently, studies have used hydrochemical methods to model and predict water quality changes throughout a catchment (e.g. Soulsby and Dunn, 2003). Chemical separation techniques can also be applied to mapping databases for the purposes of modelling ungauged catchments. Eshleman et al. (1993) were one of the first groups of researchers to relate results from chemical separation techniques to topographic map analyses with a good correlation. They found that it was mostly saturated excess overland flow contributing to storm flow in a catchment in Virginia and they were able to relate that contribution geographically to an appropriately sized area of saturated soils.

Soulsby et al. (2006) related pathway information, i.e. residence times and groundwater contribution, gleaned from chemical hydrograph separation using $\delta^{18}O$ and Gran alkalinity tracer studies, to catchment soil distribution using the UK Hydrology of Soil Types (HOST) digital Geographic Information System (GIS) database. They found that catchment soil characteristics, as mapped in HOST classes, appeared to be a more important control on flow path partitioning and residence times in the catchment than topography and catchment size. They reached the, admittedly tentative, conclusion that there may be potential for using these relationships to extrapolate understanding of hydrological function to ungauged catchments.

Understanding the changes in chemistry in a stream during a storm flow event can add significantly to the conceptual understanding that can be achieved solely from the more traditional baseflow separation techniques. Uhlenbrook and Hoeg (2003), for example, reported that in their study catchment the fast runoff components such as flow from sealed or saturated areas, with residence times of hours to days, and the deeper groundwater flow, with residence times of 6–9 years, played very little role in flood formation. Rather, it was the delayed response intermediate flow from storage in the periglacial deposits on the slopes (the soil water and shallow groundwater), with residence times of 2–3 years, which provided the most significant contribution to flood flows. This example emphasises an issue discussed by Kirchner (2003), i.e. that rapid hydrological response of catchments to precipitation during storm events produces storm runoff that is dominated by 'old' pre-event water, like baseflows, but with different geochemical characteristics to baseflows per se.

This highlights the fact that flow through the geological profile is complex and that the more traditional two-component hydrograph separation techniques are likely to oversimplify the range of hydrological pathways at work. Understanding the nature of these hydrological pathways and groundwater residence times along them is important so that environmental management strategies can be targeted more efficiently.

2.3.2 Pollutant loading and streamflow duration

As described in Section 2.2, flow duration curves have been found to be useful tools for providing information on the percentage contribution of different pathways to the flow in a stream over a given period of time. Where simultaneous water quality data are collected and related to the flow duration curves, additional insights can be achieved into (a) contaminant loadings (i.e. concentration multiplied by flow) and their relationships with the different components of the flow regime, and (b) the potential source of the contaminants, whether point source or diffuse (USEPA, 2006). Plotting loads against flow, for instance, can more tightly narrow down the range of the most important flow events for bringing large quantities of a contaminant into a stream. When pollutant concentrations decrease with increasing flow, but the loads increase, this is taken as an indication in the US that the source of the contamination may be mainly diffuse rather than point, because the diffuse sources are increasingly diluted by rainfall. Where point sources are prevalent, the loads and the concentrations will both decrease with increasing flow, assuming that there is a constant loading rate and the pollutant behaves conservatively (USEPA, 2006).

A load duration curve approach was used by the USEPA (2006) to develop total maximum daily loads (TMDLs) for contaminants of concern and to assess whether water quality standards were being met. In the Pee Dee River Basin, for instance, the instantaneous faecal coliform criterion of 400 cfu/100 ml was multiplied by the flow rate at each flow exceedance percentile to produce the maximum permissible faecal coliform load in the stream without the criterion standard being breached. A load duration curve was created which provided a simple visual method of determining whether subsequent individual faecal coliform observations were in breach of the standard or not. This approach was used to characterise water quality concentrations at different flow regimes over the course of a year. Seasonal variations in flow and their impacts on TMDLs were considered and water quality concerns were linked with key watershed processes. The relative importance of factors such as water storage or storm events on the delivery of contaminants was also determined.

One interesting application of duration curves in the US is their utility in assisting in the identification of potential contaminant source areas (USEPA, 2006). Duration curves are based on the entire range of flow conditions and consider the general hydrologic condition of the catchment. Pollutant delivery mechanisms likely to have the greatest effect on receiving waters (e.g. point sources, runoff) can be matched with potential source areas appropriate for those conditions (e.g. riparian zones, uplands, impervious zones). An example provided by the USEPA demonstrates the approach in Table 2.1, where potential source areas are assessed based on the relative importance of delivery mechanisms under the range of hydrologic conditions. The table provides an organisational framework which can be used to guide source assessment efforts. For instance, point sources in the US tend to have the most dominant effect on water quality under low flow conditions, thus the low flow zone of flows is a relatively high priority for assessment of point sources.

While further work will be required to validate the applicability of this approach in Ireland, duration curves are a useful tool to add to the 'toolbox' of methods for quantifying flow along the various pathways. Hydrochemical methods are not a panacea but they have an important role to play in better conceptualising flow through the landscape to streams. They will likely be of most use as part of a multifaceted approach that considers more than one technique and tests conceptual hypotheses from different perspectives.

2.4 Integrated Pathways Approach Using Models

In addition to attempting to decompose a river hydrograph using physical or chemical methods, the

Table 2.1. Example of potential source area identification under a range of hydrologic conditions (after USEPA, 2006).

Contributing source area	Duration curve zone				
	High flow 0–10%	Moist 10–40%	Mid-range 40–60%	Dry 60–90%	Low flow 90–100%
Point source				M	H
On-site wastewater systems			H	M	
Riparian areas		H	H	H	
Storm water: impervious areas		H	H	H	
Combined sewer overflows	H	H	H		
Storm water: upland	H	H	M		
Bank erosion	H	M			

Note: Potential relative importance of source area to contribute loads under given hydrologic condition (H: high; M: medium; L: low).

flow pathways within a river catchment can be analysed using a variety of modelling approaches. These can range from simple rainfall–runoff relationships to lumped catchment models, and on to more complex distributed numerical models. The unit hydrograph is an example of a rainfall–runoff relationship that is widely used in catchment hydrology (see e.g. Shaw, 1994). This is the river hydrograph resulting from a unit depth of effective rainfall (here defined as rainfall that produces runoff) falling in a particular time period over an entire catchment. Although its main application is in flood studies, the unit hydrograph can also be used to help separate out the overland flow component of runoff as part of a water resources study. The method was applied in the recent groundwater and surface water interactions project in Ireland to help constrain the overland flow element of the total runoff simulated using the NAM lumped parameter model (RPS, 2008) (see Section 3.5).

Examples of lumped parameter models include NAM, HBV and SMAR, many of which can be operated in either lumped or semi-distributed mode (using specific sub-catchments). These models contain a number of parameters that are varied in the calibration process, potentially resulting in non-unique solutions. Many lumped parameter models involve the routing of flows through various linear storage reservoirs within a catchment. Such models are essentially developments of unit hydrograph theory. The Danish NAM model is one example, and is based on the MIKE11 modelling suite. This deterministic model separates rainfall into four different reservoirs: snow storage (if required), surface storage, lower zone (or root zone) storage and groundwater storage (see Fig. 2.2). The three main

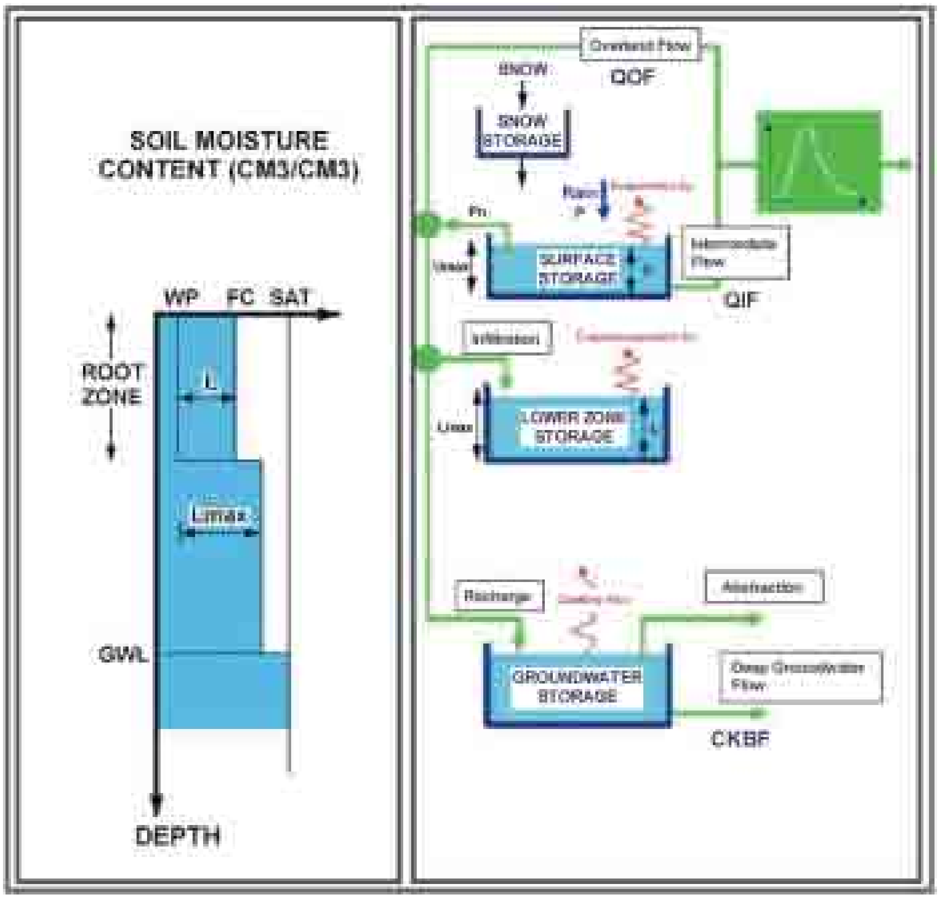

Figure 2.2. The structure of the NAM model. WP, soil moisture content at wilting point; FC, soil moisture content at field capacity; SAT, soil moisture content at saturation level; GWL, groundwater level; L, root zone storage (Lmax = maximum); U, surface zone storage (Umax = maximum); QOF, overland flow; Pn, net precipitation; QIF, interflow contribution; CKBF, time constant for baseflow. Reproduced from RPS (2008).

outputs (as contributors to total runoff) are overland flow, intermediate flow and groundwater flow. As noted in Section 3.5, in the 2008 groundwater and surface water interactions study, the intermediate flow output was considered to include both interflow and shallow groundwater flow.

An earlier routing model was described by Serenath and Rushton (1984). This model was developed for an area of chalk aquifer with overlying superficial deposits in southern England. The following pathways were included: overland flow; flow through and over the strata overlying the main chalk aquifer, including tills and glacial sands and gravels; recharge to the main chalk aquifer; and streamflow, and its interaction with groundwater.

Distributed, physically based models seek to simulate the individual component parts of a hydrological system, and may include algorithms representing overland flow, interflow and groundwater flow. Examples – of varying complexity – include models such as SHE, HSPF, SWAT, TOPMODEL, MODFLOW and FEFLOW. An example schematic for a distributed component model is shown in Fig. 2.3. This is the widely used SHE (Système Hydrologique Européen) model, which was developed by hydrologists in France, Denmark and the UK. It can be seen that this is more complex than the relatively simple storage reservoir type model illustrated in Fig. 2.2. In the SHE model, the spatial variability of a catchment can be represented by up to 2,000 horizontal and 30 vertical nodes. Finite difference numerical solutions are applied to solve flow equations along the various flow pathways.

Distributed models such as the SHE model generally require much more comprehensive data sets than lumped models. Unfortunately, such data sets are rarely available, thus limiting the applicability of distributed models. Fully distributed models also are more difficult to calibrate and even extensive data sets do not guarantee that they are the best modelling option. Nasr et al. (2007) compared models for modelling phosphorus export from three Irish catchments. The models had increasing levels of complexity, and included SHETRAN, a distributed model. The study found that no single model was consistently better at estimating total phosphorus (TP) output for all catchments. As such, whilst distributed models may have utility in this Pathways Project when undertaking a detailed investigation of flow pathways in a particular data-rich catchment, they are unlikely to feature as an integral part of a future CMT.

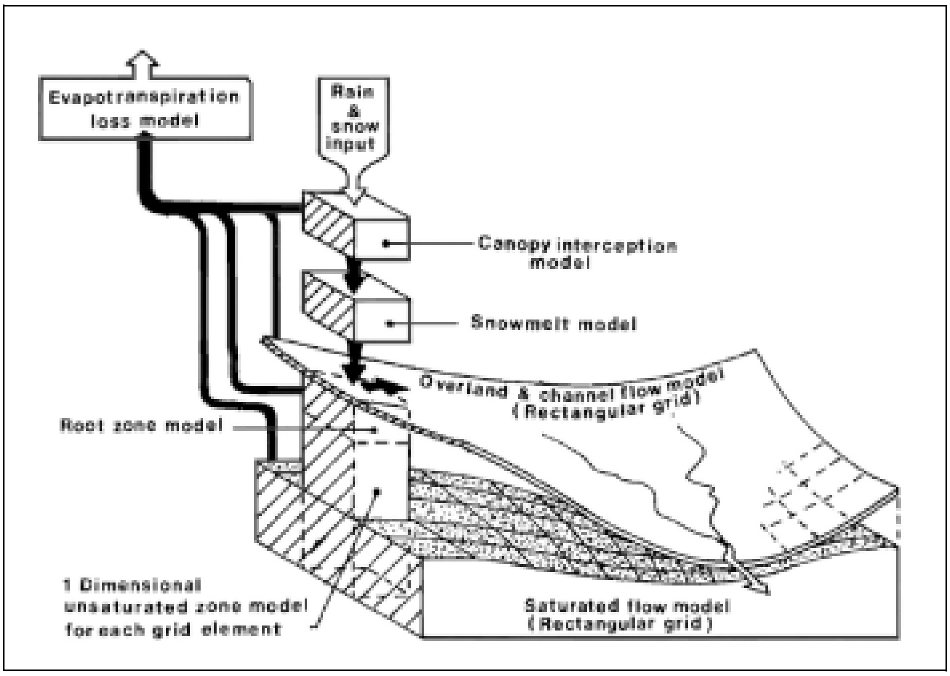

Figure 2.3. The structure of the SHE (Système Hydrologique Européen) model (Abbott et al., 1986).

The CMT will allow different modelling conceptualisations to be tested, but will require that their elements are coded into the tool and conform to its programming conventions. For instance, a model such as MIKE11 would not be integrated into the CMT, but the tool will be able to simulate the model (or any such catchment model) to assess its performance. In this sense, the CMT is flexible, which will be important for incorporating any future water quality measures that a river basin manager might want to test. This flexibility will allow comparisons of different conceptualisations of pathways, including comparing simple conceptualisations with more complex ones, and will be able to calibrate their parameters if sufficient data are available. Different conceptualisations may be needed for the different catchment settings and for achieving different outcomes.

3 Irish Hydrology and Flow Pathways

The early sections of this chapter contain a short description of the topography, meteorology, hydrology and hydrogeology of Ireland, with details of the main sources of data (Sections 3.1–3.3). The chapter then focuses on previous studies of river hydrographs and flow pathways in Ireland (Sections 3.4 and 3.5). The chapter concludes with a discussion of the proposed conceptual model for this Pathways Project, and summarises the main data gaps (Section 3.6) with recommendations for further research (Section 3.7).

3.1 Physical Setting

The following paragraphs provide a brief introduction to the physical characteristics of the country, including topography and drainage, soils and subsoils, bedrock geology and land use. Useful sources of web-based information include the WFD Ireland website (http://www.WFDIreland.ie), the EPA's ENVision site (http://maps.epa.ie), the Geological Survey of Ireland's (GSI) mapping site (http://www.gsi.ie/mapping) and a recent (April 2009) presentation by Scanlon (see: http://www.gsi.ie/Programmes/Support+Services/Information+Management/Presentations.htm).

Ireland has a mountainous rim around its seaboard, with mountains rising to over 800 m above ordnance datum (OD) in coastal counties in the east, south-west, west and north-west. The centre of the country is mainly gently undulating lowland, with elevations typically around 50–100 m OD. The country is drained by a series of river systems which have been grouped into eight RBDs for the purposes of the WFD; five of the RBDs are located entirely within the Republic, two are cross-border and the eighth is entirely within Northern Ireland. Within the RBDs, approximately 5,500 water bodies have been identified as the management units for assessing their status (both quantity and quality), comprising 4,467 river water bodies, 205 lake water bodies and 757 groundwater bodies (EPA, 2005a).

The country's topsoils are mainly derived from glacial subsoil materials. Brown Earth and Brown Podzolic-type soils are common in the midlands and south, whereas gleyed soils are more common in the north and west. The subsoils comprise glacial deposits, mainly tills (but including esker and glacio–fluvial sands and gravels), together with peat, lacustrine deposits and alluvium. The soils and subsoils maps prepared by Teagasc are available on the EPA's ENVision site and the subsoils mapping is also available on the GSI's Groundwater Public Viewer (http://www.gsi.ie/mapping). In addition, the GSI's Aggregate Potential Mapping Project has produced a summary subsoils map for the country.

The mountainous rim of the country is mainly composed of Precambrian and Lower Palaeozoic rocks, including granites and metasediments, whereas the midlands and parts of the south are underlain mainly by Carboniferous limestones and Devonian sandstones. Bedrock of younger age is found predominantly in Northern Ireland, and includes the Permian Sherwood Sandstone, Cretaceous Ulster White Limestone (chalk) and Tertiary basalts. Between 1986 and 2006 the GSI produced a series of 1:100,000 maps and memoirs describing the bedrock geology of the Republic. The maps, together with other useful GSI data sets, are now available as GIS files on CD and for download (as zipped files) from: http://www.dcenr.gov.ie/Spatial+Data/Geological+Survey+of+Ireland/GSI+Spatial+Data+Downloads.htm. A detailed account of Ireland's geological history can be found in the recently revised and updated *The Geology of Ireland* (Holland and Sanders, 2009).

The main land use in Ireland is grassland, covering approximately two-thirds of the total land area – and over 90% of all agricultural land (Brogan et al., 2002). Forestry covers just under 10% of land, mainly upland areas. Data on land use can be found at http://maps.epa.ie, which includes the Corine land cover data for 1990 and 2000.

3.2 Meteorology and Hydrology

3.2.1 Meteorology

Climate data, including precipitation and evapotranspiration, can be purchased from Met Éireann (http://www.met.ie/climate/climate-data-information.asp). There are 13 synoptic stations located throughout the country (there were 15 previously, but the stations at Clones and Kilkenny were closed in 2008). These record hourly values of precipitation, wind speed, temperature and other meteorological parameters. In addition, rainfall is measured at approximately 550 sites, 45 of which have recording gauges (Fitzgerald and Fitzgerald, 2004). Open water evaporation is measured with Class A pans at 30 sites, and evapotranspiration by lysimeters at four locations. Potential evapotranspiration (PE) is calculated from the meteorological data collected at the synoptic stations, using the Penman method and more recently the Penman–Monteith formula. Useful maps and summaries of Irish climate data are included in Collins and Cummins (1996) and Keane and Collins (2004).

Rainfall decreases across the country from west to east, with western counties receiving more than 1,200 mm annual rainfall compared with around 750 mm along the east coast. There are appreciable variations of rainfall with altitude: annual rainfall amounts increase by between 100 mm on eastern slopes and 200 mm on western slopes, for every 100 m increase in altitude (Keane and Sheridan, 2004). Whereas rainfall occurs throughout the year, without a noticeable wet or dry season, evapotranspiration ranges from less than 0.5 mm/day in December to more than 2.5 mm/day in June, leading to a soil moisture deficit (SMD) developing in the summer months. The average annual PE for the 30-year period 1971–2000 is between 440 mm and 552 mm for inland and maritime stations, respectively (Collins et al., 2004). Actual evapotranspiration (AE) is usually determined by a soil moisture balance, using methods such as the Aslyng scale, Penman–Grindley and Food and Agriculture Organization Penman–Monteith. In the absence of site-specific calculations, AE is often assumed to be approximately 95% of PE (Daly, 1994; Working Group on Groundwater, 2005; Misstear et al., 2009). The moisture surplus arising from the balance of annual total rainfall minus AE, known as the effective precipitation, ranges from less than 400 mm in parts of the east of the country to more than 800 mm in the north-west, west and south-west (Fig. 3.1). This is the water available for overland flow, interflow or groundwater recharge.

The proportion of effective rainfall that gives rise to either overland flow, interflow or groundwater recharge is influenced by factors such as rainfall intensity, topographic slope, soil infiltration capacity, land use, subsoil permeability and available aquifer storage (for accepting potential recharge). In general terms, river hydrographs tend to be ‘flashy’ in small catchments with significant land slopes, where rainfall intensity is high, and where the soils are gleyey and have limited infiltration capacity. This gives rise to a greater proportion of rainfall following surface and near surface pathways to watercourses. This in turn implies that the levels of attenuation experienced by pollutants as they travel between a source and receptor will depend more strongly on the mechanisms operating along these pathways. Less flashy hydrographs with larger baseflow components occur in catchments where the soils and subsoils are permeable, and where the catchment is underlain by a regionally important aquifer that can accept recharge and release significant quantities of baseflow. Examples of flashy and ‘non-flashy’ river hydrographs are given in Section 3.4.3, for rivers in counties Monaghan and Kilkenny, respectively. Schulte et al. (2006) summarise the complex interrelationship between soil type, climate and contaminant mobility in the Irish setting.

3.2.2 River flow data

Local authorities and the Office of Public Works (OPW) operate networks of gauges on the main rivers in Ireland. The EPA processes data collected at the local authority gauging sites, with gauges classified as automatic recorder, data logger, spot measurement, staff gauge or unknown. The data can be accessed on the EPA’s hydronet site, where the data are presented as 3-month, 1-year and complete hydrographs of both stage and flow. The EPA also maintains the Register of Hydrometric Gauging Stations in Ireland (EPA, 2007a). This includes summary details, with flow statistics, for all gauging sites in Ireland. There are

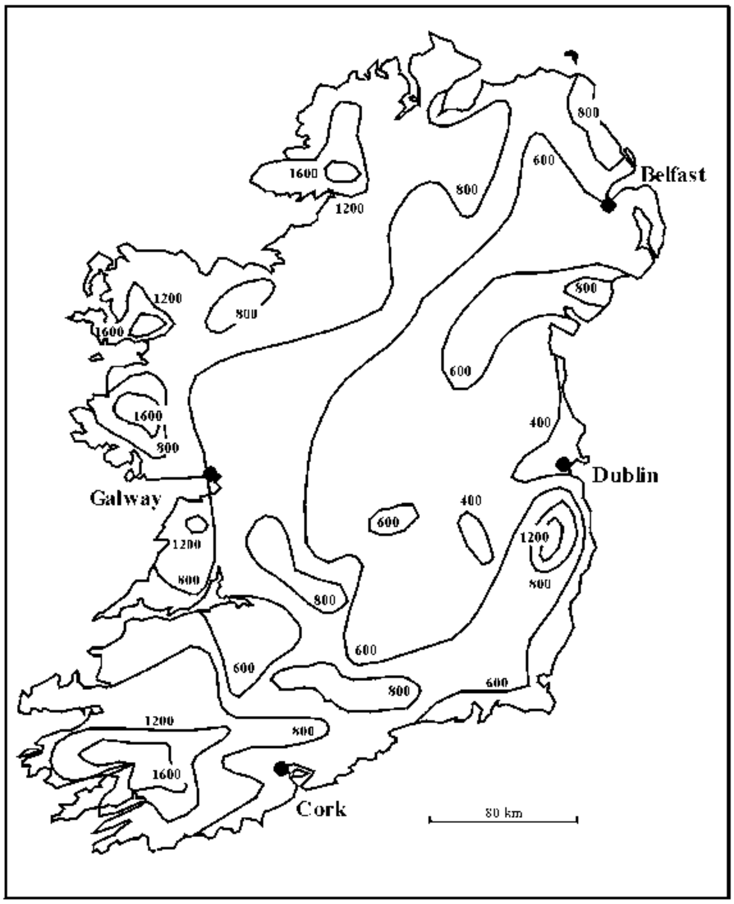

Figure 3.1. Mean annual effective rainfall, in mm (after Collins and Cummins 1996; figure compiled by David Drew, Trinity College Dublin).

1,957 gauges listed on the 2007 EPA register of gauges.

OPW data can be found on its Hydro-Data site http://www.opw.ie/hydro/index.asp. This includes a map finder option for locating gauges. By clicking on a gauge, the investigator can bring up summary statistics including stage and flow duration percentiles.

Other sources of flow data include the Electricity Supply Board (ESB), which monitors flows on rivers that feed its main power stations, and research institutions, which collect data for particular projects. In Northern Ireland, river flow monitoring is the responsibility of the Rivers Agency.

In conclusion, whereas the main rivers are well gauged, there are relatively few gauges (and especially automatic recorders) on the smaller rivers which are potentially of most interest for detailed study in this Pathways Project.

3.2.3 Climate change

Before leaving this section, it is worth mentioning climate change and how this may alter meteorological and hydrological conditions in the future. Various studies have been carried out, including those by Kiely (1999) and Steele-Dunne et al. (2008). Predictions vary according to the models and greenhouse gas emission factors used, but studies generally suggest an increase in winter rainfall, especially in the north-west of the country, and a decrease in summer rainfall, especially in the south-east. An increase in the number of extreme events is also forecast, suggesting that river hydrographs may become more flashy. Thus, changes in meteorological conditions in the future are likely to influence flow pathways and their contributions to the river hydrograph.

3.3 Hydrogeology

The country's bedrock aquifers are characterised by secondary permeability, with fissure flow (and conduit flow in some karst areas) dominant; primary, intergranular permeability is virtually absent, except in some of the younger bedrock aquifers in Northern Ireland (notably the Sherwood sandstone). The secondary permeability is best developed in the upper 10–30 m of bedrock, especially in the less productive aquifers found in the oldest geological formations (predominantly Precambrian and Lower Palaeozoic). Deeper fracturing, with deeper active groundwater circulation, can occur in the more productive aquifers, notably in some of the Carboniferous limestone formations. The effective porosity and storativity of bedrock aquifers is generally low and this, together with the presence of fissure flow, means that there is often a relatively rapid hydraulic response to both recharge and dry spells, with annual fluctuations in water-level hydrographs often exceeding 10 m. By contrast, the aquifers comprised of alluvial or glacio–fluvial sands and gravels display intergranular flow and have higher specific yield (and effective porosity), and so have more muted hydrograph responses. The contrast in effective porosity results in differences in travel times experienced by contaminants transported through each aquifer type. Under equivalent hydraulic gradients and hydraulic conductivities, lower effective porosity gives rise to more rapid contaminant transport rates, which may be important in determining levels of contaminants whose impact depends on the time taken for a pollutant to travel from a source to a receptor, e.g. pathogens.

In the National Groundwater Protection Scheme (DoELG et al., 1999), both bedrock and superficial aquifers are classified as regionally important, locally important or poor, with various subcategories defined according to their particular characteristics and extent. Under the WFD, the management unit for groundwater is the groundwater body. Each aquifer type may comprise numerous groundwater bodies and thus 757 groundwater bodies have been delineated in Ireland, approximately half of which occur in poorly productive bedrock, a quarter in karstified limestone and the remainder in productive fissured bedrock and sand and gravel (Daly and Craig, 2009). Traditionally, very little monitoring was carried out in the poorly productive aquifers but, in view of their wide occurrence, this data gap is currently being addressed by the EPA.

As well as containing a classification of the country's aquifers, the national groundwater protection scheme also includes groundwater vulnerability assessment and the delineation of protection areas around individual wells and springs. The vulnerability assessment is based mainly on the characteristics of the subsoils protecting an aquifer, especially their permeability, and also on the nature of the recharge (diffuse or point, the latter occurring in karst areas). Vulnerability maps (prepared at 1:50,000 scale), together with aquifer maps, source protection areas, information on wells and karst features, are available on the GSI's Groundwater Public Viewer (http://www.gsi.ie/mapping).

In broad terms, areas covered by thick low-permeability subsoils would be expected to have low recharge potential, and correspondingly high surface runoff (overland flow), whereas the converse should apply in those areas where subsoils are permeable and/or thin. This relationship was studied as part of a previous STRIVE project and the resultant linkages are summarised in Table 3.1. High recharge coefficient is defined as 70–90% of effective rainfall, with intermediate recharge coefficient being 30–70% and low recharge coefficient 5–30%. High recharge coefficient corresponds to low runoff, intermediate recharge to intermediate runoff, and low recharge to high runoff. Hence, for example, the high runoff category corresponds to 70–95% of effective rainfall.

Table 3.1 gives a rather simplistic picture since, in areas where subsoil conditions might suggest high groundwater recharge, other factors such as the ability of an aquifer to accept this potential recharge (which is limited in locally important and especially in poorly productive aquifers) also need to be taken into account (Misstear et al*.,* 2009). Nevertheless, the relationships can provide a useful starting point when considering major pathway contributions in a catchment.

Table 3.1 The linkages between subsoil permeability, recharge, runoff and aquifer vulnerability (Misstear et al., 2009).

Subsoil		Recharge	Runoff	Aquifer vulnerability
Permeability	**Thickness**			
High	1–3 m	High	Low	Extreme
	>3 m	High	Low	High
Moderate	1–3 m	High	Low	Extreme
	3–10 m	Intermediate	Intermediate	High
	>10 m	Intermediate	Intermediate	Moderate
Low	1–3 m	Intermediate	Intermediate	Extreme
	3–5 m	Low	High	High
	5–10 m	Low	High	Moderate
	>10 m	Low	High	Low

3.4 River Hydrograph Studies

3.4.1 Baseflow studies from the 1980s and 1990s

The following text is based mainly on Misstear and Brown (2008). Previous estimates of BFI for Irish catchments include those by Daly (1994) for the Nore Basin, MacCarthaigh (1994) for the Blackwater (Monaghan), Finn, Glyde and Dee catchments, Scanlon (1985) for the Maine and Flesk catchments and by Aslibekian (1999) for several other small catchments. Results are summarised in Table 3.2. The catchment locations are shown in Fig. 3.2.

The results presented in Table 3.2 for the Nore, Maine, and Maigue highlight an issue with respect to scale that is relevant to the Pathways Project: the soil, subsoil and bedrock geology usually vary over a much smaller scale than the size of catchment in which the river flow is gauged. The implication of this for the Pathways Project is that it will be desirable to choose study catchments that are sufficiently small to contain

Table 3.2. Selected baseflow index values from catchment studies in Ireland in the 1980s and 1990s (Misstear and Brown, 2008).

Catchment	Catchment characteristics	Baseflow index	Reference
Nore (2,388 km^2)	• Variable aquifers, subsoil and topography	50%	Daly (1994)
Monaghan Blackwater (126 km^2)	• Regionally important limestone aquifer • Thick, moderate- to low-permeability subsoils across both a lowland and upland setting	27%	MacCarthaigh (1994)
Maine and Flesk (272 km^2)	• Shale, shaley limestone and pure limestone aquifers • Variable till cover, generally thicker over the shaley limestones • Lowland and upland setting	38%	Scanlon (1985)
Maigue	• Karst limestone, thin subsoil in the lowland • Poor aquifer with thicker lower-permeability subsoils in the uplands	28%	Aslibekian (1999)
Allagaun	• Poor aquifers • Variable low-permeability peat subsoil and exposed rock • Mountain setting	10%	Aslibekian (1999)

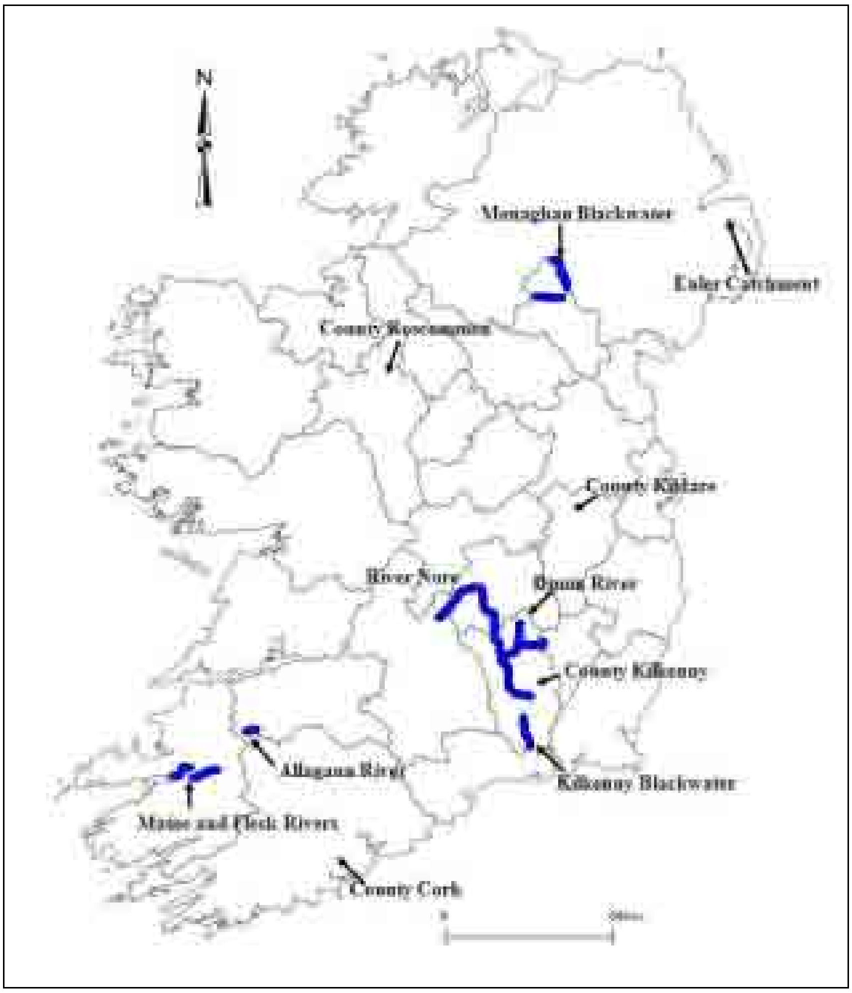

Figure 3.2. Catchment locations for baseflow studies from the 1980s and 1990s (Misstear and Brown, 2008).

relatively consistent soil and geological characteristics, yet also possess river flow gauging records.

One of the most detailed catchment studies in Ireland was that by Daly (1994) of the Nore River Basin. Daly estimated that for the gauging station at Brownsbarn Bridge on the lower reach of the Nore, approximately 41–60% of discharge was baseflow contributed from groundwater. Baseflow was assessed using the Barnes (1939) technique.

As well as the studies summarised in Table 3.2, Cawley (1994) applied a lumped model in a study of the Brosna, Nore and Suir catchments. The model computed monthly streamflow (as ‘fast discharge’ and ‘slow discharge’, the latter being regarded as equivalent to baseflow) from monthly values of precipitation and PE. The model produced good results when compared with actual (total) streamflow measurements in the study catchments.

3.4.2 A sensitivity analysis of river baseflow (Misstear and Fitzsimons, 2007)

Misstear and Fitzsimons (2007) examined the sensitivity of river hydrograph analysis to the time base parameter used in the Institute of Hydrology method (Institute of Hydrology, 1989) (see Section 2.2), and also considered the potential contributions of different subsurface pathways to a hypothetical river hydrograph. The study was based around three catchments within the Nore Basin:

1. A ‘hybrid’ sub-catchment, lying south of Kilkenny City;

2. the Kilkenny Blackwater; and

3. The River Dinin.

The hybrid sub-catchment was delineated by isolating the discharges upstream of St John's Bridge in Kilkenny City and upstream of Annamult on the King's River from the discharges downstream at Mount Juliet on the main Nore.

Using the Institute of Hydrology method the value of the 'time base' *N* was calculated from the catchment area ($N = A^{0.2}$, where *A* is the catchment area (Linsley et al. (1975)), and was then varied by no more than 2 days, giving a range of 3–5 days. For the hybrid sub-catchment, a well hydrograph was used to assess the appropriateness of the time base responses (well hydrographs were not available for the other two sub-catchments). The results of the sensitivity analysis are summarised in Table 3.3. It can be seen that, even when using only this single baseflow separation method, there is a large variation in predicted baseflow within each sub-catchment. The baseflow separations for the hybrid sub-catchment are illustrated in Figs 3.3 and 3.4. In comparing the hydrograph separations with the observed fluctuations in a nearby borehole, it can be seen that the baseflow separation using a time base (*N*) value of 3 (Fig. 3.3) represented the frequency of winter recharge events better than the analysis with a time base of 5 (Fig. 3.4).

The largest variation in BFI is in the Dinin, which is the most upland catchment, with low-permeability soils and subsoils, and underlain by a poorly productive aquifer. Therefore, the BFI values of between 46% and 65% are unlikely to represent the contribution from bedrock groundwater, and probably include contributions from interflow pathways.

Misstear and Fitzsimons also considered the influence of various potential shallow subsurface pathways on the river hydrograph, such as peat, glacial tills, and weathered rock, as well as deeper groundwater contributions. Fig. 3.5 shows some hypothetical examples of different subsurface pathways and their contribution to the overall hydrograph. In these examples, the moving averages of 3-day, 10-day and 30-day durations were calculated using effective rainfall data from the synoptic station at Kilkenny. The runoff data were taken from the hybrid catchment data set described above. In this simulation, overland flow was assumed to be insignificant and all contributions to the runoff hydrograph were assumed to come from subsurface pathways. The authors suggested that the early part of the overall storm hydrograph in Fig. 3.5 is dominated by short-term subsurface releases (e.g. from bank storage or interflow), the main portion by contributions from intermediate-term releases (e.g. from weathered rock), while the latter part is dominated

Table 3.3. Examples of the sensitivity of groundwater baseflow to the time base parameter (Misstear and Fitzsimons, 2007).

Gauge	Hydrogeological setting	Gauge catchment	Estimate of time base (*N*) from *N* = Catchment Area$^{0.2}$	Range in time base values (*N*)	Range in baseflow indices[1]
Hybrid flow record[2]	• Lowland • Typically moderate-permeability till (~5 m thickness) and some high-permeability gravel subsoils	Nore (1,140 km^2)	4	3, 5	58–68%
Scart	• Upland • Thin subsoils • Locally important fractured sandstone aquifer	Kilkenny Blackwater (108 km^2)	3	1, 3	60–76%
Castlecomer	• Poor to locally important aquifers • Generally low-permeability subsoils of varying thickness • Small gravel body occurs close to central river.	Dinin (153 km^2)	3	1, 3	46–65%

[1]Note: Baseflow was estimated by the Institute of Hydrology method (Institute of Hydrology, 1989).
[2]Derived from upstream and downstream gauges.

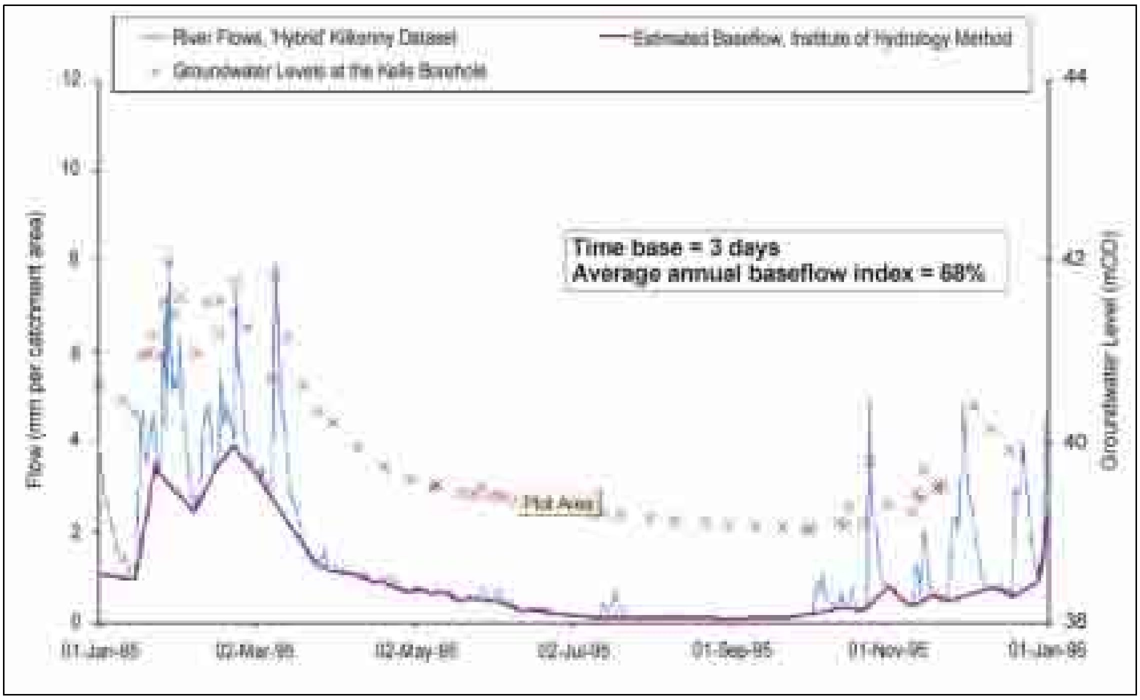

Figure 3.3. Institute of Hydrology baseflow separation for Nore hybrid catchment, using *N* = 3 (Misstear and Fitzsimons, 2007).

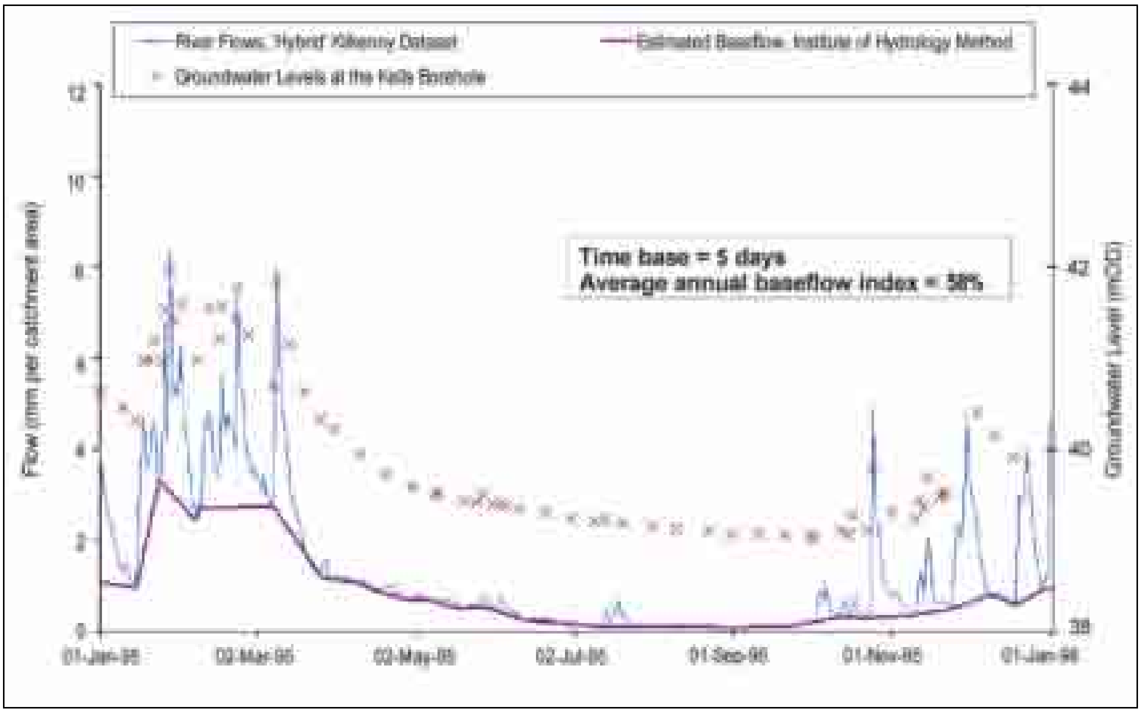

Figure 3.4. Institute of Hydrology baseflow separation for Nore hybrid catchment, using *N* = 5 (Misstear and Fitzsimons, 2007).

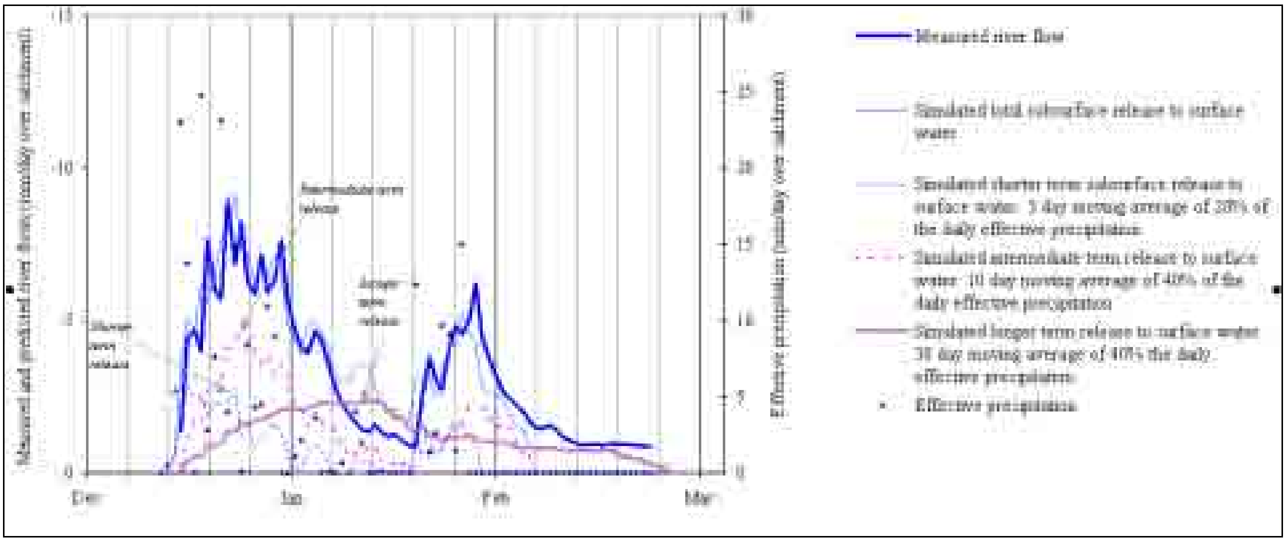

Figure 3.5. A hypothetical case depicting contributions of differing subsurface release pathways to the runoff hydrograph of a typical winter storm (Misstear and Fitzsimons, 2007).

by longer-term release (e.g. from deeper portions of a bedrock aquifer).

3.4.3 Recharge and vulnerability project (2008)

This EPA STRIVE project involved the development of a methodology for quantifying the linkage between groundwater recharge and groundwater vulnerability (especially subsoil permeability). The overall project results are described in Misstear and Brown (2008) and in Misstear et al. (2009). The project included estimations of groundwater recharge in four study areas of contrasting subsoil and aquifer properties. River hydrograph analyses were carried out in two of these areas, namely in the Knockatallon/Tydavnet area in County Monaghan and in two neighbouring catchments within the Nore Basin in County Kilkenny (including the hybrid sub-catchment described above).

An example of baseflow separation using the Institute of Hydrology method is shown in Fig. 3.6. This is for the Monaghan Blackwater, which drains part of the Knockatallon/Tydavnet area in County Monaghan. This analysis was performed using a time base value *N* of 10, and resulted in a BFI of 32%. Adjusting the time base values to 5 and 20 gave BFIs of 41% and 25%, respectively.

However, the subsoils in this drumlin area consist of thick (up to 50 m) low-permeability tills. Furthermore, the limestone bedrock aquifer is classified as locally important and water levels (at the time of analysis) had been drawn down significantly by abstractions from the local group water scheme. Therefore, the hydraulic connectivity between the bedrock aquifer and the surface drainage system would be expected to be low and groundwater discharges would be expected to be small, and so it is very unlikely that these BFIs are representative of bedrock groundwater contributions to the river. Rather, the baseflow in this case is probably indicative of interflow from glacial subsoils, releases from peat deposits and discharges from sands and gravels found along the river valley. Applying the two-parameter Boughton algorithm to the same data set gave a more plausible range of BFIs (12–15%, see Fig. 3.7), but this was achieved partly because the Boughton method allows for a great deal of flexibility in choosing values for the parameters *k* and *C* (see Section 2.2).

The effect of varying the *k* and *C* parameter values in the Boughton method is illustrated by the hydrograph in Fig. 3.8 for the King's River Catchment in County Kilkenny. The higher and lower estimates of baseflow resulting from the two sets of parameter values were 60% and 36%, respectively, but it clearly would have been possible to produce other baseflow values using this subjective method.

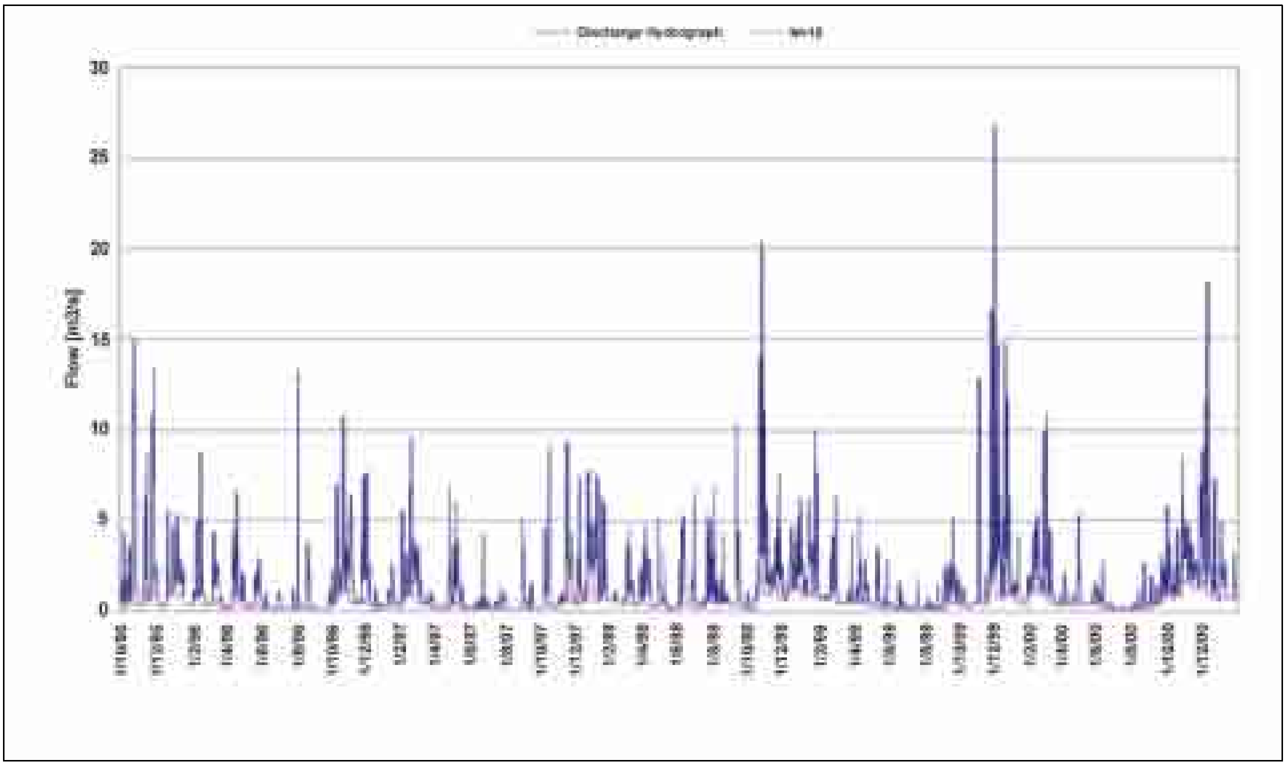

Figure 3.6. Hydrograph of the River Blackwater (Cappog Bridge gauging station) showing an example of baseflow separation using the Institute of Hydrology method of separation (*N* = 10 days) (Misstear and Brown, 2008).

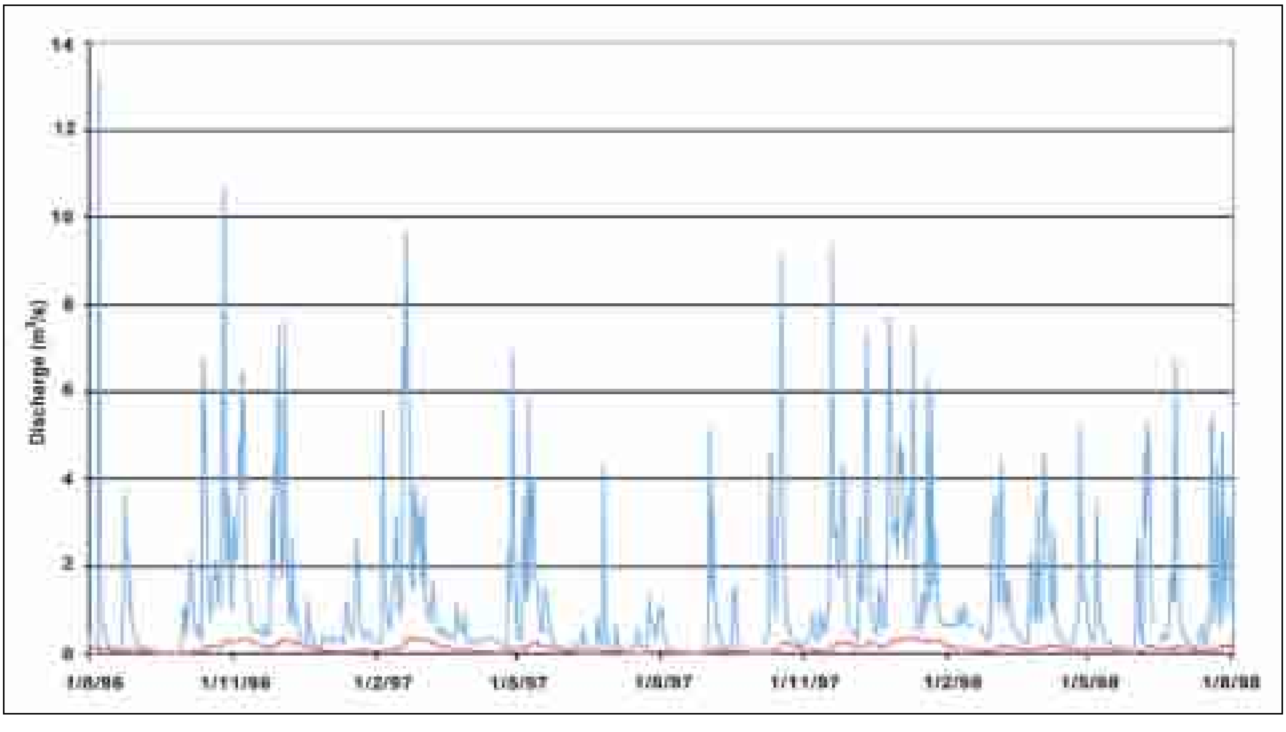

Figure 3.7. Hydrograph of the River Blackwater (Cappog Bridge gauging station) showing an example of baseflow separation using the Boughton method (Misstear and Brown, 2008).

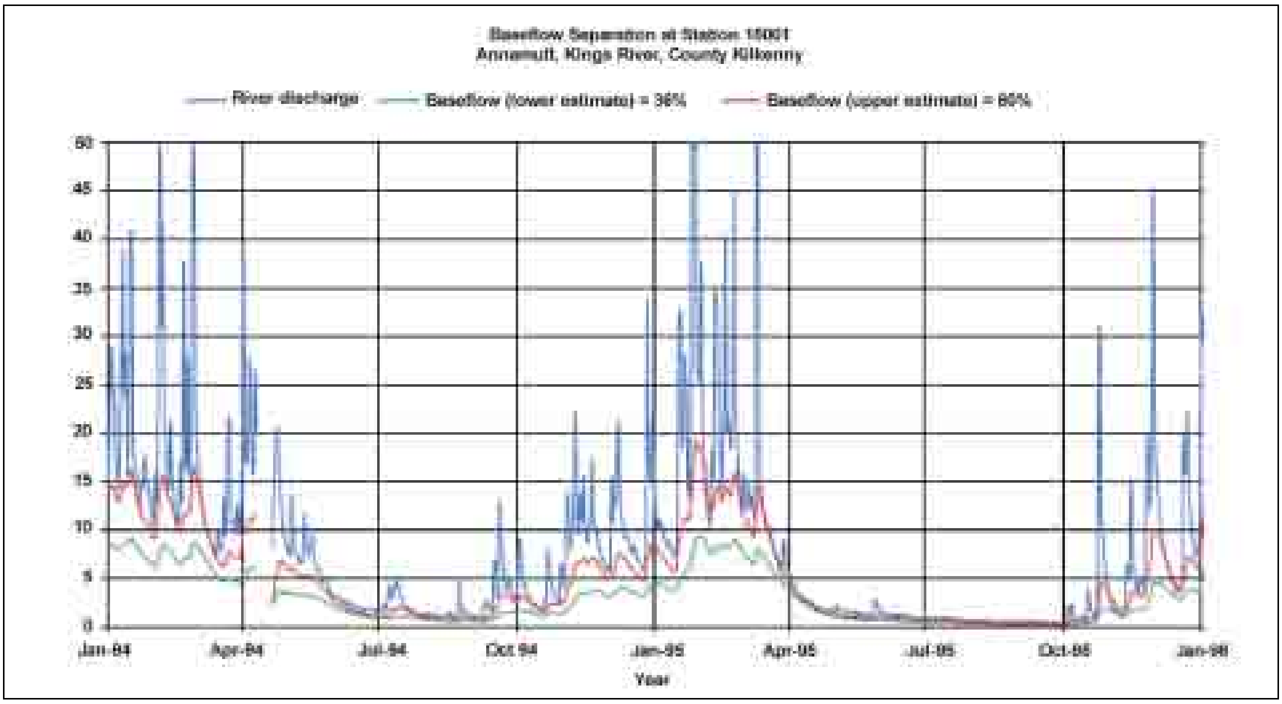

Figure 3.8. Baseflow analysis on the King's River at Annamult, using the Boughton (1995) two-parameter algorithm (k = 0.95, C = 0.028 for lower estimate; k = 0.94, C = 0.09 for upper estimate) (Misstear and Brown, 2008).

The conclusions that can be drawn from this study include:

- More than one approach should be used when analysing a river flow hydrograph;
- The methods need to back up a sound conceptual model of the catchment, including the main flow pathways; and
- The results of hydrograph separation should be subjected to sensitivity analysis.

3.4.4 Flow duration analysis

A study was carried out by ESB International for the EPA to provide a means of estimating flow duration curves for ungauged catchments in Ireland, making use of the extensive hydrometric network in the country and incorporating GIS information on topography, climate, soils and geology (ESBI, 2009).

The method involved firstly generating flow duration curves for a master set of gauging station data sets. Each station also then had a set of catchment descriptor characteristics based on GIS layers of topography/climate, soils, subsoil vulnerability/permeability and aquifers that had been generated and applied across the whole country. In ungauged catchments, the catchment descriptors were used to identify three stations from the master set which had the most similar characteristics. Flow data sets from these three stations were then used to calculate an average flow duration curve (per square kilometre) which was then applied to the ungauged catchment.

The method was found to be useful but had some limitations where rivers were impacted by abstraction and regulation, where there was conduit karst, at or near lake outfalls, and where the catchment descriptors at the ungauged site lay outside the range of the master set. The method will be improved over time as further gauging and catchment descriptor data become available.

3.4.5 Use of chemical tracer methods in Ireland

Chemical tracer methods have potential as a means of constraining the empirical parameters employed in analysing hydrograph data by physical methods (see Section 2.3).

There are just two studies in Ireland to date that have used chemical tracer methods for baseflow analysis. The more comprehensive of the two was a doctoral study carried out by Dellwyn Kane (University of Ulster, personal communication, 2009) in the Oona Catchment in County Tyrone, in which silica and SAC^{254} were used to distinguish three end members in the hydrograph: overland flow, shallow soil water (~10 cm) and deep soil water (~30–40 cm). Kane sampled at two catchment scales (~0.1 and 5 km^2) during five storm events and looked in some detail at the statistical uncertainties in the methodology. He then used the results to develop a conceptual model for the hydrology of drumlin morphology areas such as the Oona Catchment. This work was completed recently (2009), and has yet to be published.

The second of the studies was an undergraduate thesis by Dowling (2009) which looked at two storm events in the Loughlinstown River in south-east County Dublin. Dowling used pH, silica, chloride, electrical conductivity and acid neutralising capacity to separate the baseflow from the hydrograph and then compared his results with baseflow estimates using graphical (straight line, constant slope and concave) and digital filtration (Lyne and Hollick, 1979; Chapman, 1991; Eckhardt, 2005) hydrograph separation techniques. Results from all the techniques were then compared with results from MRC and frequency duration curve (FDC) analysis for the longer-term records. For the flow event that he had most confidence in, Dowling found that results from all the chemical tracers except pH were useful, and in general fell within 5–10% of the baseflow estimates generated using the MRC and FDC methods (65–66% of total storm flow). He also found that the baseflow contribution varied significantly depending on the method used (range 32–69%, excluding pH).

Artificial tracers, which can be deliberately introduced into the hydrological cycle under controlled conditions, have been used in other hydrological/hydrogeological projects in Ireland to conceptualise and quantify groundwater residence times and flow paths. The majority have been carried out at springs and sinks in karst terrains (e.g. Gunn, 1982; Drew, 1988) but there are a small number of studies that have considered flow through the unsaturated soils and subsoils into the underlying bedrock aquifer (Ryan, 1998; Tooth and Fairchild, 2003; Richards et al., 2005). A tracer study in Fermoy, County Cork, for example, applied bromide at the surface in an area underlain by 0.6 to >3 m of thin free-draining soils and Quaternary sands and gravels, overlying a shaley/cherty limestone classified as a locally important aquifer (Ballysteen Limestone, LI). The tracer was found in soil water 0.5 m below ground level (bgl) after 8 days, and in groundwater in the bedrock 23 m bgl after 34 days (Richards et al., 2005). The results showed that preferential flow in the overburden was important in delivering quick breakthrough travel times but that matrix flow in the overburden and preferential flow in the bedrock delivered the majority of the tracer to the saturated zone. Other Irish studies include the following:

- **Bowen and Williams (1972)** used tritium analyses to show recharge travel time up to 4 years in the Gort lowlands;
- **Ryan (1998)** used dye tracing to show preferential flow to a depth of 0.9 m in south-east Ireland; and
- **Tooth and Fairchild (2003)** used natural hydrochemistry to show preferential flow of hours to days through 1–2.5 m of low-permeability till to groundwater in Crag Cave, County Kerry.

3.5 Study of Interactions between Groundwater and Surface Water

The study *An Integrated Approach to Quantifying Groundwater and Surface Water Contributions of Stream Flow* (RPS, 2008) outlined a conceptual model of flow pathways in Ireland (Fig. 3.9) which was initially proposed by the Working Group on Groundwater. Five main pathways were conceptualised.

1. **Overland flow** was conceptualised as saturation excess surface runoff. Discharges from land drains were included.
2. **Interflow** was conceptualised as the subsurface water in topsoil and subsoil (with the exception of sand and gravel) that contributes to streamflow. It can occur under saturated or unsaturated conditions.
3. **Shallow groundwater flow** was conceptualised

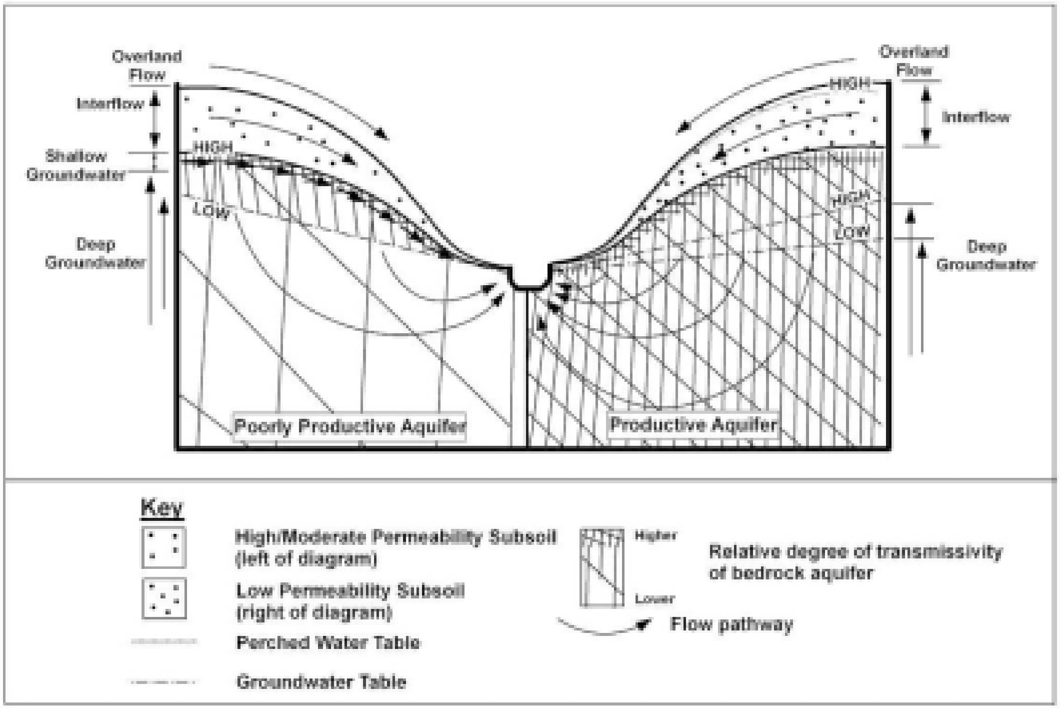

Figure 3.9. Components of surface water and groundwater flow in poorly productive (left) and productive (right) bedrock aquifer settings. Low- or high-permeability subsoil may overlie either bedrock aquifer type. This conceptual model was developed by the Working Group on Groundwater (RPS, 2008: originally devised by Daly and Hunter-Williams).

as occurring within the top few metres of weathered and fractured bedrock, and was considered to be the main flow pathway in poorly productive aquifers.

4. **Deep groundwater flow** was conceptualised as occurring in the main body of the bedrock aquifer and, as such, as being of greater importance as a flow pathway in productive (especially regionally important) aquifers than in poorly productive aquifers. It was considered to be equivalent to the long-term sustainable yield of a groundwater flow system.

5. **Discrete fault or conduit flow** was added as a further pathway in recognition of the fact that large faults or conduits (for example in karst aquifers) can transmit larger quantities of groundwater than the surrounding areas of less fractured bedrock.

Several approaches were employed to distinguish between the different hydrograph components. Unit hydrograph theory was applied to separate the overland flow from the other hydrograph components. The Boughton baseflow separation technique and MRCs (see Section 2.2) were both used to identify the deep groundwater component. The deep groundwater flow estimates were also checked against groundwater throughput calculations (using Darcy or Dupuit–Forchheimer relationships). The Danish NAM model was applied to simulate the river flow hydrograph and its main components. As described in Section 2.4, the model essentially separates rainfall into three different stores – overland flow, intermediate flow and groundwater flow – and simulates hydrograph response employing a number of empirical parameters.

The different approaches were initially applied to seven pilot catchments, representing a range of hydrogeological conditions, including catchment sizes, soil and subsoil types and aquifer types (encompassing regionally important, locally important and poorly productive aquifers). The locations of the pilot catchments are shown in Fig. 3.10.

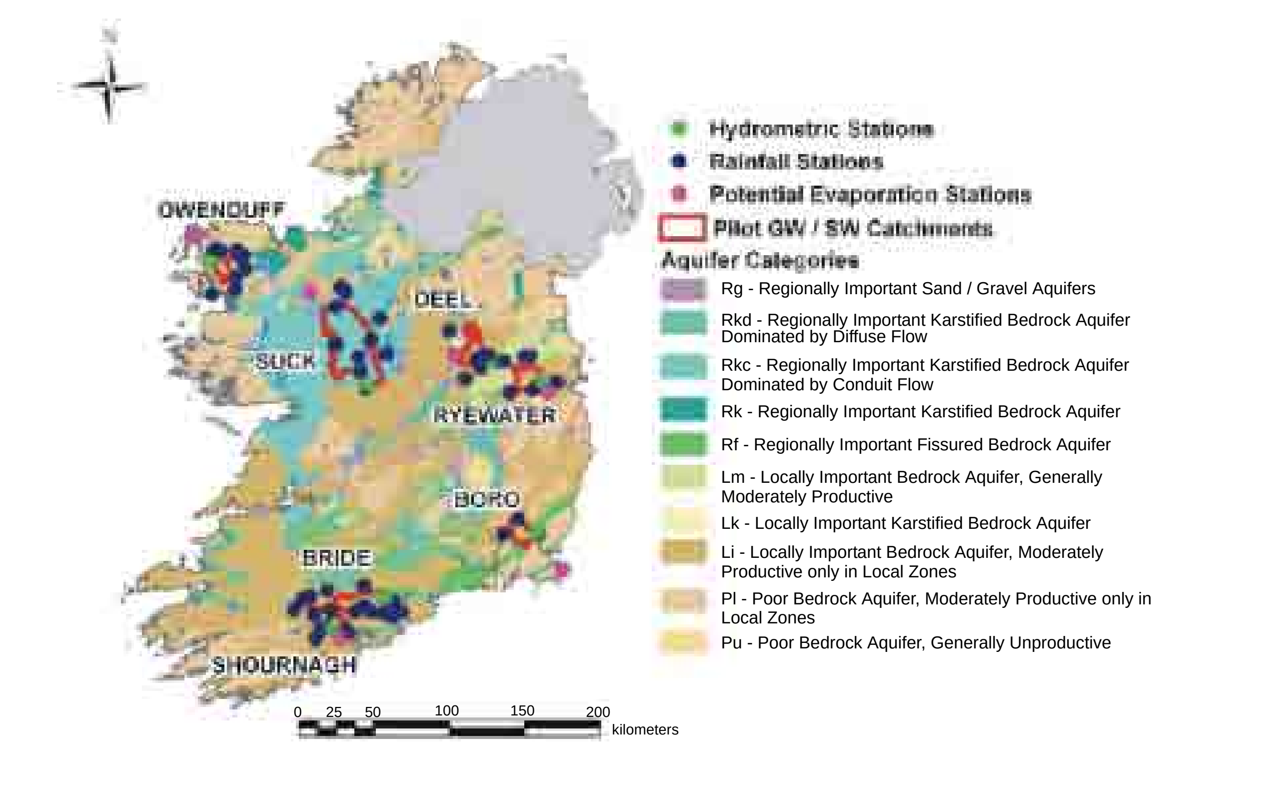

Figure 3.10. Pilot catchments selected for the surface water–groundwater interaction study, and locations of the river flow and meteorological data that were collected for their analysis (RPS, 2008).

The results of the pilot studies are summarised in Table 3.4. The use of methods analysing physical data such as the unit hydrograph, baseflow separation and throughput calculations were generally successful in constraining the empirical parameters employed in simulating outputs from the NAM model. It proved possible to develop decision tables for selecting parameters for future modelling studies; these decision tables were based on key hydrogeological descriptors, including aquifer type, subsoil and soil characteristics, topography (slope), land cover and percentage of lakes within the catchment. It was not possible, however, to separate the individual components of intermediate flow which, for a particular catchment, could include any or all of the following: interflow, shallow groundwater flow in bedrock, discrete fault or conduit flow, and discharges from peat layers.

The NAM model was subsequently applied to 32 regional catchments to estimate the contributions from overland flow, intermediate flow and deep groundwater flow.

3.6 Proposed Conceptual Model and Data Gaps

For this Pathways Project, at least for the present, it is proposed to generally follow the conceptual model and terminology developed by the Working Group on Groundwater, which was also adopted in the surface water and groundwater interactions study, as described in Section 3.5. One minor deviation is proposed at this stage: as pointed out by Nash et al. (2002), because overland flow (whether it be saturation or infiltration excess) and interflow occurring immediately below the soil surface (say between 0 and 20 mm) are ‘difficult to functionally separate’, it is proposed to use the term overland flow here to describe sheet flow on the surface together with flow in the upper few millimetres of topsoil.

A second aspect of the conceptual pathways model, namely field drainage, will require further consideration as the study progresses. In the existing conceptual model, field drainage is assumed to be included in overland flow. In certain respects it makes sense to

Table 3.4. Summary table of results for the quantification of deep groundwater flow, intermediate flow and overland flow for the pilot catchments. NAM (numerical model); MRC (Master Recession Curve); UH (Unit Hydrograph method); (RPS, 2008).

Pilot catchment	Hydrogeological scenario	Deep groundwater flow				Intermediate flow	Overland flow	
		NAM (mm/year)	MRC (mm/year)	Groundwater throughput calcs (mm/year)		NAM (mm/year)	NAM (mm/year)	UH (mm/year)
Boro	Rf Volcanic aquifer (mixed scenario: Rf/Ll/Pl)	240	388 (deep + other component)	232	330	217	231	215
Bride	'Southern Synclines' scenario (Ll and Rkd)	200	537 (deep + other component)	153	170	269	352	336
Deel	Ll Limestone	159	323 (deep + other component)	158	232	210	120	168
Owenduff	Pl Poorly Productive	128	441 (deep + other component)	73	183	318	1,322	1,074
Ryewater	Ll Limestone	121	110	158	232	85	171	191
Shournagh	Ll Old Red Sandstone	220	321 (deep + other component)	153	170	205	383	357
Suck	Karst	171	234	–	–	362	124	354

continue with this concept for the Pathways Project since, for example, flows in field drains will often respond rapidly to rainfall events and may contain suspended solids (SS), similar to overland flow. However, studies also suggest that significant attenuation of pollutants such as phosphorus and pathogens may occur in field drainage compared with overland flow (see Sections 4.1 and 5.1), suggesting that field drainage might be better placed within interflow. For the moment, this matter will be left unresolved and will be considered further once additional field data become available from this current project.

Based on the discussion of Irish hydrology and flow pathways in the previous sections of this chapter, the main data/knowledge gaps can be summarised as:

- There are relatively few reliable, long-term river gauging records for small catchments: as pointed out in Section 3.4.1, catchment properties vary over a smaller scale than the size of catchment where flow is monitored;
- There are few long-term groundwater-level records for the poorly productive aquifers that cover about half of the country (although this deficiency is currently being addressed by the EPA; see Section 3.3);
- There is very little field-based information available on the interaction of groundwater and surface water in Ireland. The recent study described in Section 3.5, although useful, was mainly a desk study;
- Very little work has been carried out in Ireland on the use of chemical tracers for hydrograph separation (see Section 3.4.4). Many of the successful studies carried out in Britain have been in upland catchments with fairly uniform (forestry) land use;
- There are very few field data available on the quantification or the quality of interflow;
- Overland flow data at the field scale (as opposed to streamflow measurements and flood event

sampling which have been assumed to be overland flow) are also limited;

- There is very limited understanding of the contribution of drains to overland flow and/or interflow; and

- Further data are required on the likely effects of climate change on Irish hydrology and, more specifically, on the flow contributions to receptors from different pathways (see Section 3.2).

3.7 Recommendations

The following are the recommendations for work to be carried out by the Pathways Project team.

- Apply a range of physical and chemical hydrograph separation techniques, and construct flow and pollutant load duration curves, to gain insights into the contributions of the different pathways to the overall flow in the four study catchments. This will be achieved by collecting and analysing river flow data, and carrying out event-based sampling using suitable chemical tracers. River flow hydrographs are a fundamental data set that will be used in the modelling and the development of the CMT as they provide the time series element that is required to fully understand and interpret the ecological response.

- Use shallow lysimeters and tensiometers to collect better information on interflow in one study catchment. Interflow is poorly understood in Ireland and field data collection will help to constrain the estimates provided by the hydrograph separation techniques.

- Use groundwater-level data and simple hydrogeological analytical equations to improve the reliability of hydrograph separation results.

- Apply lumped parameter and possibly distributed or semi-distributed models to represent flow along the relevant pathways in the study catchments. These models will then be combined with contaminant attenuation data and/or theoretical contaminant attenuation equations to generate a transport and attenuation model for use in the CMT.

Other potential relevant research which is outside the scope of the Pathways Project could include the following:

- Further characterisation of interflow across a range of hydrogeological scenarios.

- Investigation into the likely effects of climate change on the flow contributions to receptors from different pathways.

4 Sources of Nutrients

4.1 Introduction

Eutrophication, caused by nitrogen and phosphorus, is considered to pose the highest threat to water quality in Ireland. Numerous projects have been completed which focus on the CSAs of nutrients and investigate the fate and transport of nutrients to surface water bodies and the resulting impact on aquatic biota. This chapter aims to highlight the most relevant and current/ongoing research that has been undertaken in relation to hydrologic pathways and attenuation of nutrients. Particular emphasis is placed on the current knowledge and data gaps in relation to both nitrogen and phosphorus and recommendations on further research are presented, both within and beyond the scope of the Pathways Project.

4.2 Phosphorus

4.2.1 Agricultural sources

Phosphorus exported from agriculture originates from point sources, such as farmyards, and from diffuse sources arising from soil phosphorus and incidental losses to water. Runoff from farmyards and silage/manure storage areas contains a high concentration of nutrients and is a significant source of pollution, if not managed correctly. Investigation by Ryan (1991) found that the phosphorus concentrations in runoff from concreted farmyards were 21 mg/l and 52 mg/l from a beef unit and a dairy unit, respectively.

Incidental losses of phosphorus occur when runoff follows the application of organic and inorganic fertiliser which has not yet been incorporated within the soil (Preedy et al., 2001; Withers et al., 2003; Haygarth et al., 2005). Preedy et al. (2001) demonstrated that prior to treatment application, TP concentration in runoff was 100 µg/l. After the application of rock phosphate and slurry, phosphorus exports increased 30–40 times. Incidental losses of phosphorus in runoff are controlled by the rate, time, formulation, method of application (Haygarth and Jarvis, 1999) and by the distance of the application from a water body (McDowell and Sharpley, 2002).

There is a strong correlation between the soil test phosphorus (STP) concentration and phosphorus concentration in runoff (Pote et al., 1999; McDowell et al., 2001; Kurz et al., 2005a). Percentage of phosphorus saturation is also an important consideration as it takes into account the STP concentration and soil characteristics, such as the number of available binding sites on iron and aluminium oxides/hydroxides in the soil (Kuo and Lotse, 1974; Beauchemin and Simard, 1999).

Detailed reviews of phosphorus loss from agricultural soils to water can be found in Sharpley et al. (1994), Haygarth and Jarvis, (1999) and Haygarth et al. (2000).

4.2.2 Forestry sources

Phosphorus exports from forestry arise from the build-up of phosphorus in the soil due to fertilisation and from disturbance of the soil during forestry operations. Forestry is often established on upland and marginal land less suitable for agriculture (Giller et al., 1993), which frequently corresponds to areas of peat soils. Forests planted on peat soils pose a greater risk for phosphorus loss than on mineral soils due to the greater potential of mineral soils to bind phosphorus. Rock phosphate is generally applied at a rate of 250–500 kg/ha during afforestation to promote initial growth and a second application may be applied to peaty soils where nutrient deficiencies occur due to their limited ability to retain phosphorus (Campbell and Foy, 2008). The impact of fertiliser application on stream water quality has been highlighted by Binkley et al. (1999), Nisbet (2001) and Giller and O’Halloran (2004).

The increased risk of overland flow in conjunction with the disturbance of the soil structure and the breakdown of organic matter during clear-felling has a significant impact on the export of soluble and particulate phosphorus (PP) from forests. Soil compaction, as a result of the use of heavy logging machinery, increases the risk of overland flow occurring and, combined with the removal of vegetation, decreases the soil ability to retain water. The impact of clear-felling on soil hydrology is most significant in poorly drained soils such as gleys and shallow peats overlying poorly drained clay soils and deep peats (Carling et al., 2001).

Although the establishment of brash mats can help to decrease soil compaction and erosion, the decay and release of phosphorus from organic matter contributes to elevated phosphorus concentrations in runoff following clear-felling. Titus and Malcolm (1992) demonstrated that following clear-felling and establishment of a brash mat on an upland peaty soil, phosphorus loss from the site remained at 1.4 kg P/ha/year for a 7-year period. Sweeney (2007) demonstrated that phosphorus export following clear-felling could be as high as 7.2 kg P/ha/year, although this had reduced to 1.8 kg P/ha/year within 3 years of clear-felling.

More detailed reviews of phosphorus loss from forestry can be found in Binkley et al. (1999), Nisbet (2001) and Chen et al. (2008).

4.2.3 On-site wastewater treatment systems

Septic tanks are the dominant form of on-site wastewater treatment systems (OWTSs) used in Ireland (Campbell and Foy, 2008). Household effluent discharged to septic tanks is treated by sedimentation of the solids and some biological treatment of organic matter by bacteria. Subsequently, the effluent is discharged to soakaway areas where phosphorus can be removed by absorption to the soil.

Butler and Payne (1995) highlighted that the effectiveness of a septic tank is limited by a lack of desludging and an inadequate or blocked soakaway area. Irregular desludging of the tank results in a reduction in the residence time, thereby decreasing the effectiveness of the sedimentation process. The draft EPA *Code of Practice: Wastewater Treatment Systems for Single Houses* recommends that such system are visually inspected every 6 months and are desludged every 2 years (EPA, 2007b).

To ensure that oxidation of organic material takes place, septic tanks should be located in moderately permeable and well aerated soils (Canter and Knox, 1985). The effective uptake of phosphorus is dependent on the soil's ion exchange capacity, permeability, texture, depth to the unsaturated subsoil layer and depth to bedrock (McCarthy et al., undated).

Locating septic tanks at sites where the water table rises to the soil surface can result in the rapid movement of effluent through the soil (Dawes and Goonetilleke, 2003), which limits the potential for phosphorus uptake and fixation in the soil. A depth of 0.3–0.4 m to a restrictive soil horizon is required for adequate treatment of effluent (Dawes and Goonetilleke, 2003; Karathanasis et al., 2006). The problem of inadequate site drainage is further exacerbated if tanks are not located at a sufficient distance from watercourses (Dawes and Goonetilleke, 2003), as saturated conditions may result in a direct pathway for the transport of phosphorus to lakes and rivers. For groundwater, the risk of pollution is greater in areas where the subsoil beneath the site has a high permeability (Gill et al., 2009a). A detailed review of OWTSs can be found in Butler and Payne (1995), Gill et al. (2004) and Beal et al. (2005).

4.2.4 Controls on mobility

4.2.4.1 Hydrological controls

A number of studies have shown that the majority of phosphorus is lost during low-frequency, high-intensity storm events (Nash et al., 2000; Tunney et al., 2000). Tunney et al. (2000) found that 40% of the annual dissolved reactive phosphorus (DRP) exported from field plots occurred during a period of 4 days. Sharpley et al. (1981a) demonstrated a linear relationship between rainfall intensity and the loss of phosphorus in overland flow.

Overland flow is a major pathway of phosphorus loss from soil to water (Haygarth et al., 2000) and in Ireland and the UK occurs predominantly as saturated excess overland flow (Haygarth et al., 2000; Diamond and Sills, 2001). Saturation excess overland flow is generated in variable source areas (VSAs) (Dunne and Black 1970; Sharpley and Rekolainen, 1997) which occur in areas of high antecedent soil moisture conditions, particularly in areas where the water table is close to the surface of the soil. Where VSAs occur in association with high STP concentrations, CSAs of phosphorus develop (Gburek and Sharpley, 1998; Pionke et al., 2000). CSAs can account for as little as 20% of the catchment area.

In free-draining soil phosphorus loss can occur through subsurface pathways especially where re-adsorption does not occur due to build-up of phosphorus in the soil profile (Sims et al., 1998; Heathwaite and Dils, 2000) or in soil where preferential flow channels exist (Stamm, 1997). In more poorly drained soils where artificial drainage systems are installed, phosphorus can be transported rapidly through the soil profile and away from the source via the drainage system (Haygarth et al., 1998; Bilotta et al., 2008).

Sims et al. (1998) suggested that phosphorus leaching occurs in deep, well-drained sandy soils, in soil with excessive organic matter or also in soils with elevated STP concentrations. Holman et al. (2008) carried out a detailed review of phosphorus in groundwater in the UK and Ireland and found that a significant number of monitored groundwater samples had phosphorus concentrations in excess of the required threshold limit. They concluded that phosphorus in groundwater may play a more significant role in eutrophication of surface water than previously expected.

4.2.4.2 Soil physico–chemical controls

Phosphorus in the soil solution is the most freely available form of phosphorus and can be in the form of inorganic orthophosphates (Sharpley, 1995) or organic phosphorus such as phosphate esters, phospholipids and nucleic acids. Labile, moderately labile and stable forms of phosphorus are available to be lost from the soil following desorption into the soil solution or erosion of PP at the soil–water interface. While occluded phosphorus is unavailable to be lost in dissolved forms, in an erosive environment it can be lost as PP; however, its bioavailability in a water body is limited except over extended periods of time (Sharpley, 1985a).

Soil texture and the composition of the clay fraction affect the number and type of binding sites available for adsorption/desorption of phosphorus (Griffin and Jurinak, 1974). Soils with a high percentage of clay provide more available binding sites for phosphorus (Sparks, 1995; Evangelou, 1998), while the presence of organic matter increases the availability of phosphorus as it competes with and displaces phosphorus from binding sites on soil particles. (Daly et al., 2001). Soil pH has a strong effect on phosphorus sorption and desorption through its control of speciation and surface charge (Bhatti and Comerford, 2002), with phosphorus sorption to aluminium and iron decreasing with increasing pH (Sparks, 1995).

4.2.4.3 Control at the soil–water interface

As water moves across or through the soil in the form of overland flow, interflow and leachate, turbulence mixing occurs that results in the mobilisation of dissolved phosphorus. Desorption, diffusion, mass transfer and hydrodynamic dispersion result in the phosphorus moving from the soil solution and particles into the moving mass of water. A key process in the mobilisation of dissolved phosphorus at the soil–water interface is the formation of the depth of interaction between the soil surface and runoff. The depth of interaction with overland flow decreased exponentially from the soil surface (Ahuja et al., 1981) and varies depending on slope, soil type, vegetation, rainfall intensity and rainfall duration (Sharpley, 1985b). Havis et al. (1992) found that the depth of interaction was a linear function of rainfall intensity. Sharpley (1985b) suggested that the impact of raindrops on the soil surface increases turbulent mixing in the thin surface zone and that the formation of the initial depth of interaction is a function of the degree of soil aggregation.

The export of PP depends on erosion/detachment of soil particles at the soil–water interface and entrainment in runoff. On bare soil, the energy created by raindrop impact and overland flow are key factors in the detachment of soil particles (Fraser et al., 1999). With vegetation cover, the impact energy of raindrops is dissipated by the presence of the vegetation canopy and the shear strength requirement for detachment of soil particles from the soil surface is increased. While the presence of vegetation, such as grass, greatly modifies the erosion processes occurring at the soil–water interface (Prosser et al., 1995; Carroll and Tucker, 2000), there is still the potential for the erosion and entrainment of particles. The erosion of soil particles is selective, with smaller clay-sized particles first to be moved once the shear strength of the soil is exceeded (Quinton et al., 2001). The importance of these fine slow-settling particles cannot be overlooked due the high affinity of phosphorus to clay particles in the soil (Proffitt and Rose, 1991).

A detailed review of soil phosphorus dynamics and mobilisation processes can be found in Sharpley (1995), Haygarth and Jarvis (1999) and Haygarth et al. (2000).

4.2.5 Studies in Ireland

Phosphorus research in Ireland has largely been based on the sources–pathway–receptor model, with much of the early research focused on individual components of this model. In recent years, a more integrated approach to phosphorus research has been adopted in which the links between the sources of phosphorus, the pathways of delivery and the resultant impact on water quality were investigated. These studies were carried out over a range of scales and now form the basis for much of the regulations controlling phosphorus loss from agriculture forestry and OWTSs.

4.2.5.1 Soil phosphorus

Tunney et al. (2000) reported that STP concentrations in Ireland have increased 10-fold over the past 50 years. Data collected by Teagasc in 1998 suggested that the average STP (Morgan's P) concentration in samples sent by farmers for analysis was 8.1 g/l (Morgan's P). Up to 25% of the soils analysed were at Index 3, while a further 24% were at Index 4 (Brogan et al., 2001). However, more recently concern regarding eutrophication and a change in the agronomic advice has resulted in a 30% reduction in phosphorus fertiliser use between 1995 and 2001 (Power et al., 2005).

Prior to 2007, the target phosphorus index for the optimum agronomic production in grasslands was Index 3 (Morgan's P 6.1–10 mg/l), with the risk of phosphorus loss to water increasing significantly above an STP concentration of 10 mg P/l. Schulte and Herlihy (2007) revised the recommendations, which resulted in Index 3 ranging from 5 mg/l to 8 mg/l (Table 4.1). A review by Schulte and Lalor (2008) demonstrated that the new recommendations minimised the risk of phosphorus loss to water while maximising agronomic productivity.

Different STP index classifications are used in the Republic of Ireland and Northern Ireland (Tables 4.1 and 4.2). Foy et al. *(*1997) demonstrated that the relationship between Morgan's P (Republic of Ireland) and Olsen's P (Northern Ireland) is not linear (Eqn 4.1), particularly at Morgan values of >10 mg/l:

$$\text{Olsen's P} = 5.96 \text{ Morgan's P}^{0.773} \qquad \text{Eqn 4.1.}$$

In agreement with much of the international research, a significant correlation between STP and phosphorus loss to water has been demonstrated in a number of studies in Ireland (Daly et al., 2001; Kurz et al., 2005a; Styles et al., 2006; Tunney et al., 2007; Watson et al., 2007a). Daly et al. (2001) demonstrated that the degree of phosphorus saturation of soils increases significantly at higher Morgan's P concentrations, making them more vulnerable to phosphorus loss due to desorption. The STP concentrations at the three sites in the study of Kurz et al. (2005a) had Morgan's P concentrations of 4, 8, 17 mg P/l and the corresponding average flow-weighted DRP

Table 4.1. Soil phosphorus index (Morgan's P) for soils in the Republic of Ireland post-2007.

Morgan's P index	Morgan's P range (mg/l)
1	0.0–3.0
2	3.1–5.0
3	5.1–8.0
4	>8.0

Table 4.2. Soil phosphorus index (Olsen's P) for grassland mineral soils in Northern Ireland.

Olsen's P index	Olsen's P range (mg/l)
0	0–9
1	10–15
2	16–25
3	26–45
4	46–70
5	71–100
6	101–140
7	141–200
8	201–280
9	>280

concentration for each site ranged from 0.01 to 0.05 mg/l, 0.08 to 0.32 mg/l and 0.12 to 5.1 mg/l, respectively. This relationship was also highlighted by Watson et al. (2007a) who demonstrated an increase in phosphorus loss in both overland flow and subsurface drains in response to Olsen's P accumulation in six hydrologically isolated drumlin field plots in Northern Ireland. Watson et al. (2007a) found that TP export from the plots increased from a range of 0.19–1.55 kg P/ha for the plot receiving zero phosphorus to 0.35–2.94 kg P/ha for the plot receiving 80 kg P/ha/year.

4.2.5.2 Soil type

Research in Ireland has demonstrated that soil type is a key determinant of the risk of phosphorus loss (Daly et al., 2001; Daly and Styles, 2005; Jordan et al., 2005). Mineral soils in Ireland have been shown to have a higher potential to absorb phosphorus than peat soils due to the ability of aluminium and iron oxides to bind with phosphorus (Daly et al., 2001; Jordan et al., 2005). Daly et al. (2001) demonstrated that phosphorus sorption capacity correlates negatively with percentage organic matter in Irish soil. Due to low sorption capacities and binding energies, peat soil with an organic matter content of >20% poses a greater threat of phosphorus loss following the surface application of phosphorus (Daly and Styles, 2005; Carton et al., 2008).

The process of sorption and desorption in non-calcareous mineral soils is controlled by soil variables such as pH, aluminium, iron and percentage organic matter (Daly and Styles, 2005). Jordan et al. (2005) demonstrated the greater risk of desorption from the Dripsey Catchment soils than the soils in the Oona Catchment due to the highly adsorptive and strongly binding aluminium concentration in the Oona soils as opposed to the highly adsorptive but weakly binding iron concentration in the Dripsey soils. Figure 4.1 illustrates that at 25% the degree of phosphorus saturation (DPS) equated to Index 3 (Morgan's P) in the Dripsey soils compared with Index 4 in the Oona soils, which indicates that phosphorus saturation in the Dripsey soils is likely to be greater per unit concentration of STP.

Non-calcareous mineral soils (pH < 6) pose a higher risk of phosphorus desorption to soil solution than calcareous mineral soils at similar STP concentrations (Daly and Styles, 2005; Daly and Mills, 2006; Carton et al., 2008). Jordan et al. (2005) suggested that the process of uptake and release of phosphorus with calcium involves precipitation/desorption reactions instead of adsorption/desorption, which decreases the risk of phosphorus desorption to the soil solution.

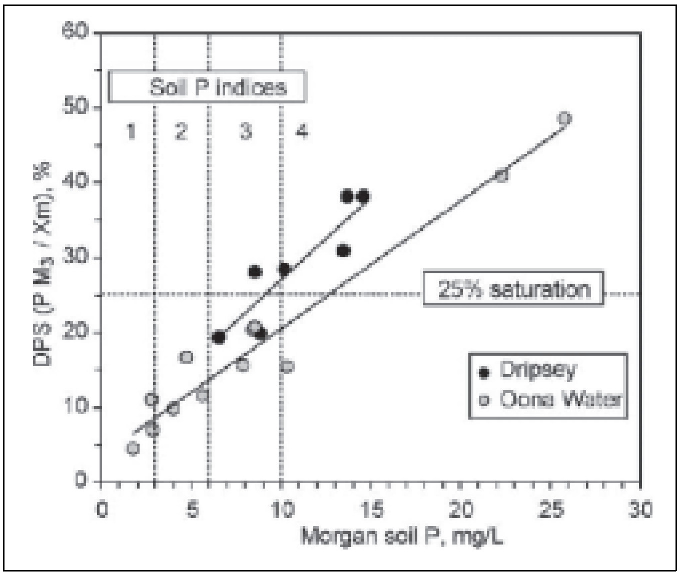

Figure 4.1. Morgan's P concentration and percentage phosphorus saturation for soil from the Oona and Dripsey catchments (source: Jordan et al., 2005).

Gill et al. (2009b) highlighted that subsoil clay mineralogy and specific surface area played an important role in the subsoil's phosphorus attenuation capacity. Gill et al. (2007) found in their investigation that the risk of groundwater pollution from septic tanks is greater for systems located where high-permeability subsoils underlie the site. Septic tanks should be installed in subsoil with a hydraulic conductivity in the region of 0.08–4.2 m/day (Gill et al., 2007). Where subsoil permeability is too low to allow sufficient soakage of effluent, the risk of phosphorus export to groundwater and surface water increases significantly (Gill et al., 2004).

4.2.5.3 Land-use and management practices

Agriculture

A recent synthesis report by Carton et al. (2008) summarised the findings of a national phosphorus project that provided evidence of the potential contribution of grassland agriculture to eutrophication due to fertiliser use, slurry spreading, elevated STP and grazing. Due to the limited distribution of arable land in Ireland, it has received much less attention than grassland agriculture despite having a significantly higher phosphorus export coefficient. The mean export coefficient for non-irrigated arable land was reported by Jordan et al. (2000) as 4.88 kg TP/ha/year while a figure of 0.83 kg TP/ha/year was calculated for grassland agriculture (Table 4.3). Smith et al. (2005) estimated that 1,023 t/year of phosphorus was export from agriculture in Northern Ireland to fresh water and coastal waters. The Department of the Environment, Heritage and Local Government (DoEHLG) report (DoEHLG, 2005) submitted to the EU under Article 5 of the WFD demonstrated that agriculture was contributing on average 33.4% of the phosphorus load to Irish water bodies. This figure ranged from 56.6% in the Neagh/Bann RBD to as low as 4.2% in the Eastern RBD.

Kurz et al. (2006) investigated the impact of grazing on phosphorus loss from grassland soils and concluded that although grazing did increase the export of organic phosphorus from the soil, it had a more significant impact on soil hydrology than on nutrient export. A grazing intensity of 2 LU/ha[1] resulted in a 57–83% decrease in macroporosity, an increase of 8–17% in bulk density and an increase of 27–50% in resistance to penetration. However, Tunney et al. (2007) suggested that under good grazing practice, grazing animals were not a major risk factor in phosphorus loss from soil and that the accumulation of phosphorus in the soil due to slurry and fertiliser application was a more significant risk associated with phosphorus loss at the field scale.

Incidental losses of phosphorus from soil to water in Ireland occur due to the spreading of inorganic and organic fertiliser prior to rainfall and runoff events (Kurz et al., 2005b; Carton et al., 2008). Carton et al. (2008) concluded that the application of slurry and fertiliser above the rates advice for agronomic purposes increases the risk of phosphorus loss to water and the timing of application is a key factor in controlling this risk. Kurz et al. (2005b) found evidence of an increase in phosphorus concentration in overland flow and subsurface flow following the application of slurry to an experimental grassland site. In the Republic of Ireland, restriction on slurry spreading commences on 15 October across the country and runs until 12 January in Zone A (Southern) and until 31 January in Zone C (Northern) (Fig. 4.2). The restriction on fertiliser spreading commences on 15 September and continues until the same dates as slurry spreading in all three zones. In Northern Ireland, the closed periods for both slurry and fertiliser spreading equate to those of Zone C in the Republic of Ireland, with 22 weeks of slurry storage required to cover this period.

The division of the Republic of Ireland into three zones is based on soil type, rainfall and the length of the growing season. Schulte et al. (2006) concluded that although the risk of phosphorus loss was controlled by pressure factors such as STP in the south-eastern parts of the Republic of Ireland, in the north-western regions, pathway factors, such as soil drainage and rainfall, play a more significant role in determining the risk of phosphorus loss from soil to water. The western and northern areas have the highest incidence of intense drainage events and the shortest grass growing periods, hence making them more susceptible to phosphorus loss (Schulte et al., 2006). Holden et al. (2004) determined the probability of safe spreading days in Ireland and concluded that in the eastern part

1. LU/ha, livestock units per hectare.

Table 4.3. Export coefficients used for nutrient load prediction for Northern Ireland catchments (source: Jordan et al., 2000).

Corine land cover	Export coefficient ranges (kg/ha/year)			
	Total phosphorus		Soluble reactive phosphorus	
	Min.	Max.	Min.	Max.
1.1.1. Continuous urban fabric[1]	0.3	2.1	0.05	0.3
1.1.2. Discontinuous urban fabric	0.3	2.1	0.05	0.3
1.2.1. Industrial or commercial units	0.9	4.1	0.11	0.49
1.2.2. Road and rail networks and associated land	0.3	2.1	0.05	0.3
1.2.3. Seaports	0.9	4.1	0.11	0.49
1.2.4. Airports	0.9	4.1	0.11	0.49
1.3.1. Mineral extraction site	0.9	4.1	0.11	0.49
1.3.2. Dump	0.9	4.1	0.11	0.49
1.3.3. Construction site	–		–	
1.4.1. Green urban areas	0.66	1	0.17	0.43
1.4.2. Sport and leisure facilities	0.3	2.1	0.05	0.3
2.1.1. Non-irrigated arable land	3.76	6	1.58	3
2.1.2. Permanently irrigated land	–		–	
2.1.3. Rice fields	–		–	
2.2.2. Fruit trees and berry plantations	–		–	
2.2.3. Olive groves	–		–	
2.3.1. Pastures				
2.3.1.1. Good pasture	0.66	1	0.17	0.43
2.3.1.2. Poor pasture	0.4	0.9	0.17	0.55
2.3.1.3. Mixed pasture	0.65	0.9	0.25	0.4
2.4.1. Annual crops associated with permanent crops	0.66	1	0.17	0.43
2.4.2. Complex cultivation patterns	2.05	2.6	0.86	1.21
2.4.3. Land principally occupied by agriculture	0.38	0.6	0.16	0.34
2.4.4. Agro-forestry areas	–		–	
3.1.1. Broadleaved forest	0.11	0.4	0.05	0.21
3.1.2. Coniferous forest	0.32	0.4	0.01	0.09
3.1.3. Mixed forest	0.11	0.4	0.05	0.21
3.2.1. Natural grassland	0.4	0.9	0.17	0.55
3.2.2. Moors and heathlands	0.05	0.2	0.05	0.15
3.2.3. Sclerophyllous vegetation	–		–	
3.2.4. Transitional woodland scrub	0.11	0.4	0.05	0.21
3.3.1. Beaches, dunes, sand	0	0	0	0

Table 4.3 *contd*.

Corine land cover	Export coefficient ranges (kg/ha/year)			
	Total phosphorus		Soluble reactive phosphorus	
	Min.	Max.	Min	Max
3.3.2. Bare rocks	–		–	
3.3.3. Sparsely vegetated areas	0	0	0	0
3.3.4. Burnt areas	–		–	
3.3.5. Glaciers and permanent snowfields	–		–	
4.1.1. Inland marshes	0.06	0.4	0.06	0.42
4.1.2. Peat bogs				
4.1.2.1.Unexploited peat bogs	0.06	0.4	0.06	0.42
4.1.2.2. Exploited peat bogs	0.06	0.4	0.06	0.42
4.2.1. Salt marshes	0	0	0	0
4.2.2. Salines	–		–	
4.2.3. Intertidal flats	0	0	0	0
5.1.1. Stream courses	0	0	0	0
5.1.2. Water bodies	–18	–9.2	–9.3	–3.9
5.2.1. Coastal lagoons	–		–	
5.2.2. Estuaries	0	0	0	0
5.2.3. Sea and ocean	–		–	

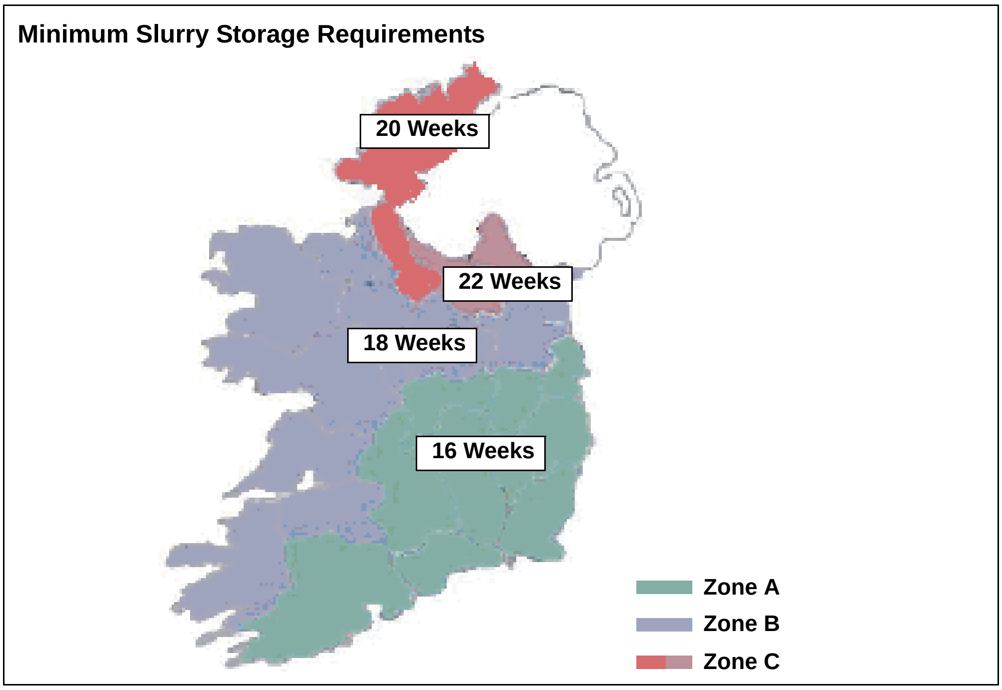

Figure 4.2. Slurry spreading zones in the Republic of Ireland.

of the country safe slurry spreading in winter would be possible for 5–6 years in every 10 years. This was reduced to 3–4 in 10 years in the northern part of the island.

Jordan, C. et al. (2007) developed a slurry acceptance map for Northern Ireland in which the risks associated with slurry spreading were based on soil and site parameters such as SMD and slope. Soil drainage is a key determinant of the risk of incidental loss of phosphorus. Schulte et al. (2005) developed a simple hybrid model which accurately predicted the temporal patterns of SMD in three soil types (well drained, moderately drained and poorly drained soils in Ireland). Schulte et al. (2006) used this hybrid model to develop a drainage map of Ireland based on the three soil types identified in Schulte et al. (2005) (Fig. 4.3).

Forestry

Although agriculture has been the focus of much of the phosphorus research in Ireland, the impact of forestry management practices, such as clear-felling and fertilisation, on water quality has also received attention (Giller and O'Halloran, 2004; Machava et al., 2007; Rodgers et al., 2008). Rodgers et al. (2008) carried out monitoring, pre-clear-felling and post-clear-felling, of a 20-ha sub-catchment in the Burrishoole Catchment in County Mayo. In the 3 years of monitoring, 80% of phosphorus exported was in dissolved form. The mean total reactive phosphorus (TRP) concentration increased from 6 µg/l pre-clear-felling to a maximum recorded concentration of 429 µg/l post-clear-felling. However, below the confluence with the larger Srahrevagh Stream, the dilution factor resulted in the TRP concentration remaining below 10 µg/l. In the first year after clear-felling, annual phosphorus export was estimated to be 2.24 kg TRP/ha/year as compared with 0.02 kg TRP/ha/year prior to clear-felling.

Machava et al. (2007) carried out a similar study on phosphorus loss from forestry at two sites on the Ballinagee River in Wicklow and at Crossmolina in County Mayo. During the 2-year monitoring period, little evidence was found to suggest that forestry operations, such as afforestation and thinning, were having a significant impact on phosphorus concentration in the receiving water bodies. The TRP concentration in the Ballinagee Catchment was generally below 20 µg/l, despite forestry accounting for

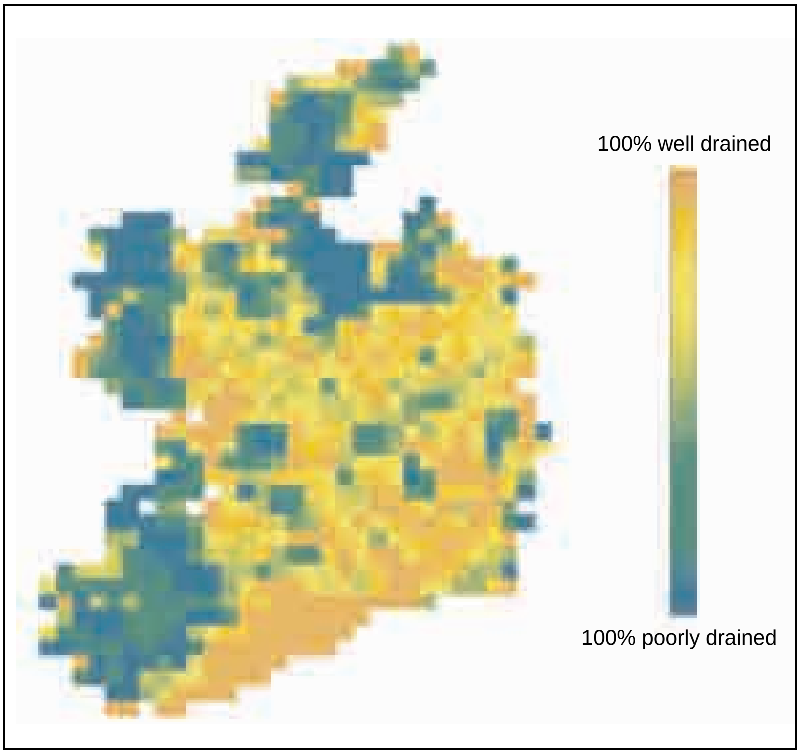

Figure 4.3. Indicative drainage map of Ireland (source: Schulte et al., 2006).

51% of the 3.6-km^2 catchment. Annual TRP export rates for the forest area were estimated at between 0.05 and 0.07 kg/ha/year which is slightly higher than reported by Rodgers et al. (2008) but less than the 0.14 kg/ha/year reported during the Three Rivers Project (Three Rivers Project, 2002; Machava et al., 2007).

Machava et al. (2007) monitored the 3-ha Crossmolina site prior to and following afforestation. The site had previously been used for intensive agriculture and had a Morgan's STP value of 13.5 mg/l (Index 4). Soil disturbance at the site during site preparation for afforestation did not result in an increase in TP transport during the following months. In fact, with the installation of subsurface drainage during afforestation, the occurrence of runoff decreased, which resulted in a corresponding decrease in TP from the site. Clenaghan et al. (1998) also reported that phosphorus concentration was generally low in an afforested sub-catchment of the Douglas River in County Cork.

Machava et al. (2007) cautioned against using the result of this study for other sites, quoting a previous study of Cummins and Farrell (2003a) at the Cloosh Forest in western Ireland in which recorded phosphorus concentrations were high, particularly following fertilisation and clear-felling. Machava et al. (2007) suggest that differences arise due to scale, the intensity of forest operations and the attenuation process in streams, which was supported by Giller and O'Halloran (2004) in their review of the impact of forestry on Irish aquatic ecosystems.

Although the study of Machava et al. (2007) investigated the impact of afforestation on phosphorus concentration, no results were presented that isolated the potential impact of fertiliser application in new forest plantations on water quality. Giller and O'Halloran (2004), in their review of forestry and the aquatic environment, found only one study, an unpublished report by Giller et al. (1994), that investigated the impact of forest fertilisation on eutrophication. It demonstrated that in the Clydagh Catchment in West Cork there was evidence of cultural eutrophication in upland streams as a result of aerial fertilisation.

OWTSs

In rural Ireland, the prevalence of low-density housing results in 1.6 million people using septic tanks to treat their household waste (NS Share, 2007). Correct siting and maintenance of OWTSs are vital for the effective removal of phosphorus from household effluent. McGarrigle and Champ (1999) highlighted that septic tanks can pose a significant threat to water quality in Ireland, particularly in areas of wet soils. Smith et al. (2005) concluded that septic tanks were contributing 7% of the phosphorus export to watercourses in Northern Ireland.

Arnscheidt et al. (2007) suggested that clusters of poorly sited and maintained septic tanks were having an impact on phosphorus concentration during periods of low flow in a sub-catchment of the River Blackwater. However, it was concluded that the role of septic tanks in a more complex catchment was less evident (Arnscheidt et al., 2007). Of the 113 septic tanks surveyed by Arnscheidt et al. (2007), 35% were classified as high risk in relation to water quality. Campbell and Foy (2008) reported on a survey of 49 septic tanks in the Lough Melvin Catchment, in which 46% of the septic tanks surveyed were over 20 years old. The results of the survey demonstrated that 50% of septic tanks had never been desludged and only 12% were desludged in the 12 months prior to the survey (Campbell and Foy, 2008). In addition, 66% of the septic tanks surveyed discharged directly into a drain and 8% into a stream. The results of the Arnscheidt et al. (2007) and Campbell and Foy (2008) studies raise concerns regarding the effectiveness of the treatment of household effluent in these catchments; however, due to a limited availability of data on the siting and maintenance of OWTSs in Ireland, the representativeness of these results cannot be gauged. McCarthy et al. (undated) carried out a detailed survey of 154 households in the Milltown Lake Catchment in County Monaghan. The results from this study will be available mid-2009 (Valerie McCarthy, Dundalk Institute of Technology, personal communication, 2009) and will aid in determining the role of septic tanks in eutrophication.

4.2.6 Pathways

Although significant quantities of phosphorus have been reported in subsurface flow, in Ireland overland flow is considered the main pathway of phosphorus loss from soil to water (Tunney et al., 2000; Kurz et al., 2005a; Watson et al., 2007a). A recent investigation by Watson et al. (2007a) of phosphorus losses from six hydrologically isolated drumlin field plots demonstrated that although overland flow accounted for only 11–35% of water exported, average annual flow-weighted mean concentrations of phosphorus in overland flow were up to 10-fold higher than phosphorus in drain flow. They reported average DRP and TP flow-weighted mean concentrations in overland flow from grassland plots receiving 0 kg P/ha/year over 5 years as 0.391 mg/l and 0.668 mg/l, respectively. The DRP and TP values increased to 0.898 mg/l and 1.325 mg/l, respectively, for an adjacent plot receiving 80 kg P/ha/year.

The importance of overland flow in determining CSAs of phosphorus has been identified by a number of authors (Hughes et al., 2005; Doody et al., 2006; Magette et al., 2007). In response to the need to identify agricultural CSAs at field and catchment scales, Hughes et al. (2005) developed a phosphorus risk index which was subsequently updated by Magette et al. (2007). The phosphorus risk index incorporated both sources and transport factors and takes into account the concept of connectivity between the sources of phosphorus and watercourse. In the Lough Melvin Catchment, 31% of fields surveyed using the phosphorus risk index developed by Magette et al. (2007) were classed as high risk for phosphorus loss, with a further 25% classified as medium risk (Campbell and Foy, 2008). Connectivity was a key determinant of this risk as 60% of the fields in the catchment were within 200 m of a watercourse (Campbell and Foy, 2008). Kurz et al. (2005b) found that where the same management practices were applied under the same conditions to two grassland sites in Wexford, the site with the greater hydrological connectivity had a significantly bigger impact on the phosphorus concentration in the stream draining the site.

Watson and Matthews (2008) investigated phosphorus loss in drain flow from a drumlin grassland hillslope in a 10-year study and demonstrated that the annual TP load exported in drainage waters ranged from 0.28 kg/ha/year to 1.73 kg/ha/year, with the TP concentration ranging from 0.187 mg/l to 0.273 mg/l. Smith et al. (2003) investigated phosphorus loss in drain flow from a 9-ha intensively managed grassland mini-catchment in Northern Ireland with a phosphorus surplus of 23.4 kg/ha/year. The mean concentrations of soluble reactive phosphorus (SRP) and TP in drainage water ranged from 0.026 mg/l to 0.067 mg/l and 0.070 mg/l to 0.298 mg/l, respectively. Kurz (2000) carried out a short-term study of a 24.5-ha grassland site in which the Morgan's STP ranged from 4 mg/l to 12 mg/l and report that DRP and total dissolved phosphorus (TDP) export were 0.412 kg/ha and 0.56 kg/ha, respectively, for the 5-month duration of the study. This compared with DRP and TDP losses in overland flow of 0.15 kg/ha and 0.392 kg/ha, respectively, from a low phosphorus site (STP 4 mg/l) and 1.25 kg/ha and 1.71 kg/ha from a high phosphorus site (STP 17 mg/l) monitored during the same period (Kurz, 2000).

Kilroy and Coxon (2005) suggested that the phosphorus in groundwater had received limited attention in Ireland. The limited availability of phosphorus data for groundwater bodies in Ireland was also highlighted in the Scottish & Northern Ireland Forum for Environmental Research (SNIFFER) report (2008). No data were available for 37% of groundwater bodies, which was partially due to a lack of monitoring of unproductive aquifers in Ireland (SNIFFER, 2008). A total of 28% of this monitored area in the Republic of Ireland has a phosphorus concentration exceeding 30 µg/l, with only 0.2% exceeding 60 µg/l. In Northern Ireland, there were 513 groundwater samples analysed for phosphorus from 2000 to 2006 and, of these, 35 had phosphorus concentrations of 30 µg/l or above. A background phosphorus level of 20 µg/l was set nationally in a report by O'Callaghan Moran & Associates (2000) (cited in SNIFFER, 2008) as groundwater was not considered to be influenced by lithology.

Karstified limestone of varying degrees underlies approximately 50% of Ireland and with significant interaction between surface and subsurface systems, groundwater contributions from such areas can have a significant impact on phosphorus concentrations recorded in surface water bodies (Coxon and Drew, 2000; Drew, 2008). While in much of Europe karst areas are confined to upland regions, in Ireland karst underlies much of the lowland regions which are more heavily populated and where intensive agriculture operates on the productive soils overlying the karst bedrock (Drew, 2008). The high level of anthrogenic activity in karst regions in Ireland has potential implications for both groundwater and surface water quality in such areas (Fig. 4.4).

SNIFFER (2008) reported that high phosphorus concentrations of between 35 and 70 µg/l were

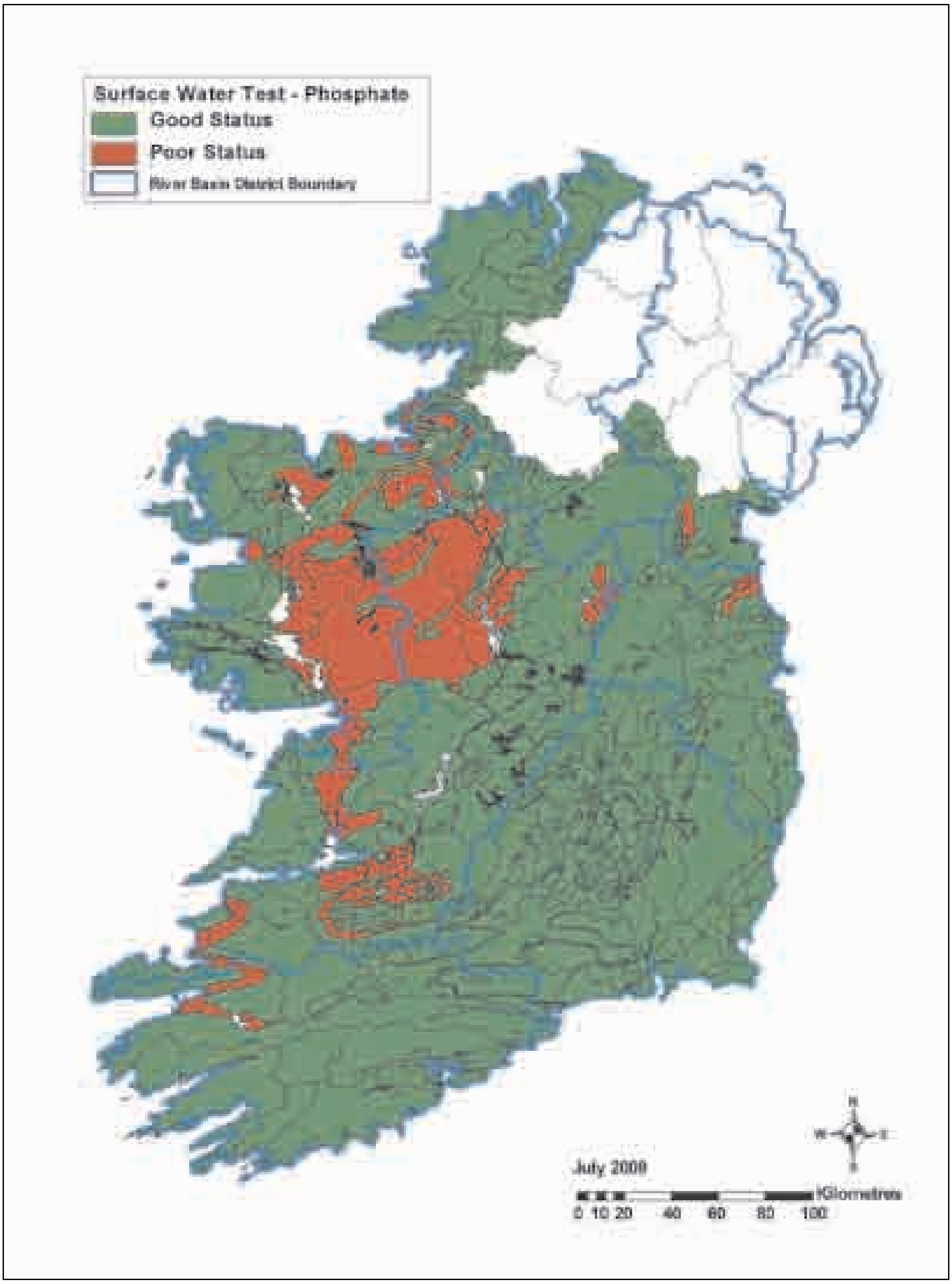

Figure 4.4. Groundwater bodies with poor status (red) based on the contribution of molybdate-reactive phosphorus from groundwater to rivers (source: RPS, 2009).

recorded in the mid-west of Ireland in karstified Carboniferous limestone aquifers, which are dominated by conduit flow. Kilroy and Coxon (2005) reported that phosphorus concentration in karstified areas of western Ireland often exceed the limits at which eutrophication can occur. The rapid transfer of contaminants in conduit flow pathways means that often there is little attenuation of contaminants along the flow pathway (Coxon and Drew, 2000).

Kilroy and Coxon (2005) monitored eight Carboniferous limestone karst springs in the west of Ireland and reported TP increases of 45–107 µg/l in response to rainfall. During one localised pollution event, a TP concentration of 1,814 µg/l was recorded in one of the karst springs monitored. With a typical phosphorus concentration of 560 mg/l, effluent from silage clamps in the Burren are one potential point source of such a high phosphorus concentration recorded by Kilroy and Coxon (2005). Drew (1996) estimated that of 92% of silage clamps in the Burren are at risk of leaching effluent to groundwater, with 60% of all silage clamps considered high risk for groundwater contamination.

Jordan et al. (2005) carried out an investigation into the patterns and processes of phosphorus loss in three catchments in Ireland. Approximately 80% of phosphorus transport in the Oona, Dripsey and Clarianna catchments occurred between October and February and the largest losses were associated with storm events (Kiely et al., 2007). The phosphorus concentration in the Dripsey Catchment during baseflow periods was very low, indicating that groundwater was not contributing significant quantities of phosphorus. In contrast, in the Oona Catchment Jordan et al. (2005) reported chronically high phosphorus concentrations during low flow periods. However, it was highlighted that, due to the surface till layer that forms the gley drumlin, the aquifer is isolated from the surface hydrology and so groundwater is unlikely to be causing the high phosphorus concentration during baseflow periods. Instead, it was suggested that this was due to the significant input of phosphorus from septic tanks in the Oona Catchment (Jordan et al., 2005). The Clarianna Catchment is located on a Carboniferous limestone formation and the overlying soil type is predominantly free-draining (Jordan et al., 2005). Kiely et al. (2007) report that in the Clarianna Catchment, due to the well-drained calcareous soil, phosphorus loss in surface water was 10 times lower than in the Dripsey or Oona Catchment; however, a significant phosphorus concentration in groundwater was recorded in the Clarianna Catchment.

Jordan, P. et al. (2007) identified three types of events associated with phosphorus loss in the Oona Catchment. The first type was associated with baseflow periods and, except for peaks in TP associated with other event types, the rising trend in TP concentration peaked in July and August when baseflow was lowest. Type 2 events occurred during storm events and accounted for the majority of phosphorus exported. Menary (2004) reported that over 70% of the phosphorus loss in the Oona Catchment was during such infrequent high flow events while Jordan, P. et al. (2007) reported that this figure could be as high as 90% as 255 kg of the 278 kg TP exported during the study were due to Type 2 events. Type 3 events are discrete high-magnitude TP transfer events unrelated to rainfall or changes in stream discharge which were potentially due to discreet pollution events in the catchment (Jordan, P. et al., 2007).

4.2.6.1 Forms of phosphorus exported

The forms of phosphorus exported vary with land use, management activities and pathways. The dissolved fractions of phosphorus have been demonstrated by a number of authors, at both field and catchment scales, as the dominant form of phosphorus exported from grassland soils in Ireland (Tunney et al., 2000; Jordan et al., 2005; Kurz et al., 2005a; Kiely et al., 2007; Watson et al., 2007a). However, Menary (2004) reported that in the Oona Catchment PP was the dominant fraction of phosphorus exported. This is possibly due to the flashier nature of this catchment as demonstrated by the higher Q5/Q95 ratio compared with the Clarianna and Dripsey catchments (Jordan et al., 2005). Due to erosion of soil on arable land, PP is the dominant fraction exported due to this land use.

Despite a significant export of suspended sediment as a result of forestry management activities, Rodgers et al. (2008) demonstrated that 80% of phosphorus exported was in dissolved forms. The impact of clear-felling on the export of suspended sediment had ceased after 1 year but the dissolved phosphorus concentration in the stream draining the site was still at 100 µg/1 over a year after a clear-felling event as compared with 6 µg/1 post-clear-felling (Rodgers et al., 2008).

The TP concentration of effluent discharged to a soakaway is typically 10 mg/l (EPA, 2007b), with 50–70% of the solids retained within the septic tank (Gill et al., 2004). Bouma (1979) (cited in Gill et al., 2004) found that 85% of phosphorus entering the percolation area was in the form of orthophosphate.

4.2.6.2 Scale

The impact of scale on the processes of phosphorus loss has to date received limited attention in Ireland. Jordan et al. (2005) reported that in the Dripsey Catchment phosphorus export decreased with increasing scale from 2.65 kg/ha/year at 0.17 km^2 (with no point sources) to 1.60 kg/ha/year at 14 km^2. This decrease took place despite the cumulative input of eight farmyards and it was suggested that this was due to the input of groundwater as the scale increased. In the Oona Catchment, phosphorus loads increased with scale from 2.40 kg/ha/year at 0.62 km^2 to 3.12 kg/ha/year at 88.50 km^2 (Jordan et al., 2005). Because of the isolation of the aquifer from the surface hydrology in the Oona Catchment, due mainly to the surface till layer that forms the gleyed drumlins, it was suggested that this was due to significant input of phosphorus from septic tanks (Jordan et al., 2005).

Rodgers et al. (2008) suggested that due to dilution factors, the impact of clear-felling on phosphorus concentration in a first-order stream draining the forest area decreased significantly to below 10 µg/l on entering a larger second-order stream. They concluded that knowledge of the area for clear-felling, potential dilution factors and nutrient concentration could be used as an indicator for sizing of clear-felling areas that would have a minimum impact on receiving water bodies.

4.2.7 Knowledge gaps

Phosphorus loss from soil to water has been the focus of much research in Ireland, which has provided a detailed understanding of the sources and pathways of diffuse phosphorus loss at a range of scales (Table 4.4). Although a number of projects have investigated phosphorus loss at the catchment scale (Menary, 2004; Jordan, P. et al., 2005, 2007; Arnscheidt et al., 2007; Kiely et al., 2007; Machava et al., 2007; Rodgers et al., 2008), much of the research has adopted a smaller-scale reductionist approach whereby phosphorus loss processes are investigated at laboratory, plot and field scales (e.g. Tunney et al., 2000; Kurz et al., 2005a; Doody et al., 2006; Watson et al., 2007a). The strengths of a small-scale reductionist approach lie in the ability to isolate processes and to test hypotheses, both of which help to inform understanding at larger scales (Haygarth et al., 2005). However, due to the inherent heterogeneity and complexity of catchment-scale processes, there is still significant uncertainty related to linking the processes observed at these smaller scales to changes in water quality observed at catchment scale. Haygarth et al. (2005) highlighted the increasing complexity and uncertainty associated with increasing scale and advocated the need for detailed case studies that integrate research across scales.

An understanding of the impact of scale is vital if the effect of mitigation measures, implemented at field, household, farm and forest plantation scales, are to be linked to changes in water quality observed at catchment scale. Sharpley et al. (2007) suggested that there has been little catchment-scale evaluation of best management practice for reducing phosphorus loss from soil to water. Mitigation measures are often investigated under controlled experimental conditions (Cherry et al., 2008); however, there are limited data available in Ireland to demonstrate the effectiveness of phosphorus mitigation measures at the catchment scale. Cherry et al. (2008) suggested that there has been a failure to effectively assess mitigation measures using individual methods such as phosphorus budgets, risk assessments, water quality monitoring, and modelling, and that a more integrated approach which combines these methods across different scales is required. In the agricultural sector, the Teagasc Agricultural Catchment Project, which aims to investigate the effectiveness of the Nitrates Action Plan, will help to improve the current understanding of the link between farm-scale

Table 4.4. Phosphorus data available from monitoring programmes at plot and catchment scales.

Catchment	Project	Hydrology data	Land-use data	Water quality data	Phosphorus data	Met Office data	Groundwater data	Scale	Sampling frequency	Number of years of data
Oona	EPA LS-2 Projects	Yes	Yes	Yes	Yes	Yes		Sub-catchment and catchment	Flow proportional storm sampling	2–3
Blackwater	INTERREG TRACE Project	Yes	Yes	Yes	Yes	Yes		Sub-catchment and catchment	Up to 10-min sampling	2–3
Clarianna	EPA LS-2 Projects	Yes	Yes	Yes	Yes	Yes	Yes	Sub-catchment and catchment	Flow proportional storm sampling	2–3
Dripsey	EPA LS-2 Projects	Yes	Yes	Yes	Yes	Yes		Sub-catchment and catchment	Flow proportional storm sampling	2–3
Colbrook	AFBI/DARD	Yes	Soil sampling	Yes	Yes	No	No	Sub-catchments	Fortnightly	3–4
Upper Bann	AFBI/DARD	Yes	No	Yes	Yes	No	No	Sub-catchments	Fortnightly	3–4
Lough Melvin	Lough Melvin Nutrient Reduction Programme	Rivers Agency	Yes	Yes	Yes	Met Office	No	Sub-catchment and catchment	Bi-monthly	3
Boyne	Three Rivers	Yes		Yes	Yes	Met Office	Yes	Sub-catchment and catchment	24-h composite samples	?
Suir	Three Rivers	Yes		Yes	Yes	Met Office	Yes	Sub-catchment and catchment	24-h composite samples	?
Liffey	Three Rivers	Yes		Yes	Yes	Met Office	Yes	Sub-catchment and catchment	24-h composite samples	?
Burrishoole	Quantification of Erosion and Phosphorus Release from a Peat Soil Forest Catchment (EPA STRIVE)	Yes	Yes	Yes	Yes	Yes	No	17.7 ha catchment	Up to hourly	2
Four Mile Burn River	AFBI/DARD	Yes	No	Yes	Yes	Met Office	No	597 and 1,968 ha sub-catchments	Daily	4–5
Ballinagee	PEnrich	Yes	Yes	Yes	Yes	Yes	No	14.4-km^2 catchment	Up to daily	20 months
Crossmolina	PEnrich	Yes	Yes	Yes	Yes	No	No	3.5-ha catchment	Up to daily	21 month
Ardvarney	PEnrich	Yes	Yes	Yes	Yes			27-m^2 field plots		20 months
CENIT Site	Ongoing	Yes	Yes	Yes	Yes	Yes	Drainage flow data	Field scale	Up to every 20 min during storm flow	>10
Foleshouse Field Site	Ongoing	Yes	Yes	Yes	Yes		Drainage flow data	Field scale	?	

AFBI, Agri-Food and Biosciences Institute (UK); DARD, Department of Agriculture and Rural Development (UK).

processes and changes in water quality at the catchment scale.

An international phosphorus conference in Denmark (IPW5) (Heckrath et al., 2007) focused on mitigation options and the ecological effects in river basins of diffuse phosphorus losses. The testing of mitigation measures at catchment scale is also the focus of the EU COST 869 Action (http://www.cost869.alterra.nl/), established in 2005, which aims to evaluate mitigation options for nutrient losses to surface water and groundwater at the river basin scale. Similarly the MOPS (Mitigation of Phosphorus and Sediment) project aims to investigate the effectiveness of mitigation measures such as ponds and wetlands for the control of sediment and phosphorus from agricultural land (http://www.lec.lancs.ac.uk/research/catchment_and_aquatic_processes/mops.php). The focus of these research projects on mitigation measures and ecological impact highlights the need to link the implementation of measures with water quality response at the catchment scale.

The research of Machava et al. (2007) and Rodgers et al. (2008) has improved the current understanding of the impacts of forestry on water quality; however, as with agriculture, how these studies relate to larger catchment-scale processes is still unknown. Machava et al. (2007) suggested that further research is required to elucidate the processes of phosphorus retention and release and that extensive monitoring is needed at catchment scale to determine the temporal and spatial contribution of forestry to phosphorus loss from soil to water.

Edwards and Withers (2007) suggested that the potential significance of point sources of pollution, such as farmyards, is poorly understood and potentially underrepresented in modelling exercises. This may also be the case with septic tanks in Ireland as current estimates of the contribution of phosphorus from septic tanks are largely based on PE values from systems that are correctly installed and maintained. Jarvie et al. (2008) concluded that the impact of septic tanks needs to be further investigated in the UK to determine the impact on water chemistry and ecology. Beal et al. (2005) highlighted that there are growing concerns that septic tanks are having an impact on water quality; however, there are few studies that have demonstrated this impact. In Ireland, the National On-Site Wastewater Treatment study being carried out by the National Centre for Freshwater Studies in Dundalk Institute of Technology (http://ww2.dkit.ie/research/ncfs) will provide more detailed data on the impact of on-site water treatment facilities on surface water quality in Ireland. The results of Arnscheidt et al. (2007) and Campbell and Foy (2008) highlighted that often septic tanks are incorrectly installed and maintained so further research is required to determine if their results are representative of unsewered areas in Ireland. This information is also required to gain a better understanding of the connectivity of septic tanks to watercourses.

Discharge of effluent from septic tanks may over time have an impact on the soil's ability to treat effluent and warrants further investigation. For example, effluent discharges to soils with a low calcium/magnesium ratio can decrease drainage efficiency due to dispersion and structural breakdown of the soil over time (Dawes and Goonetilleke, 2003). Further research is also required on biogeochemical processes in soils in order to understand their potential to buffer against diffuse pollution of watercourses. For example, Tunney et al. (2007) demonstrated an annual 'wash-out' of phosphorus from grazed grassland during the autumn and winter months. Phosphorus concentration in overland flow was highest during the autumn and decreased over a couple of months until an equilibrium phosphorus concentration was achieved. The soil processes controlling this peak in availability of phosphorus during the autumn months are unknown. In addition, a more detailed understanding of the cycling of phosphorus between the soil and herbage would provide a better understanding of the contribution of herbage to phosphorus loss from grassland sites.

Further research is required on the attenuation and remobilisation of phosphorus during transport so as to provide a better understanding of the lag time between implementation of measures and subsequent changes in water quality (Collins and McGonigle, 2008). This is of particular importance in the context of achieving 'good ecological status' in water bodies in Ireland by 2015. Similarly, research on the internal cycling and attenuation of phosphorus in rivers is required to elucidate the link between the sources of phosphorus and the downstream ecological impacts of phosphorus loss from soil to water (Jarvie et al., 2008; McDaniels et al., 2009; Withers and Jarvie, 2008).

Although studies to date in Ireland have demonstrated that dissolved phosphorus is often the dominant phosphorus fraction exported to water bodies from surrounding land uses, further research is required on the role of sediment in the mobilisation, attenuation and transport of phosphorus to water bodies. Suspended sediment can be mobilised in runoff and re-deposited over short distances, and can act as a mediating substance in the export of dissolved phosphorus depending on the STP concentration of the suspended sediment and the equilibrium phosphorus concentration of the runoff (Sharpley et al., 1981a,b). Recent studies have demonstrated that in intensively managed grassland soils, despite the stabilising and filtering effect of the grass sward, significant quantities of sediment can be exported during individual rainfall events (Chapman et al., 2005; Bilotta et al., 2008). These authors have demonstrated that the export of suspended sediment and associated phosphorus was particularly important in artificially drained grassland sites. Bilotta et al. (2008) reported that only 8–18% of the TP exported during their study was in dissolved form, highlighting the significant role that sediment can play in the export of phosphorus from grassland sites. Walling et al. (2008) reported that, in five sub-catchments of the Wye River in the UK, channel/subsurface sources contributed 40–55% of the overall SS flux and 21–43% of the PP flux from the catchments, further highlighting the potential contribution of subsurface pathways in PP loss from catchment land uses.

The importance of preferential flow in phosphorus transport has been highlighted by a number of authors (Stamm, 1997; Ball Coelho et al., 2007; Fuchs et al., 2009). However, in Ireland, limited research has been carried out on the role of preferential flow channels in nutrient export from soil. Kramers et al. (2009) studied three grassland soils in Ireland and demonstrated the existence of preferential flow channels in all three soils to a depth of 75 cm. They concluded that the preferential flow pathways observed could result in significant movement of water and dissolved solutes in the soil profile. In light of the findings of Kramers et al. (2009) there is a need for further investigation into phosphorus transport through this pathway.

The SNIFFER (2008) report highlighted the limited data available on phosphorus in groundwater bodies in Ireland. The results from Kilroy and Coxon (2005), Kiely et al. (2007) and the SNIFFER (2008) report demonstrate that phosphorus is a contaminant of concern in karstified Carboniferous limestone aquifers and so further research is required to identify the pathways and sources of phosphorus in these systems. Limited data are available on phosphorus in poorly productive aquifers in Ireland and so increased monitoring of these systems is required.

The application of fingerprinting techniques would provide important information on the pathways and sources of phosphorus within Irish catchments. Walling et al. (2008) used physico–chemical fingerprinting techniques to identify the sources and pathways of sediment and PP in Ireland, while Arnscheidt et al. (2007) used faecal matter and grey water fingerprinting techniques to trace the sources of phosphorus at low flow in the Oona Catchment. The use of biochemical fingerprinting bacteria was also proposed by Ahmed et al. (2005) as a method to provide direct evidence of septic tank failure. The work of Arnscheidt et al. (2007) and Jordan, P. et al. (2007) has also demonstrated the value of high-resolution monitoring for understanding the phosphorus loss process at the catchment scale. Such high-resolution monitoring is resource and time intensive; however, accurate source apportionment justifies investment in such intensive monitoring programmes at the catchment scale in order to cost-effectively target and implement migration measures.

4.2.8 Recommendations

4.2.8.1 Recommendations for the Pathways Project

- Although studies to date in Ireland have demonstrated that dissolved phosphorus is often the dominant phosphorus fraction exported to water bodies from surrounding land uses, further research is required on the role of sediment in the mobilisation, attenuation and transport of phosphorus to water bodies.

- Further research is required on the role of septic tanks in diffuse pollution at the catchment scale. Currently there are limited national data available on the installation, maintenance and connectivity of septic tanks to water bodies. As part of the Pathways Project, a survey of septic tanks should be carried out in the selected catchments to determine their potential contribution to changes in water quality observed in these catchments. The potential risk posed to water quality by septic tanks should be assessed based on soil type, topography, connectivity to watercourses, structural integrity of the tanks, condition and location of the percolation area, and frequency of inspection and desludging. The development of a risk assessment tool similar to the phosphorus risk index approach used in agriculture (Magette et al., 2007) would be a worthwhile outcome from the project.

- Due to the limited data available on phosphorus in groundwater in Ireland, further investigation is required. In particular further investigation into the interaction between groundwater and surface water in karst areas should be carried out so as to elucidate the role of groundwater quality in eutrophication of surface water bodies in such areas.

4.2.8.2 Recommendations for future research

- Due to the inherent heterogeneity and complexity of catchment-scale processes, there is still significant uncertainty related to linking the processes observed at smaller scales to changes in water quality observed at the catchment scale.

- Further research is required on the attenuation and remobilisation of phosphorus during transport so as to provide a better understanding of the lag time between implementation of measures and subsequent changes in water quality.

- An understanding of the impact of scale on phosphorus loss processes is vital if the effect of mitigation measures, implemented at field, household, farm and forest plantation scales, are to be linked to changes in water quality observed at the catchment scale.

- Research is required on the impact of septic tank effluent on the soil's physico–chemical properties, and subsequent changes in the soil's ability to mitigate against phosphorus export.

- An increased understanding of biogeochemical soil processes and their buffering capacity would provide an insight into the potential of soils to mitigate against diffuse pollution of watercourses.

- Research is required on the internal cycling and attenuation of phosphorus in rivers to help interpret observed changes in water quality.

- In Ireland, limited research has been carried out on the role of preferential flow channels on nutrient export from soil to water and, hence, this warrants further research.

4.3 Nitrogen

Among the four major forms of nitrogen in the environment (nitrogen gas, organic nitrogen, ammonia (NH_4) and nitrate (NO_3)), nitrate is recognised as a widespread contaminant in groundwater and surface waters. Elevated concentrations in groundwater are of significant concern in many countries across the European Union (EEA, 2000) and over the past years an increasing number of Irish public water supplies have exhibited elevated levels of nitrate (Page et al., 2009). While it has generally been documented that rising levels of nitrate in the aquatic environment can be primarily attributed to diffuse pollution from intensive farming (Foster and Young, 1980), a number of other sources have been identified to contribute to the overall pollutant load.

The rationale for investigating the sources and fate and transport of nitrate in the environment is linked to the serious nature of the potential impacts of elevated nitrate levels on human health, animal welfare and aquatic ecosystems.

- **Human health effects**
  While nitrate is not directly toxic to humans, excessive consumption of nitrate in drinking water has been associated with the risk of methaemoglobinaemia ('blue-baby syndrome'; Fan and Steinberg, 1996), linked to the reduction of ingested nitrate to nitrite (NO_2) in the human gut

and subsequent passage of nitrite ions into the bloodstream affecting the capacity of haemoglobin molecules to transport oxygen. In view of this risk to human health, the EU standard for nitrate in potable water of 11.3 mg N/l has been set by the EU Drinking Water Directive. Nitrate is furthermore identified as a possible cancer risk due to its degradation to nitrite in the body, which in turn can combine with organic compounds to form *N*-nitroso compounds, which have been shown to be potent animal and human carcinogens.

- **Animal health/welfare**
  Consumption by livestock of water containing elevated nitrate concentrations may result in nitrate poisoning. At high nitrate concentrations (>300 mg NO_3/l), nitrate poisoning may result in animal death. At lower concentrations, nitrate poisoning may increase the incidence of stillborn calves, cystic ovaries, lower milk production and reduced weight gain (Faries et al., 1991).

- **Aquatic ecosystems**
  Excess nitrate concentrations can cause eutrophication (nutrient enrichment), which may in turn affect biodiversity by favouring plants that need, prefer, or can survive in nutrient-rich environments. Certain algal species such as freshwater cyanobacteria and marine dinoflagellates thriving under these enriched conditions produce toxins that may seriously affect the health of mammals, birds and fish (WHO, 1999). Eutrophication may also adversely affect a wide variety of water resources used for potable supplies, livestock watering, irrigation, fisheries, navigation, angling and nature conservation. The full impact of eutrophication depends primarily on the balance between nitrogen and phosphorus concentrations in a water body. In the freshwater environment, excess nitrate particularly affects oligotrophic waters (Mason, 2002). In estuarine and coastal environments, nitrate eutrophication tends to trigger the growth of smothering algal mats across the inter-tidal zone as well as blooms of toxic, nuisance algae (Vitousek et al., 1997; Levine et al., 1998). Even at relatively low concentrations, nitrate can have adverse effects on common eelgrass (Hauxwell et al., 2003), which supports many commercially important aquatic vertebrate and invertebrate species (Beck et al., 2001).

4.3.1 Sources in the environment

While agricultural sources are attributed to 82% of nitrogen loads in Irish rivers and estuaries (EPA (2004) in Schulte et al., 2006), a number of other sources contribute to the overall nitrogen load.

Nitrogen may be added to the subsurface through various processes and may undergo chemical transformations before it is transported into groundwater. The major divisions of the nitrogen cycle are (Brady and Weil, 2002):

- Mineralisation;
- Immobilisation;
- Nitrogen fixation;
- Ammonification;
- Nitrification; and
- Denitrification.

The conversion of mobile nitrogen species to some organic forms is termed immobilisation or microbial and plant assimilation. Mineralisation is the conversion of complex organic nitrogen to more simplified inorganic forms. Nitrogen may be present in the soil in the form of ammonia, which may be metabolised by organisms, assimilated by plants, adsorbed by clay minerals and/or organic matter, and oxidised to nitrate. Nitrification is the biochemical oxidation of ammonia to nitrate. In the presence of specific bacteria and oxygen, ammonia is enzymatically oxidised in a stepwise process to nitrite followed by nitrate. In Ireland, the rate of net mineralisation (i.e. the difference between gross mineralisation and immobilisation) was observed to range from 56 kg N/ha/year to 220 kg N/ha/year as a function of soil texture, soil depth, organic matter content and soil water status (O'Connell and Humphreys, 2005).

Nitrification will only occur in oxidising environments. Secondary parameters affecting nitrification include temperature, moisture content, bacterial populations and pH. Denitrification is the biochemical reduction of nitrate-nitrogen to nitrogen gas in the absence of oxygen (refer also to Figs 4.5 and 4.6).

In an approach to an integrated assessment of agriculture and waters, the EEA completed a source apportionment exercise for nitrogen and phosphorus across a number of EU Member States (EEA, 2005). The sources covered in this report include point sources, such as discharges from urban wastewater, industry and fish farms, as well as diffuse sources, including background losses (e.g. natural land), losses from agriculture, losses from scattered dwellings and atmospheric deposition.

Edwards and Withers (2007) provide an overview of sources of potential sediment and nutrient loss with certain general characteristics (Table 4.5).

Table 4.6 provides an overview of total nitrogen (TN) concentrations, as well as TP and SS concentrations for various sources.

With regard to agricultural nitrogen, the CSA concept applies to many catchments, where much of the exported nitrogen originates from relatively small areas. Typically, these CSAs result from a combination of high hydrologic activity due to climate, topography and geology, with high nutrient loss potential due to intensive agricultural activity. While phosphorus export is typically associated with surface runoff during storm events that occurs in close proximity to catchment streams, Pionke et al. (2000) observed that most nitrate exported to streams originated as subsurface flow entering the soil or groundwater at some distance away from the stream, predominantly during non-storm flow periods. In many humid, temperate climate landscapes, VSA hydrology (Ward, 1984) controls where surface runoff occurs leading to spatial variability. Similar, but to a lesser degree, groundwater recharge varies spatially across individual catchments.

4.3.1.1 Atmospheric deposition

Atmospheric nitrogen originates from a variety of natural and anthropogenic sources and is deposited on land both under wet and dry deposition. Natural sources include nitric acid created from nitrogen gas and water vapour by lightning and natural ammonia emissions from rotting biomass. Anthropogenic

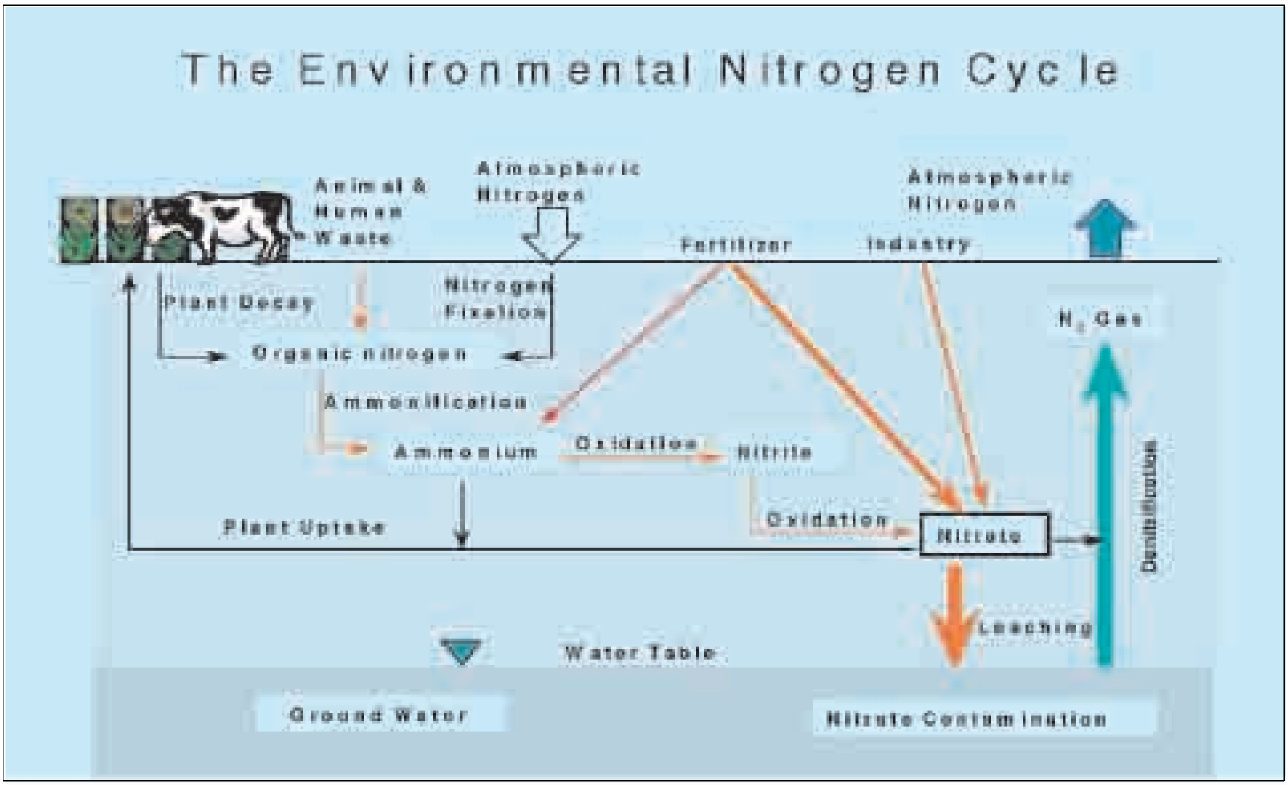

Figure 4.5. The nitrogen cycle (source: ITRC, 2000).

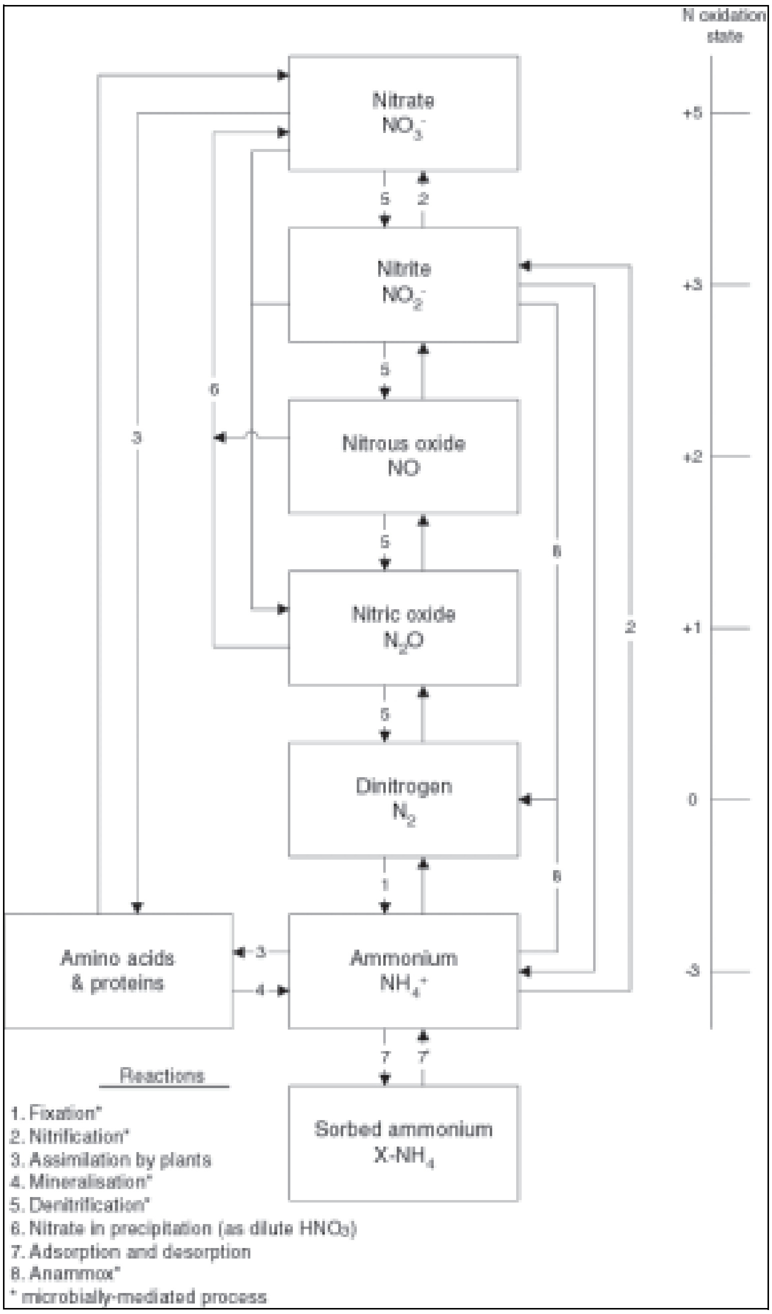

Figure 4.6. Chemical species in the nitrogen cycle (based on O'Neill, 1985).

sources include nitrogen oxides (NO_X) from the combustion of fossil fuels (which in turn are converted to nitric acid by lightning) and industrial emissions. Anthropogenic sources generally outweigh natural sources in rainfall nitrogen (Jordan, 1997). With regard to nitrogen loading, examples from the UK show that approximately 10 kg N/ha/year is deposited by precipitation (Goulding et al., 1990). However, dry and particulate deposition can increase TN deposition to 35–40 kg N/ha/year.

4.3.1.2 Geological nitrate

Organically bound nitrogen can be found in organic-matter-rich sediments. This organic nitrogen can be mineralised to ammonium during diagenesis (Rodvang and Simpkins, 2001). If this ammonium is nitrified, it can produce high levels of nitrate that are entirely natural. Because of groundwater flushing in aquifers, this nitrate tends only to survive in aquitards. This source of nitrate can be distinguished from agricultural nitrate, for example by its stable isotope signature

Table 4.5. Various sources of potential sediment and nutrients and certain general characteristics (Edwards and Withers, 2007).

Source type	Hydrological		Chemical composition
Source	Discharge	Rainfall dependency	
Point			
STW/Industry	Continuous	Low	Concentrated
CSOs	Episodic	High	Concentrated
Intermediate			
Septic tanks	Semi-continuous	Low	Variable
Field drains	Semi-continuous	Low–high	Variable
Road/Track runoff	Episodic	High	Variable (high SS)
Farmyards	Episodic to semi-continuous	Low–high	Variable
Diffuse			
Surface runoff	Episodic	High	Variable (high SS)
Subsurface runoff	Episodic	High	Dilute
Groundwater	Continuous	Low	Dilute

STW, sewage treatment works; SS, suspended solids; CSO, combined sewer overflow.

Table 4.6. Comparison of total nitrogen, total phosphorus and suspended solids concentrations (mg/l) in various sources with range shown in brackets (Edwards and Withers, 2007).

Source type	No.	Total nitrogen	Total phosphorus	Suspended solids
Farmyard runoff	33	183 (0.7–1021)	30.80 (0.02–247)	982 (690–1284)
Pig slurry	3	209 (200–218)	41.10 (39.4–43.6)	637 (519–873)
Road runoff	2	2.8 (2.3–3.2)	0.26 (0.18–0.34)	102 (55–149)
Septic effluent	16	69.6 (9.2–210)	10.20 (1–22)	47.7 (5.0–129)
STW effluent	132	No data	2.90 (<DL–13.10)	27.4 (1.5–600)
Track runoff	13	3.2 (0.7–13.8)	2.69 (0.24–7.30)	642 (70–2,764)

STW, sewage treatment works; No., minimum number of samples; <DL, less than detection limit.
Sources of data:
Farmyard runoff – Dunne et al. (2005), Chadwich and Chen (2002), Tanner et al. (1995), Cumby et al. (1999), Newmann et al. (2000), Kern and Idler (1999) and Mantovi et al. (2003) – all cited in Edwards and Withers (2007).
Pig slurry – Lee et al. (2004) – cited in Edwards and Withers (2007).
Road runoff – Mitchell (2001) – cited in Edwards and Withers (2007).
Septic effluent – Grennway and Woodley (1999), Kerna and Idler (1999), Luederitz et al. (2001), Gschlossl et al. (1998) – all cited in Edwards and Withers (2007).
STW effluent – Jarvie personal communication – cited in Edwards and Withers (2007).
Track runoff – Withers personal communication – cited in Edwards and Withers (2007).

which is different from that of agricultural nitrate (see Section 3.3).

4.3.1.3 Fertilisers

Increased leaching of nitrogen from topsoil and the removal of nitrogen by crops interrupts the natural nitrogen cycle. Leguminous crops (e.g. clover, alfalfa or beans) are able to convert elemental nitrogen in the atmosphere to forms of nitrogen useful to other crop types. Soil nitrogen stores can thus be replenished by crop rotation, including leguminous crops ploughed into the soil. However, this does not necessarily maximise the potential crop yield and import of nitrogen is still required for continuous cultivation. Nitrogen can be imported as manure, dairy washings or as biosolids; in modern agriculture most nitrogen is imported as mineral fertilisers. Nitrogen is the most common element used as a fertiliser supplement for agricultural, turf and garden use. Artificial nitrate fertilisers are applied as ammonium nitrate (34% nitrogen), ammonium sulphate (21% nitrogen), calcium ammonium nitrate (27% nitrogen) or urea (46% nitrogen), depending on the needs of the crop. Most of the ammonium is converted to nitrate in the soil zone. Nitrate's high solubility and low sorptivity allows infiltration beyond the root zone when over-applied or overwatered. As a result, elevated groundwater nitrate levels have occurred in heavily farmed areas. Studies on the application of nitrogen fertiliser versus soil leaching (Addiscott, 1996) have indicated, however, that fertiliser nitrogen is not necessarily the direct source of nitrate pollution. During spring application, less than 10% of nitrogen applied is likely to be lost to leaching since most of the applied nitrogen is taken up by the crop and converted to organic forms. In wet and warm autumn soils, decaying organic matter is rapidly mineralised and nitrified to nitrate and is therefore prone to leaching by winter infiltration. However, where excessive amounts of nitrogen fertiliser are applied to the soil, direct loss of nitrate can result. The parameters governing the relationship between crop yield and fertiliser application are dependent upon the soil (texture, pH, organic content), crop variety and its method of planting and fertiliser application (Goulding, 2000). Figure 4.7 illustrates a typical crop nitrogen response curve and nitrate leaching losses.

In the context of fertilisers, production/handling facilities may be regarded as potential industrial point sources, as discharges of ammonium and/or nitrate may be associated with these facilities. Groundwater impacted from weathered fertiliser stockpiles has been reported to show concentrations of ammonium up to 1,500 mg N/l, with concentrations of nitrate over 300 mg N/l (Barcelona and Naymik, 1984).

4.3.1.4 Land-use changes

Land-use changes may lead to a mobilisation of soil-bound nitrogen. Ploughing, e.g. due to conversion of pasture to tilled land for arable cultivation, exposes soil-bound ammonium compounds and organically bound nitrogen to the atmosphere. These are mineralised to nitrate, which is readily leached by rainfall runoff and infiltration. Table 4.7 summarises some nitrate leaching rates for ploughed grassland.

Table 4.7. Nitrate leaching rates of ploughed grassland (collated in Wakida and Lerner, 2002).

Vegetation type	Nitrate leaching (kg N/ha/year)
Temporary pasture	36
Grass ley	33
Ploughed grass	93
Temporary leguminous pasture	72–142

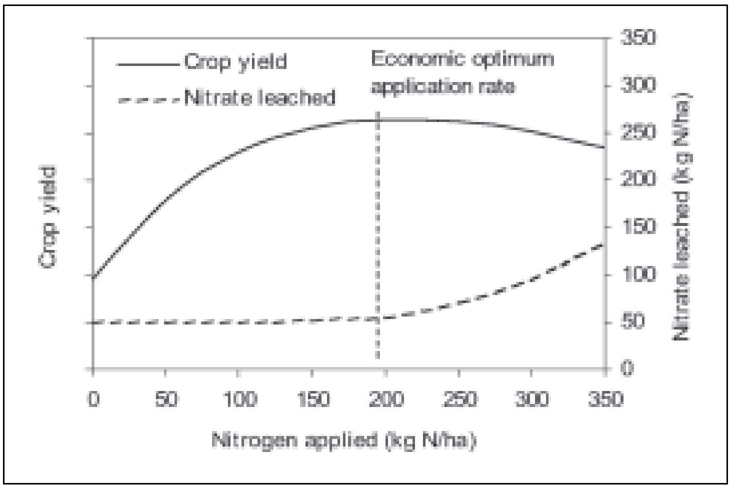

Figure 4.7. Typical crop nitrogen response curve and nitrate leaching losses (based on Addiscott, 1996).

4.3.1.5 Urban sources

In an urban environment, the disturbance of ground by construction can trigger the leaching of soil-bound nitrogen as described above. Wakida and Lerner (2002) estimated the average nitrate load from exemplary construction sites in the city of Nottingham to be 65 kg N/ha. However, at any one time, only a limited amount of construction earthworks are ongoing across a given city and so diffuse urban sources such as leaking sewers (Fukada et al., 2004), contaminated land in general and nitrogen oxides from vehicle emissions are likely to contribute the majority of the nitrogen load to urban groundwater. Lerner et al. (1999) suggest that the total annual loading of nitrogen to groundwater from the Nottingham urban area is 21 kg N/ha, comprising leaking mains (37%), leaking sewers (13%), soil leaching (9%) and other sources such as contaminated land and industrial discharges (41%).

4.3.1.6 Point sources

Point sources of nitrogen pollution are commonly associated with a hydraulic surcharge that drives the contaminant into the subsurface, for example in septic tank soakaways or landfills (Lyngkilde and Christensen, 1992; Harman et al., 1996). These sanitary sources often discharge nitrogen in organically bound forms under reduced conditions. These are quickly mineralised to ammonium and under aerobic conditions this can be oxidised to nitrate.

The identification of individual point sources can be affected by scale, e.g. small nitrate plumes from individual septic soakaways can be dispersed in the aquifer to form no observed plume.

4.3.1.7 Other sources

Other potential sources of nitrate impact may be associated with the manufacture/storage of ammonium-nitrate-containing explosives and ordnance testing. Nitrogen compounds are furthermore widely used in industrial settings such as plastics manufacturing, metal processing (Ford and Tellam, 1994), the textile industry, petroleum refining, pharmaceutical industries and a range of other manufacturing processes. Nitrate contamination may result from the improper handling, disposal and use of the applied nitrogen compounds.

4.3.2 Controls on mobility/pathways

4.3.2.1 Nitrate leaching

Numerous studies have shown that the soil zone can act as both a source of nitrate and as a zone of active denitrification (Parkin, 1987; Goulding et al., 1993; Bakar et al., 1994). Organically bound nitrogen in the soil is mineralised to ammonium, and then quickly nitrified to nitrate. This nitrate is then available for leaching. The soil zone is also the most active area of nitrogen cycling, both by microbial denitrification and plant uptake. Once nitrate is leached below the rooting zone, it is normally lost from an agricultural system (Whitehead, 1995). Denitrification rates in agricultural soil are highest in the autumn, when soil is moist but still warm (Addiscott, 1996). A number of soil leaching models have been developed in the past (Smith et al., 1996; Wriedt et al., 2005) to predict concentrations of nitrate leaching from agricultural regions. Soil texture and type affect nitrate leaching rates, with coarser more permeable soils allowing more leaching through larger better connected pore spaces (Goss et al., 1998). Clayey soils have high nitrogen retention (Hubbard et al., 2004) but this nitrogen can subsequently be released on ploughing. Macropores may facilitate bypass flow around the shallow root zone area of most active denitrification. However, Casey et al. (2001) and Jørgensen et al. (2004) found elevated denitrification rates where macropores provided preferential pathways for limiting nutrients, including nitrate and organic carbon.

4.3.2.2 Physical transport processes

Recharge and the unsaturated zone

As a non-sorbing solute, nitrate moves at the same velocity as the water in which it is dissolved. Transport of nitrogen from agricultural soils is hence more related to the general vertical movement of water through the soil profile. Consequently, groundwater recharge (and nitrate leaching) will only occur when water input to the soil from rainfall (or artificial irrigation/liquid fertiliser application) exceeds water removal by evapotranspiration and storage in dead-end soil pores. Under Irish climatic conditions this typically occurs from late autumn to early spring. Recharge rates will vary depending on soil properties and environmental conditions, with deeper soils with heavier, less well-drained subsoils showing longer travel times. Artificial drainage may however significantly affect travel times and the potential for nitrate attenuation (see Section 3.3). Large volumes of rainfall can have either of two effects on nitrogen loss: (i) reducing the proportion of nitrate retained in a soil, or (ii) diluting nitrate concentrations (Scholefield et al., 1993; Tyson et al., 1997). Although mechanical dispersion may affect the passage of nitrate through the unsaturated zone with regard to lithological heterogeneities at varying scales, a reasonable body of evidence suggests that as a simplification most of the nitrate moves through the unsaturated zone in a piston-flow-like manner, undergoing only moderate dispersion with the result that the most important zone of mixing occurs beneath the water table in the saturated zone (BGS, 1999).

Slow movement of recharge and solutes through thick unsaturated zones can lead to the accumulation of significant nitrogen stores in the unsaturated zone (Foster and Bath, 1983). Typical nitrate concentrations in unsaturated zone pore waters range from 20 to 100 mg N/l (BGS, 1999).

Transport in groundwater

Like all solutes undergoing advection, nitrate is subject to hydrodynamic dispersion and diffusion. In fractured, porous aquifers, solute movement is primarily by advective flow through fractures, but is attenuated by diffusion into the matrix leading to typical dual porosity solute breakthrough curves. These effects are also observed in porous media with connected macropore features (e.g. root/worm holes or desiccation cracks). They are commonly observed in near-surface soils and subsoils where such features remain open (Brady and Weil, 2002). Fracture flow through clay tills were observed to a depth of approximately 6 m (McKay et al., 1993), beneath which the fractures were closed by the overburden pressure. Gerber et al. (2001), however, observed transmissive fractures throughout the depth of a 60-m thick till aquitard. The relationship between matrix- versus fracture-dominated flow will affect the nitrate depletion potential of aquifer systems.

Sorption

Sorption of the negatively charged nitrate ion is usually not observed. However, sorption of nitrate has been noted in soils that contain poorly crystallised oxide or hydroxide minerals (Katou et al., 1996). Sorption of nitrite in soils is commonly observed and may be related to nitrite reacting with the aromatic ring structure of dissolved organic matter to produce dissolved organic compounds (Davidson et al., 2003). These in turn may then be adsorbed to soil or taken up by plants and bacteria. As an attenuation mechanism for nitrate, this requires that nitrate is firstly converted to nitrite via denitrification.

Nitrate depletion/attenuation

The key mechanism for the depletion of nitrate in groundwater is microbial denitrification. Other processes such as dissimilatory nitrate reduction to ammonium and assimilation of nitrate into microbial biomass may also contribute to nitrate depletion to a minor degree, subject to the specific environmental conditions.

Denitrification is the process whereby nitrate is converted via a series of microbial reduction reactions to nitrogen gas (Fig. 4.8). The organisms that contribute to this process tend to be common in surface water, soil and groundwater (Beauchamp et al., 1989). These denitrifiers are mostly facultative anaerobic heterotrophs (obtaining both their energy and carbon from the oxidation of organic compounds). Some denitrifying bacteria are autotrophs (obtaining their energy from the oxidation of inorganic species). In general, the absence of oxygen and the presence of organic carbon, reduced sulphur, or iron facilitates denitrification.

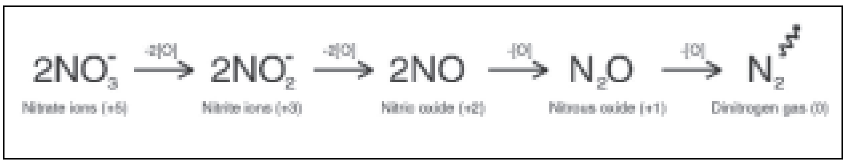

Figure 4.8. Denitrification reaction chain (Brady and Weil, 2002).

Although the denitrification process has a stable end point at nitrogen gas, it can be halted at any of the intermediate stages (Fig. 4.9), depending on a number of factors. This is of importance insofar as nitrite is significantly more toxic and reactive than nitrate. In natural waters, nitrite rarely occurs at concentrations comparable to those of nitrate except temporarily under reducing conditions. Typical background concentrations tend to be two to five orders of magnitude below those of nitrate.

When oxygen levels are very low, nitrogen gas is the end product of the denitrification process, but where they are more intermediate or variable the reaction may be halted at the formation of nitrogen oxide gases. Nitrogen oxides (nitric oxide and nitrous oxide) are environmentally harmful gases contributing to acid rain, promote the formation of ground-level ozone and contribute to global warming. Nitrous oxide is often used in wetland studies as an indicator that denitrification is occurring (Delaune and Jugsujinda, 2003). However, it is equally produced as an intermediate product in the nitrification of ammonium and to this end the presence of nitrous oxide is not necessarily a conclusive indicator for denitrification. Some studies (Fontes et al., 1991) have used nitrogen gas concentrations as 'excess nitrogen' (the nitrogen gas concentration above the expected equilibrium concentration with the atmosphere) to quantify denitrification in deep confined aquifers.

The other 'by-product' of the denitrification process is the oxygen rejected at each stage, typically as the bicarbonate ion and carbon dioxide (if carbon is the electron donor) or the sulphate ion (if a sulphide mineral is the electron donor). This can provide favourable circumstances for the denitrification process as the production of bicarbonate and carbon dioxide buffer the groundwater pH around neutral conditions, which are most favourable for the process.

With regard to heterotrophic denitrification, many factors are known to affect the complex reactivity of soil, or organic matter, towards oxidants, including environmental conditions such as pH, temperature and oxidant concentrations, physical protection and chemical composition (Hartog et al., 2004). The rate of denitrification is most often related to the amount of DOC in porewater or groundwater (Fig. 4.10).

Solid-phase organic carbon (as solid organic matter (SOM) or fraction of organic carbon (f_{OC})) of soil or geologic deposits may also provide an indication for the potential for denitrification (Brettar et al., 2002).

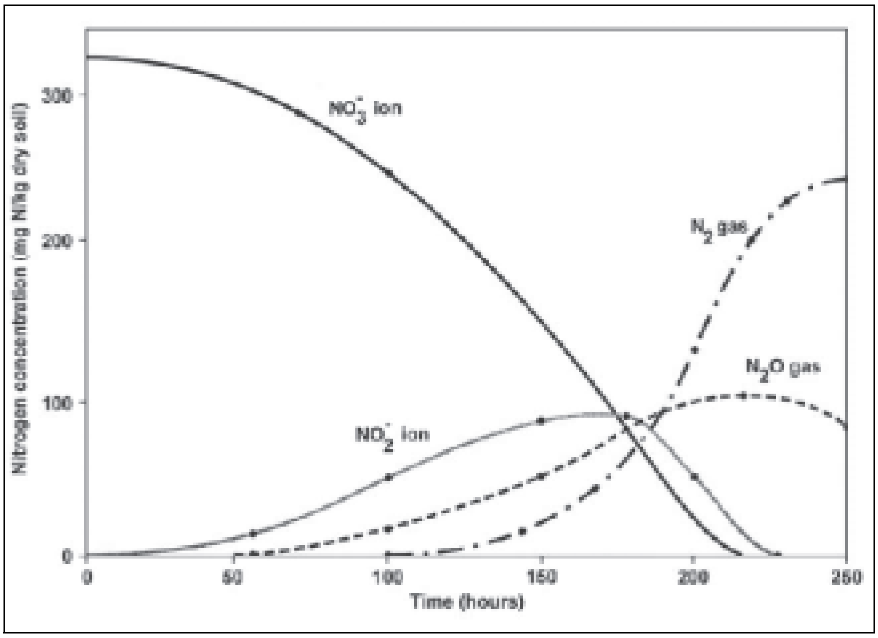

Figure 4.9. Nitrogen speciation during the nitrification process in a moist soil incubated under anaerobic conditions (Brady and Weil, 2002).

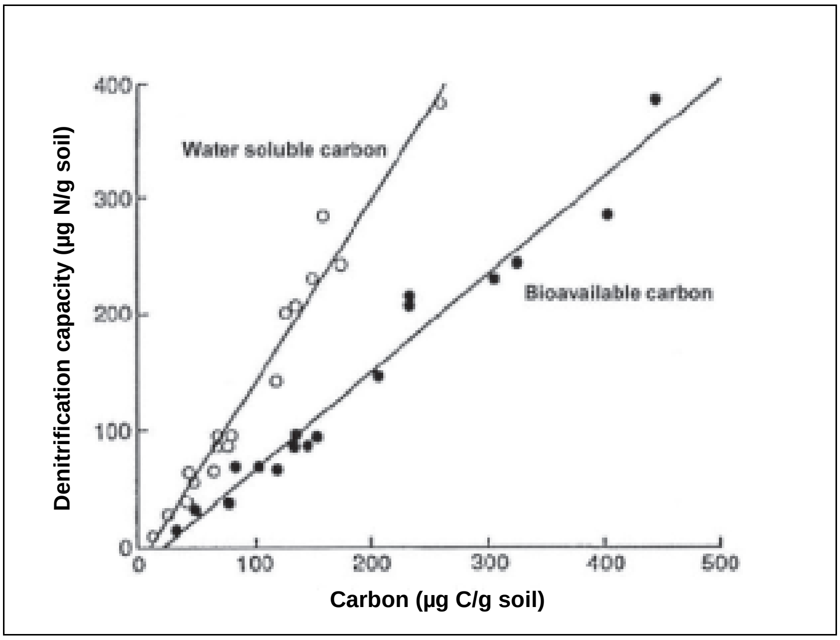

Figure 4.10. Relationship between the denitrification capacity of soil and the content of water-soluble and bioaccessible carbon (Burford and Bremner, 1975).

Eppinger and Walraevens (2005) however highlight that the pore throat size and the clay content of a rock mass may make certain parts of the SOM physically inaccessible to micro-organisms, even if it is bioaccessible. Fine-grained sediments, even if rich in SOM, may not contribute significantly more to denitrification than coarser-grained deposits for this reason. Considering the type of SOM in sediments, Hartog et al. (2004) showed that sediments with more oxidised organic matter were less reactive (microbial mediated) to dissolved oxygen. Sediments that had been exposed to aerobic conditions during depositions and diagenesis thus yielded SOM with lower reactivity.

With regard to sewage effluent, it has been documented (MacQuarrie et al., 2001) that although raw sewage contains considerable amounts of labile organic carbon, much is oxidised co-incidentally with or prior to ammonium oxidation in the unsaturated zone. Nitrate-rich, well-oxidised effluent may therefore contain only small amounts of carbon that might act as an electron donor.

A number of environmental factors affect the efficacy of the denitrification process:

- **Nitrate concentrations**
  A number of studies indicate that the kinetics of denitrification at concentrations >1 mg N/l are independent of concentration (Smith and Duff, 1988; Korom et al., 2005); the relative concentrations of nitrate versus organic carbon can control whether nitrate is depleted by denitrification or dissimilatory reduction to ammonium.

- **Oxygen concentration**
  Denitrification is principally an anaerobic process; it will only start when dissolved oxygen levels fall below a certain threshold, generally believed to fall around 1–2 mg/l (Bates and Spalding, 1998; DeSimone and Howes, 1998; Böhlke et al., 2002).

- **Nutrient availability**
  Denitrifying bacteria require a number of additional trace nutrients for the construction of their cellular structure (e.g. boron, copper, iron, manganese, molybdenum, zinc, chlorine); deficiency in these micronutrients may limit bacterial growth; in some environmental systems phosphorus may be a key limiting factor (Hunter, 2003). The presence of sulphide in soils has been shown to facilitate

dissimilatory nitrate reduction versus denitrification (Hiscock et al., 1991).

- **pH**
  The preferred pH range for heterotrophic denitrifiers lies between 5.5 and 8.0 (Rust et al., 2000); acidic environments (pH < 5) may arrest the denitrification process leading to the formation of nitrite and nitrous oxide (Brady and Weil, 2002). In non-calcareous aquifers, mineralisation of organic carbon and nitrification of ammonium in organic waste can reach pH 4.9 (DeSimone and Howes, 1998).

- **Temperature**
  The optimum temperature range for denitrification lies between 25°C and 35°C, with a viable range of 2–50°C; reaction rates are commonly assumed to double for every 10°C increase in temperature. Changes in the denitrification rate due to seasonal temperature fluctuations may be masked by variations in the rate of organic carbon flux (Cannavo et al., 2004).

- **Salinity**
  High salinities inhibit denitrification; however, denitrification in estuarine and marine environments is less affected by salinity (Magalhàes et al., 2003) and is facilitated by halo-tolerant strains.

- **Toxins**
  Heavy metals, pesticides and pesticide derivatives have been shown to inhibit denitrification (Hunter, 2003); however, other studies have also indicated that pesticides may even stimulate denitrification as a source of organic carbon (Jørgensen et al., 2004).

- **Pore size**
  Small pore spaces may inhibit microbial growth. Where the available pore spaces fall below 1 µm (typical diameter of a microbial cell), microbe penetration may be precluded; on the other hand, where large open fractures dominate aquifer flow paths, the biodegradation activity will be limited by the small surface area for microbial growth relative to the fracture volume and by comparatively short hydraulic residence times (Mather, 1989), as well as by relatively high flow velocities in open fractures inhibiting the growth of biofilms by shear stresses.

While the analysis of concentrations of key redox species is a common approach to identify denitrification processes, study of the chlorine/nitrate ratios provides a further simple technique for identifying potential denitrification. As chloride and nitrate behave conservatively (except where nitrate may undergo denitrification), study of the chlorine/nitrate ratio rather than the absolute concentration of redox species can compensate for changes in nitrate concentrations caused by mixing of different groundwater components. A further increasingly commonly implemented approach to identify and quantify denitrification processes is to use stable isotope techniques. The stable isotope composition of nitrate is known to be indicative of its source and can be used to identify biological denitrification. $\delta^{15}N$ is used in this approach ($^{15}N/^{14}N$ ratio of sample compared with standard – nitrogen in air). This approach can assist in delineating individual sources of contamination (Fukada et al., 2004) exhibiting the characteristic isotope signature (see Table 4.8) and in determining groundwater denitrification zones within aquifer systems.

The $\delta^{15}N$ approach is often combined with other lines of investigation, such as microbial indicators, $\delta^{11}B$ or $^{87}Sr/^{86}Sr$. On a catchment scale, $\delta^{15}N$ has been used in conjunction with $\delta^{13}C$, $\delta^{34}S$, chlorofluorocarbons and ^{3}H to determine the application history and fate and transport of nitrate (Böhlke and Denver, 1995). The combination of $\delta^{15}N$ and $\delta^{18}O$ provides further information to characterise the denitrification processes by reflecting the isotope fractionation processes associated with biological denitrification.

Table 4.8. Ranges of $\delta^{15}N$ signatures (based on BGS, 1999; Fukada et al., 2004; Widory et al., 2004).

Source	$\delta^{15}N$ (‰)
Inorganic nitrate fertilisers	–7 to +5
Ammonium fertilisers	–16 to –6
Natural soils	–3 to +8
Sewage	+7 to +25

Aquifer studies of nitrate attenuation processes by employing environmental isotope analysis (Schwientek et al., 2008; Vitoria et al., 2008) have successfully shown a link between denitrification and pyrite oxidation analysing $\delta^{18}O$ (NO_3), $\delta^{34}S$ (SO_4), $\delta^{18}O$ (SO_4) and $\delta^{18}O$ (H_2O) signatures.

While anaerobic denitrification represents the key process for nitrate depletion, dissimilatory nitrate reduction to ammonium (DNRA) is a further anaerobic reduction reaction that can be used by fermentative bacteria (Korom, 1992). DNRA occurs under similar conditions as denitrification but is less commonly observed. The partitioning between DNRA and denitrification is controlled by the availability of organic matter. Once ammonium or nitrite generated by DNRA is released back into an aerobic environment it will quickly be oxidised back to nitrate or taken up by vegetation. However, sorption and ion exchange of ammonium and nitrite (Davidson et al., 2003) is significant in many aquifer systems so that DNRA may lead to an apparent attenuation of nitrate. DNRA should, however, not be considered as a sink for nitrate nitrogen but may lead to elevated concentrations of nitrite in groundwater and surface waters.

4.3.2.3 *Nitrate attenuation in hydrogeological environments*

Unsaturated zone denitrification

Denitrification in the unsaturated zone of many aquifers is not commonly observed, as replenishment of oxygen provides for generally aerobic conditions. Where air exchange is limited by lithological heterogeneities or where electron donors (such as organic wastes) are in high abundance, denitrification may, however, occur locally. This is mainly associated with anaerobic 'micro-sites' within a generally aerobic environment (Lloyd et al., 1987). Denitrification mostly occurs in or near the soil zone, principally because it is the region with the highest concentrations of organic carbon (Brady and Weil, 2002). Availability of DOC may vary seasonally and is associated with greater fluxes in autumn from plant die-off. Warm, wet and organic-rich autumn soils provide an environment for rapid denitrification (Addiscott, 1996). Through the profile of the unsaturated zone, DOC concentrations tend to decrease downwards due to gradual mineralisation to carbon dioxide. Anaerobic micro-environments in typically aerobic unsaturated zones may be formed in pore spaces within clumps of finer-grained aggregates or in fine-grained sediments. In low-permeability environments, the denitrification process is facilitated by solute transport to these anaerobic micro-environments via macropores (Casey et al., 2004), whose frequency and size have been observed to decrease with depth (Jørgensen et al., 2004). An increase of first-order half-lives from the ground surface to 3.5 m depth from 7 to 35 days was observed beneath forest soils and from 1 to 7 h beneath agricultural soils (Jørgensen et al., 2004). The differing rates were associated with the different concentrations of water-soluble carbon and denitrifying bacteria in the two environments.

Saturated zone denitrification

While denitrification in the saturated zone of unconfined aquifers has been described locally (Roberts and McArthur, 1998), mainly associated with an excess abundance of DOC, the widespread aerobic conditions in unconfined aquifer systems do not favour denitrification. Confining layers of impermeable material limit the entry of oxygenated recharge and the diffusion of atmospheric oxygen to aquifers. A supply of nitrate and a suitable electron donor thus provides more favourable conditions for denitrification in such confined environments. A number of studies on regional aquifer systems have described a classic down-dip redox transition across the confined zone of the aquifer, as dissolved oxygen, then nitrate and sulphate are reduced, with this trend being generally associated with biologically mediated reactions with aquifer organic matter (Howard, 1985; Lawrence and Foster, 1985). The efficacy of the denitrification process within these aquifer systems may be affected by individual environmental factors as summarised in Section 3.3. In dual porosity systems, potential pore size exclusion of denitrifiers from the aquifer matrix and inhibition of biofilm formation along fracture conduits due to high flow velocities (Seiler and Vomberg, 2005) are particular aspects to be considered in the assessment of denitrifying potential. Roy et al. (2007) identify a clear seasonal link between nitrate concentrations, groundwater levels and effective rainfall, suggesting that rainfall-induced leaching and rises in capillary zone level partly control saturated zone nitrate concentrations. Figure 4.11

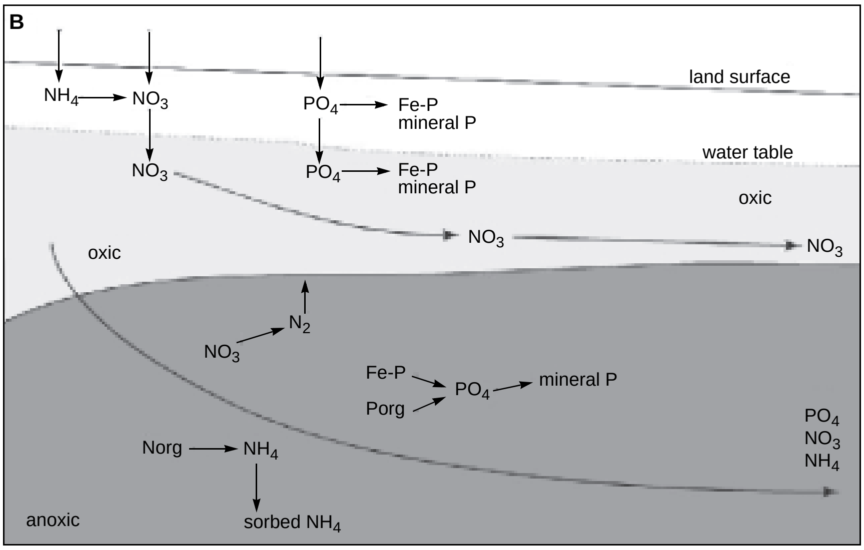

Figure 4.11. Schematic representation of the processes affecting nitrogen and phosphorus in oxic and anoxic aquifers (Slomp and Van Cappellen, 2004).

illustrates the processes affecting nitrogen and phosphorus in oxic and anoxic aquifers.

In their study of shallow groundwater environments, Varsanyi et al. (2005) observed organic matter to be the key electron donor for denitrification processes within sedimentary aquifers, while in basement aquifers pyrite served as the key electron donor. Tarits et al. (2006) highlighted the effect of autotrophic denitrification processes occurring in pyrite-bearing fractures on nitrate and sulphate concentrations in bedrock aquifers. Aquifer-scale autotrophic denitrification via pyrite oxidation was observed by Bottrell et al. (2001). Pauwels et al. (2000) described the zonation within a schist bedrock aquifer, with autotrophic denitrification considered to be the key process in the unweathered schist while heterotrophic processes may occur in the overlying weathered zone.

Aquitards

Typically, the concentration of suitable electron donors in aquitards exceeds that of adjacent aquifers and can provide significant protection to underlying aquifers if the physical conditions bring reactants and micro-organisms in contact (Robertson et al., 1996). Glacial tills for example may contain significant amounts of disseminated pyrite and organic carbon, which can act as electron donors for the denitrification process, providing local protection for underlying aquifers (Foster et al., 1985).

Groundwater–surface water interface

Riparian zones and wetlands may provide buffers to surface water bodies from non-point source pollutants such as nitrates. They are characterised by dynamic zones of horizontal and vertical heterogeneity, where reducing conditions and near-constantly saturated sediments, high in labile organic carbon, can facilitate denitrification (Cirmo and McDonnell, 1997).

Riparian zones, wetlands and hyporheic zones are strongly influenced by their position in the larger topographic and hydrogeological environment. Their position in the landscape will determine some of the inherent local conditions and affect nitrate levels by controlling surface and groundwater delivery, nutrient fluxes and local groundwater flows. The size of upland aquifers governs the amount of groundwater flow to the riparian zone and the magnitude of water table fluctuations. Large, deep aquifers up-gradient of the riparian zone can significantly decrease nitrate concentrations by dilution with older, nitrate-poor waters (Spruill and Galeone, 2000). Local hydrology can also play a distinct role, where drainage ditches can bypass the riparian zones and discharge nitrate-laden runoff or interflow directly into water bodies (Puckett, 2004).

The depositional environment of river alluvium is very variable, creating heterogeneous matrices of clay, silt and sand. These are associated with permeability contrasts, differing organic carbon contents, cracks and fissures, and varying surface topography. Both denitrification and carbon degradation require some residence time in an aquifer, which is influenced in part by sediment permeability. Geologically heterogeneous alluvial deposits therefore potentially act as both a conduit and barrier to groundwater flow. Permeable alluvial deposits favour slow subsurface flow, allowing for attenuation of nitrate under the right conditions, whereas low-permeability alluvium can deflect groundwater via a lower, more permeable aquifer or across the surface, limiting attenuation (Puckett, 2004). Heterogeneous alluvial deposits will contain a mixture of both high- and low-permeability sediments, and flow patterns within the deposit will be complex. At a small scale, flow patterns within the alluvial sediment may permit bypass (via preferential flow along gravel lenses) or concentration (via shallow aquitard horizons) of nitrate-rich groundwater (Fig. 4.12) through zones of greater denitrification potential.

The amount of organic carbon present in riparian zones is one of the key factors for making them effective zones for denitrification. Carbon stocks are replenished by seasonal natural leaf fall, plant die-off, root turnover and exudates. However, as for non-riparian soils and subsoils, the denitrification potential decreases with depth in riparian zone soils (Burt et al., 1999). Plant uptake may contribute significantly to nitrate attenuation but microbial denitrification is likely to be the dominant process (Hinkle et al., 2001). Riparian forests show higher biomass increases with

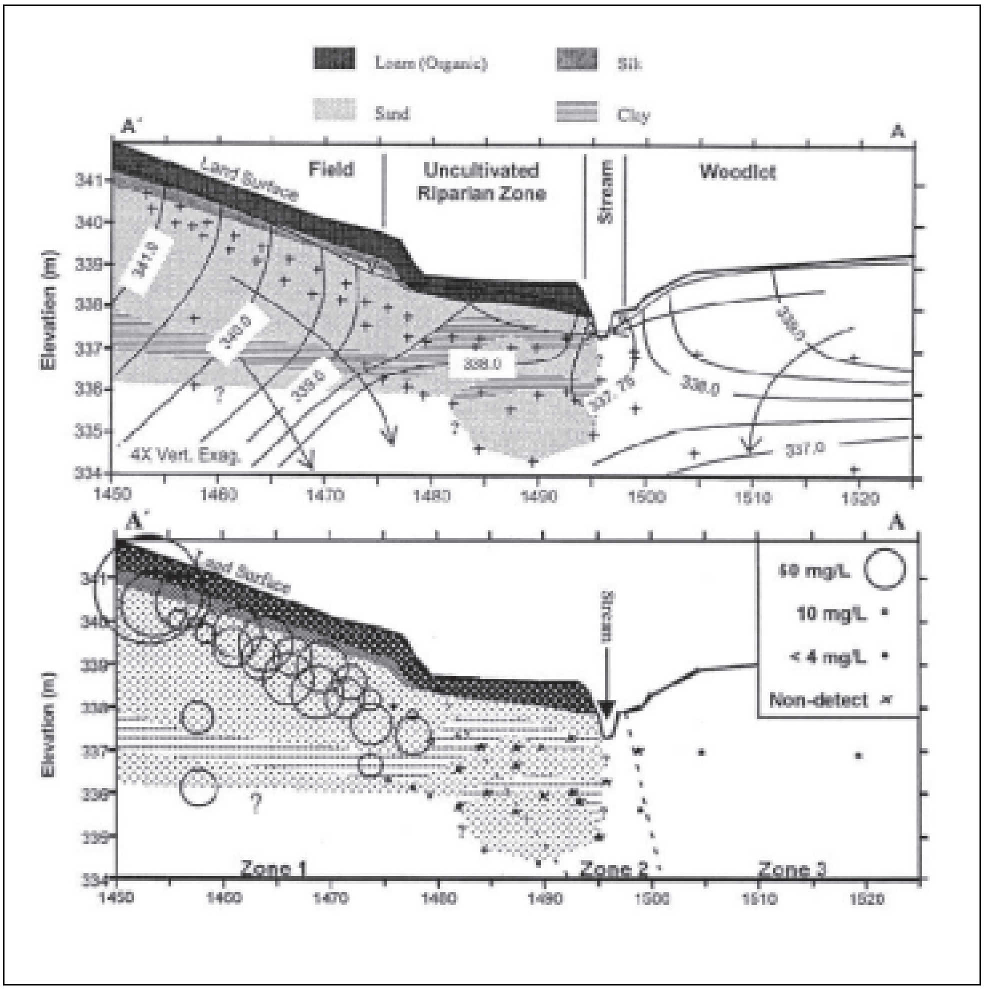

Figure 4.12. Cross section through a riparian zone (Cey et al., 1999); *upper section:* hydraulic head equipotentials (m) and indicative flow direction; *lower section:* groundwater nitrate concentrations (mg NO_3/l).

higher groundwater nitrate inputs. This effect diminishes though with increasing maturity of the forest and is thus most significant with younger forests (<30 years old) (Hill, 1996). Regardless of the seasonal fluctuations of the nitrate input to groundwater, riparian zones exhibit seasonal variations in nitrate attenuation due to water table fluctuations, varying inputs of nitrate and organic carbon and the plant growth cycle. Seasonal fluctuations in the water table elevation govern the anaerobic capacity of soils through which groundwater flows (Burt et al., 1999). Carbon inputs vary seasonally with the growth cycle of vegetation and the amount washed through by infiltration and flood waters. Root exudates are a significant source in the summer, whilst plant die-off and decomposition of leaf litter are highest in autumn. The elevation of the water table, and therefore the thickness of the unsaturated zone, also affects the amount of mineralisation of organic matter as it infiltrates. As a consequence, DOC levels tend to be higher in winter. Nitrate levels are also higher in winter since plant uptake is minimal and the high infiltration washes nitrates down to the groundwater (Burt et al., 1999). These factors indicate that denitrification activity in riparian wetlands is likely to be highest in the winter months.

The hyporheic zone is permanently saturated. The direction of transfer between groundwater and surface water is governed by local hydraulic gradients and stream bed topography. Heterogeneous stream bed sediments may lead to complex flow patterns and the patterns of discharge/recharge can be very complex at fine spatial scales (<10 m) and over the course of a hydrological event (Malcolm et al., 2002). Hyporheic exchange increases hydrologic residence times and the volume of water in contact with sediment biota, thus enhancing biological reactions. The interstitial water in the hyporheic zone is often enriched with nutrients relative to both surface and groundwater, including inorganic nitrogen, DOC and phosphorus (Sheibley et al., 2003). Carbon stocks in this zone are high with high DOC fluxes through the hyporheic zone and seasonally variable replenishment by stream-borne DOC (Chapman et al., 2005). Denitrification in the hyporheic zone still depends on anaerobic conditions. Hence, redox gradients still occur in the zone, albeit over short distances (Hinkle et al., 2001). In view of the above heterogeneity of this zone, denitrification may be localised, leading to discrete regions within a hyporheic zone in which nitrogen transformation occurs. In addition to the above factors leading to the heterogeneous nature of the hyporheic zone, geological conditions are also critical with regard to the potential for nitrate attenuation. Grimaldi and Chaplot (2000) found that while nitrates were depleted in a stream bounded by sandy peat on granite, no attenuation was observed where the stream was bounded by low-permeability loam overlying schists. It was concluded that the low permeability of the loam/schist hyporheic zone limited the input of stream water towards the denitrifying sites and the return of denitrified water towards the stream. Current research in the University of Sheffield, UK, is focusing on nitrate attenuation in the hyporheic zone with particular attention being paid to attenuation in alluvium and clay. Results from this project will be available by October 2010 (Nick Riess, University of Sheffield, personal communication, 2009).

Surface waters

Increased fluxes of nitrate in many streams and rivers can be related to changes in land use and agricultural practices (see Section 4.3.1) but these relations are complicated due to nitrogen transformations within the drainage network. A number of small-scale field and laboratory studies have indicated that nitrate in oxygenated surface waters can be reduced by benthic denitrification, in which bacteria reduce nitrate to nitrogen gas at or below the sediment–water interface (Seitzinger, 1988; Kemp and Dodds, 2002). Scholefield and Butler (2002) observed a distinct diurnal periodicity in nitrate concentrations, in particular under low flow conditions. Rather than to fluctuations of the source term, this periodicity was mainly attributed to effects of temperature on river hydrology and/or in-stream biology. Larger-scale regional models and statistical analyses have indicated that nitrogen loads in streams and rivers are reduced substantially by a variety of processes, amongst which benthic denitrification is thought to be a major component (Howarth et al., 1996; Seitzinger et al., 2002). However, accurate estimates of reach-scale nitrogen losses in streams and rivers are difficult to obtain. Böhlke et al. (2004) provide a reach-scale study employing ^{15}N-enriched nitrate as an in-stream tracer identifying denitrification processes along the reach. The study furthermore showed that despite increasing nitrate loading within the studied reach, denitrification was a substantial permanent sink for nitrogen leaving the agricultural watershed during low flow conditions.

Transitional/Coastal waters

Transitional and coastal waters are naturally nutrient-rich environments; however, large amounts of nitrate discharged from agricultural watersheds can enter nitrogen-sensitive estuaries and coastal marine waters and contribute to increased primary productivity, excessive deep-water oxygen demand and hypoxia (Goolsby et al., 2001; Rabalais et al., 2001). In both environments, the greatest impacts of increasing nutrient conditions have been at sites with restricted water exchange (Carvalho et al., 2002). The processes affecting nitrate fluxes in these environments are linked to nutrient loading of the water column and sediment-bound processes. In some estuaries, the attenuation of the nitrogen load seems significant (Seitzinger, 1988, 1990), while in others it appears to be small. Balls (1994) suggested that the degree of nitrate attenuation within an estuary may be related to the flushing time of the estuary. Ogilvie et al. (1997) studied a typical hypernutrified, turbid muddy estuary, draining fertile, artificially fertilised agricultural land to the North Sea. This study identified insignificant transformations of nitrogen in the water column and observed nitrification processes in the sandy sediments at the mouth of the estuary with nitrate export from the sediment. However, denitrification processes were observed in the muddy sediments higher up in the estuary providing significant sinks for nitrate. The study furthermore identified a seasonal cycle with maximum denitrification occurring during early winter, when nitrate in the water column was greatest and low temperatures favoured denitrification. Tobias et al. (2003) investigated the nitrogen cycling within an estuarine environment using ^{15}N-enriched nitrate tracers, showing that ^{15}N storage in sediments and marsh macrophytes accounted for 50–70% of the ^{15}N assimilated in the estuary which may sequester watershed-derived nitrogen in the estuary for timescales of months to years.

4.3.3 Studies in Ireland

4.3.3.1 Sources

The quality of Irish surface waters can be classified as relatively good by European Standards, with over 69% of Irish rivers classified as ‘unpolluted’ (Toner et al., 2005). Monitoring carried out by the EPA (Clabby et al., 2008), however, illustrates elevated levels of nitrate in surface waters in the south-east of Ireland in particular that are likely to be associated with a higher degree of agricultural land under tillage. Surface water monitoring as part of the Tellus Programme in Northern Ireland has shown that the highest nitrate concentrations were observed in areas of arable farming, with slightly lower concentrations being observed in areas of pastoral farming (Fig. 4.13).

Groundwater monitoring completed by the EPA (Clabby et al., 2008) reflects the observation of higher nitrogen loading in the environment in the south-east of Ireland, with a greater proportion of monitoring points showing elevated nitrate concentrations (Fig. 4.14) (Clabby et al., 2008). Groundwater monitoring completed in Northern Ireland (DoENI, 2009) showed that average nitrate concentrations (2000–2006) were less than 50 mg NO_3/l at approximately 95% of monitoring locations (Fig. 4.15). Elevated concentrations were similarly observed in areas of tillage farming and in proximity to point source waste discharges.

A detailed assessment of the trophic status of Irish coastal waters/estuaries (EPA, 2001) highlighted that a number of coastal areas were breaching the quantitative eutrophication criteria as outlined in the document, including dissolved inorganic nitrogen (DIN) concentrations. With regard to median DIN concentrations, the EPA (2001) document sets out eutrophication criteria of >2.6 mg/l N, >1.4 mg/l N and >0.25 mg/l N for tidal fresh waters, intermediate waters and full salinity waters, respectively. The main sources of nutrients to estuaries are river runoff, sewage discharges, atmospheric inputs and groundwater discharges (Maier et al., 2009). Given that the mean nitrate concentration in Ireland exceeds 5 mg/l in the majority of the EPA monitoring network (Fig. 4.14), groundwater discharge of nitrogen is likely to have a significant impact on Irish estuaries.

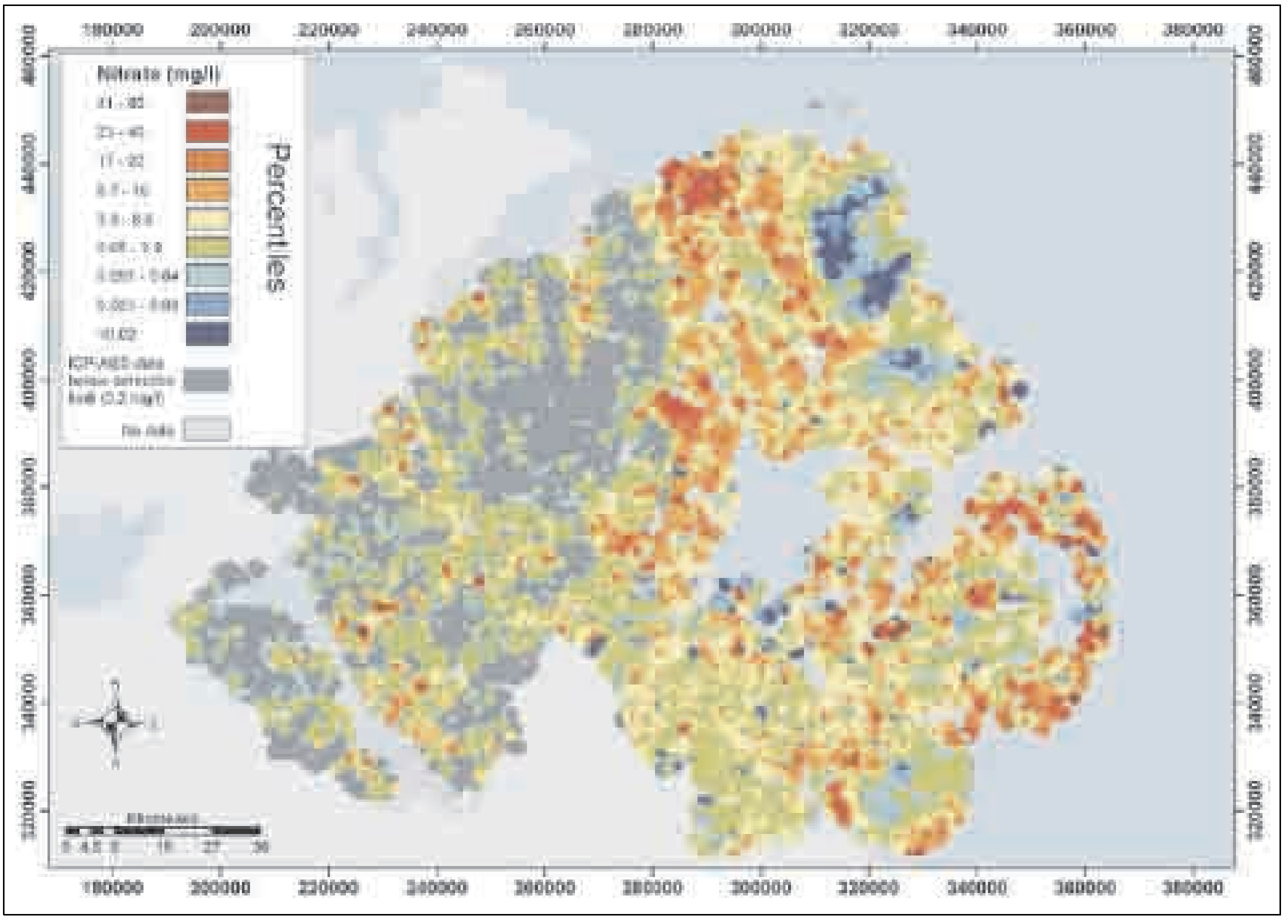

Figure 4.13. Map of nitrate concentrations in stream waters in Northern Ireland (Ander, 2007).

4.3.3.2 Agriculture

Agriculture is seen to contribute significantly to the eutrophication of Irish rivers and estuaries, with up to 82% of nitrogen loads attributed to agricultural sources (EPA, 2004).

A number of studies in Ireland have addressed agricultural practices and their effects on nitrate leaching and nitrate loading to surface and groundwater. Land-use patterns have been shown to be the main cause of regional differences in water quality. Ryan and Fanning (1999) found nitrate concentrations to be 60% higher in areas under tillage, compared with cut grass. Similar findings are reported by Thomsen and Christensen (1998). In tillage systems, the ploughing of soil stimulates mineralisation of soil organic matter, releasing nitrogen (Addiscott, 1996). Furthermore, during the winter months fallow land can continue to release nitrogen at a time of year when there is little plant uptake due to the absence of crops. Neill (1989) showed that mean nitrogen losses to rivers in the south-east was 76 kg N/ha/year for ploughed land, with a significantly lower value of 2 kg N/ha/year for unploughed land.

With regard to fertiliser application required to sustain animal grazing, dairy farming can be considered to be most likely associated with high rates of nitrate leaching due to high stocking densities and high fertiliser applications (Ryan, M. et al., 2006).

Richards et al. (2007) compared nitrate leaching from an intensive beef farm (210 kg/ha organic N) with a less-intensive beef farming practice under the Rural Environment Protection Scheme (REPS) (170 kg/ha organic N). Reduction of the stocking rate of grazing animals and fertiliser application has been shown to significantly reduce the amount of nitrate leaching (Richards et al., 2007).

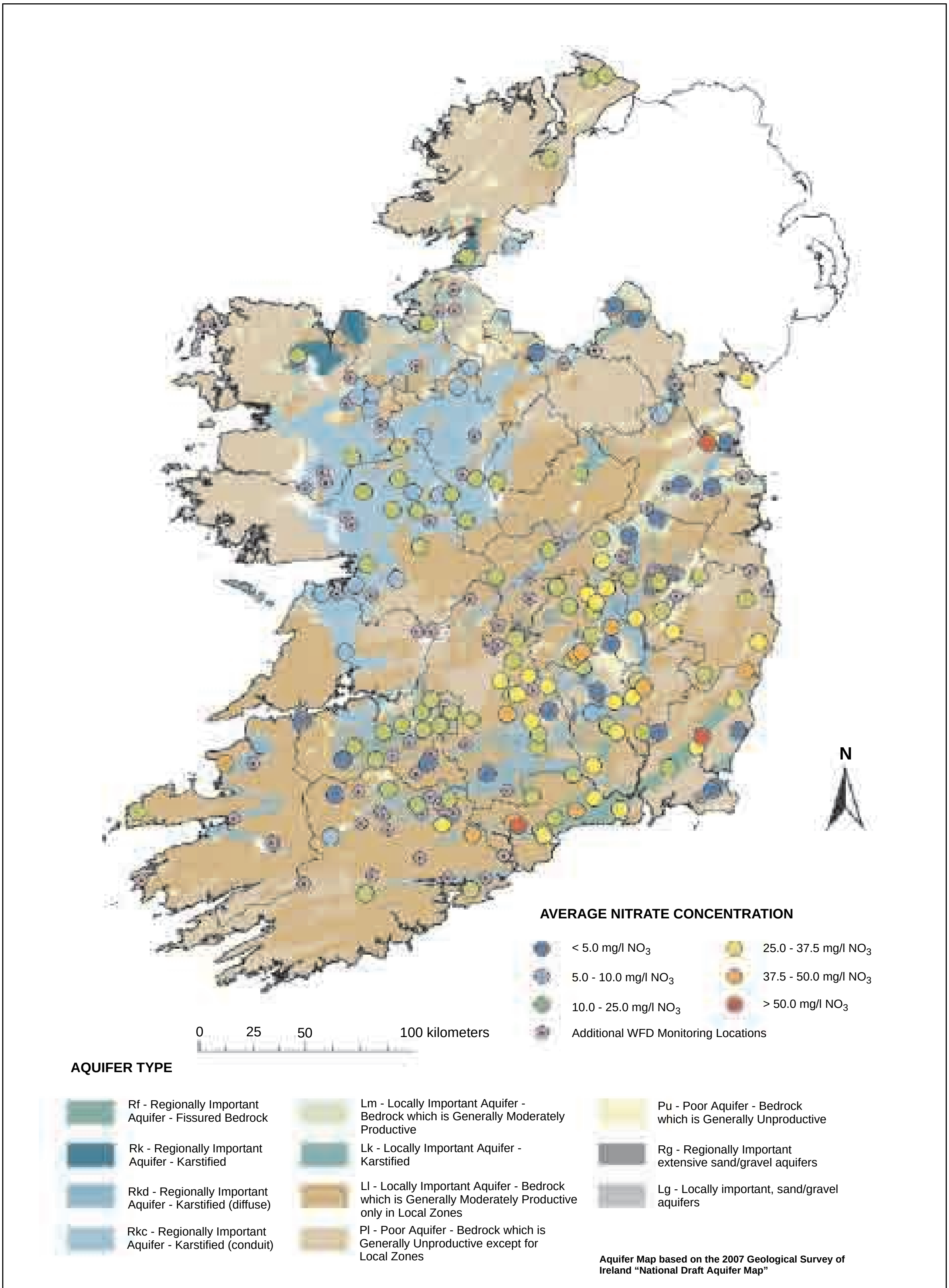

Figure 4.14. Mean nitrate concentrations in groundwater 2004–2006 (Clabby et al., 2008).

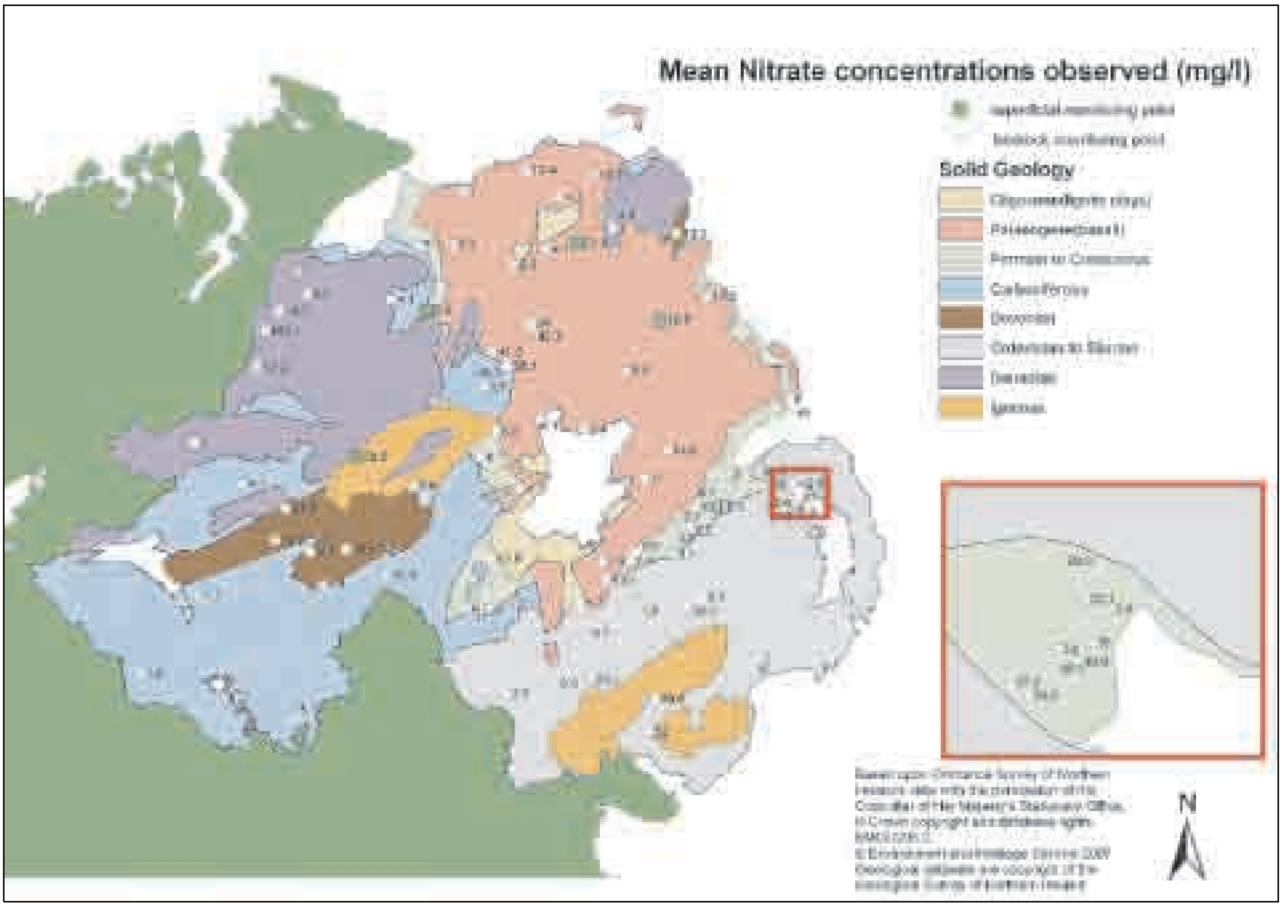

Figure 4.15. Map of the mean nitrate concentrations (EHS, 2006).

Over recent years, a number of individual studies have been completed in Ireland under the LS-2 Projects *Eutrophication from Agricultural Sources*, commissioned by the DoEHLG through the EPA under the National Development Plan 2000–2006. In particular, the studies completed under the programme section LS-2.3 *Effects of Agricultural Practices on Nitrate Leaching* provided a comprehensive assessment of factors affecting nitrate leaching in the context of agricultural practices.

The studies completed as part of the LS-2.3 project aimed to quantify nitrate leaching from an intensively managed dairy farm located on a soil type typical of nitrate-vulnerable zones in Ireland. Within this context, the individual studies (Bartley and Johnston, 2006; Gibbons et al., 2006; Ryan, M. et al., 2006) focused on nitrate leaching to soil pore water and groundwater, farm-scale nitrogen loading and field-scale effects of farming practices.

Bartley and Johnston (2006) identified variable responses in groundwater nitrate concentrations dependent on individual farm management areas, with highest concentrations observed beneath 'grazed dirty water irrigation' areas. The study furthermore identified a positive correlation between average nitrate concentration in groundwater and the number of plot grazing days. Gibbons et al. (2006) showed that nitrogen fertiliser applications of less than 300 kg/ha/year did not result in an exceedance of the 11.3 mg N/l threshold value in soil pore water. However, fertiliser applications in late September and excessive application in early spring resulted in the threshold value being exceeded, particularly when the application was followed by heavy rainfall. Furthermore the study showed that dirty water application during winter can result in an exceedance of the threshold value in soil pore water, while similar applications during the summer did not result in exceedances.

Across the individual studies, TN loads ranging from 465 kg/ha to 538 kg/ha were observed, with highest loadings associated with ‘grazed dirty water irrigation’ areas (up to 719 kg/ha). Between 54% and 60% of the total loading was associated with fertiliser nitrogen. Estimated annual nitrogen losses represented 7–11% of the inputs from applied fertiliser, slurry and dirty water over the 3-year study. These estimated losses were lower than previously reported Irish estimates of 13–14%.

In their study examining the environmental impacts of nitrogen and phosphorus use by the grassland-based agricultural industry in Northern Ireland, Watson and Foy (2001) investigated the losses associated with nitrogen inputs to grazed grasslands.

Schulte et al. (2006) present a comprehensive study evaluating regional, seasonal and temporal variations in the risk of nutrient loss from Irish agriculture to water in response to spatial and temporal patterns of the most important pressure (soil nutrient levels, land use, length of grass growing season and droughts) and pathway factors (soil drainage capacity, quantity and seasonality of net rainfall, rainfall intensity and number of trafficable days).

Hooker et al. (2008) investigated the effect of winter cover crops on nitrate leaching and showed that TN losses in the winter can be reduced by between 18 and 83% by the use of winter cover crops.

Watson et al. (2007b) studied the impact of grazed grassland management on TN accumulation in soils. They studied nitrogen balances and TN and carbon accumulation in soil with varying fertiliser nitrogen inputs on reseeded grazed grassland. Among the findings, they observed a redistribution of nitrogen within the soil profile affecting the development of longer-term nitrogen balances.

4.3.3.3 Forestry

With approximately 10% of its area, Ireland has a below-average forest cover compared with other EU countries (30%) (Machava et al., 2008), with Northern Ireland showing an even smaller level of forest coverage (6%) (Forestry Commission, 2002). Clear-felling is identified as the forestry activity that has the greatest potential to cause a release of nutrients (Campbell and Foy, 2008).

Similar to agricultural nitrate leaching, Ryan et al. (1998) observed an increase in soil inorganic nitrogen in Irish forest soils after drought.

Although primarily focusing on phosphorus loss from forestry operations in three study catchments, Machava et al. (2008) provide some limited data on mean nitrate concentrations for surface sampling points in the Crossmolina study catchment. These were generally very low, with mean concentrations ranging from 1.25 mg/l to 1.81 mg/l. Studies in the Lough Melvin catchment (Campbell and Foy, 2008) have similarly observed that while forested areas within the catchment were showing among the highest phosphorus export rates in the catchment, at the same time they showed some of the lowest nitrate export rates. Furthermore, Campbell and Foy (2008) observed that on the whole nutrient exports from forestry were lower than those recorded from agricultural land. Cummins and Farrell (2003b) observed an increase in ammonium nitrogen and some increases in nitrate in forest drains following clear-felling during a 5-year study in blanket peatland forests in western Ireland.

The ongoing HYDROFOR project financed under the current EPA STRIVE 2007–2013 Programme is investigating the impact from forestry operations on the ecological quality of water in a number of study catchments over the coming years.

4.3.3.4 Other sources

In Ireland, over one-third of the population’s domestic wastewater is treated by on-site systems such as septic tanks. Northern Ireland shows a lower percentage of the population being served by on-site systems more in line with the UK average of 5% (Wakida and Lerner, 2004) (see Chapter 5.2 for further details).

Gill et al. (2008) monitored the performance of six separate septic tank percolation areas to assess the attenuation effects of the respective subsoils with regard to OWTSs. With regard to the potential nitrogen loading to groundwater, significant differences were observed across the sites. The average nitrogen loading after 1.0 m depth of unsaturated soil ranged from 3.2 to 5.5 g TN/day/capita for those sites receiving secondary-treated effluent and from 0.3 to 4.2 g TN/day/capita for the sites receiving raw septic tank effluent. In a separate study, Gill et al. (2007) investigated the attenuation effects of Irish subsoils at four percolation areas treating domestic wastewaters.

Foy and Girvan (2004) highlight that a former Irish Fertiliser Industry (IFI) facility has been a major historical source for nitrogen loading to the River Lagan. Similarly, the DuPont facility in Maydown, County Derry, has historically been the largest single source of nitrogen input into the River Foyle (Foy and Girvan, 2004). However, the nitrogen input from the facility has significantly decreased since 1993 by 93% (Foy and Girvan, 2004).

Foy and Rosell (1991) investigated the fractionation of nitrogen loadings from a Northern Ireland fish farm. The study identified the fractions of the TN loading to be: 62.1% ammonium nitrogen, 26.6% soluble organic nitrogen, 8.9% particulate organic nitrogen and 2.4% nitrite + nitrate nitrogen. The study furthermore observed an increase of the soluble organic nitrogen proportion in the effluent with temperature within the temperature measuring range (4–22°C).

Bashir et al. (2008) present a comprehensive study of background air quality and the ionic composition of precipitation as sampled at Valentia Observatory, including trends in atmospheric nitrate deposition. Abdalmogith et al. (2006) provide additional data on particulate nitrate concentrations in Belfast.

4.3.3.5 Controls on mobility/pathways

The LS-2.3 studies (Carton et al., 2006) highlighted that winter precipitation and subsequent groundwater recharge is a major driver of nitrate concentrations in vulnerable receiving waters. Recharge velocities estimated for the free-draining sandy loam soil/subsoil at the study site yielded a range from 1 mm/day to 7 mm/day for summer and winter seasons, respectively. The study furthermore concluded that additional hydrological loading, such as from dirty water irrigation during winter, can increase the potential for nitrate impact on groundwater. It was estimated that an additional irrigation of 25 mm can increase the recharge rate by 8%. Tracer studies completed at the study site (Bartley and Johnston, 2006) indicated that secondary preferential pathways existed at the site in addition to soil matrix flow. However, the findings of Gibbons et al. (2006) did not necessarily support these observations.

Numerous studies have observed a link between drought and increased nitrate leaching. Tyson et al. (1997) and Richards (1999) found a strong linear increase of nitrate levels in groundwater with increasing SMD during the previous summer months. This was associated with diminished grass growth and, hence, limited nitrogen uptake by grass. Unused fertiliser could thus be accumulated in the soil and then leached through subsequent soil re-wetting.

Schulte et al. (2006) highlight that the risk of nitrogen loss to water is greater in well-drained soils. Their study showed that nitrogen losses to water are pronounced in southern and eastern areas of Ireland, as large parts of this region are characterised by well-drained soils facilitating nitrate leaching. Furthermore, net annual precipitation in these regions tends to be sufficient to ensure full soil recharge each winter and thus provide a pathway for nitrogen transport below the rooting zone. At the same time an approximate net precipitation of 300 mm in this region provides only limited dilution of nitrate concentrations.

In their study of quantities of mineral nitrogen in soil and concentrations of nitrate in groundwater at four grassland-based systems of dairy production, Humphreys et al. (2008) found that low losses of nitrate to groundwater were primarily attributed to high rates of denitrification associated with a heavy soil texture, wet anaerobic soil conditions, relatively high organic carbon contents throughout the soil profile and mild soil temperatures throughout the year. The study furthermore found that nitrogen uptake by herbage over the winter made an important contribution to low nitrogen losses.

The impact of cattle on nutrient concentrations in overland flow and soil hydrology (bulk density, macroporosity and resistance to penetration) was investigated by Kurz et al. (2006).

Donohue et al. (2005) studied the importance of spatial and temporal patterns with regard to the risk assessment of diffuse nutrient losses to surface waters. In a study area of the Lough Mask Catchment, the authors found the nutrient–streamflow relationship to vary seasonally for both phosphorus and nitrogen.

As part of the LS-2.3 project, the NCYCLE_IRL model, based on the empirical mass balance NCYCLE model, was developed to assess the impact of soil type, cutting and grazing management, dairy or beef enterprise and fertiliser nitrogen inputs and nitrate leaching at a farm scale (DelPrado et al., 2006).

Within the scope of a study investigating six predominantly grassland catchments, Watson et al. (2000) assessed the loss of organic nitrogen in land drainage. Field observations and nitrogen balances suggested that a large proportion of the organic nitrogen in river water was originating from land drainage.

Wang and Yang (2008) present an improved GIS-based D-DRASTIC approach for groundwater risk assessment from diffuse agricultural sources. For the Upper Bann case study area in Northern Ireland, the authors identify 5% and 11% of the case study area to be at 'very high' or 'high' risk, respectively, with regard to groundwater nitrate risk.

Helliwell et al. (2007) investigated the role of catchment characteristics in determining surface water nitrogen in upland catchments, including the Mourne Mountains in Northern Ireland. The study highlighted that those catchments dominated by mineral soils (in contrast to peaty-soil-dominated upland catchments) are potentially more susceptible to nitrate leaching, linked to the smaller carbon pool within these catchments.

Minet (2007) illustrated the application of stable isotope techniques ($\delta^{15}N/\delta^{18}O$) as a tool to investigate nitrate sources in Irish groundwater. Jones et al. (2004) investigated the nitrogen stable isotope composition in upland lakes in Northern Ireland with differing nutrient status, suggesting that $\delta^{15}N$ could be developed as a simple integrating measure of the degree of nitrogen limitation in lakes.

4.3.4 Data availability

Both the Irish EPA and the Northern Ireland Environment Agency hold comprehensive monitoring data sets with regard to surface water and groundwater quality. For Northern Ireland, the Tellus Project provides additional analytical data for stream sediment and water sampled at an average of one site per 2 km^2. While a large number of previous studies have focused their investigations on nitrate leaching and nitrate loadings associated with individual sources and subsurface on a farm or field/site scale, respectively (see Sections 4.1–4.2), several previous investigation programmes into nutrient loss to waters have studied and instrumented a number of study catchments. Although a large number of these studies may not have had nitrogen as a focus of their research and hence only limited historic data may be available with regard to nitrogen species for these catchments, available hydrological/hydrogeological and meteorological data, as well as information with regard to subsurface characterisation, could support more nitrogen-focused studies within these 'established' catchments (see also Table 4.4). Such study catchments include those listed in Table 4.9.

Details of a number of relevant UK catchment studies and nutrient management (including nitrate) projects are available through the online UK Agricultural Diffuse Aquatic Pollution Toolkit (UK ADAPT).

Details and references for catchment studies at varying scales across Europe, as well as approaches

Table 4.9. Established research catchments which may support further detailed nitrogen-focused studies.

Study catchment	Project
Oona	EPA LS-2 Project
Dripsey	EPA LS-2 Project
Clarianna	EPA LS-2 Project
Lough Melvin	INTERREG IIIa Project
Ballinagee	EPA PEnrich Project
Crossmolina	EPA PEnrich Project
Ardvarney	EPA PEnrich Project
Lough Sheelin	Shannon Regional Fisheries Board

to source apportionment with regard to nutrient losses to the aquatic environment, are summarised in EEA (2005).

As part of the ongoing EPA/COFORD HYDROFOR Project and the Teagasc Agricultural Catchment Programme, which will investigate nutrient loss from farming activities with particular focus on Sources–Mobilisation–Pathways–Transfer–Impact linkages, a number of study catchments will be investigated over the coming years. Furthermore, catchment instrumentation installed by the EPA/QUB and contributing to the QUB Griffith Geoscience Project into Poorly Productive Aquifers across Ireland will provide for a number of potential sites suitable for more detailed investigations of nitrogen loss and associated subsurface processes/impacts on aquatic receptors on a small- to medium-sized catchment scale. Close collaboration with these parallel programmes will help to maximise research efficiency and avoid duplication of research effort.

4.3.5 Knowledge gaps

There is a sound understanding of the processes controlling nitrate attenuation in the unsaturated soil zone. However, in groundwater, the geochemical conditions that determine whether denitrification will take place are not well established beyond a broad appreciation that denitrification is unlikely to be significant under well-oxygenated conditions. Similarly, little is understood about the groundwater conditions that control the rate and extent of denitrification.

As denitrification provides the primary attenuation process for nitrate the following knowledge gaps may warrant further research effort:

- Distribution of DOC in confined and unconfined aquifers and its bioavailability;
- Occurrence of denitrification across the fracture/ weathered matrix/matrix sub-zones;
- Assess whether small-scale studies of denitrification in fracture networks can be scaled up to regional aquifer/catchment scale;
- Influence of pore size (incl. pore size exclusion and bioavailability of porous matrix organic carbon);
- Application of stable isotope techniques (including $^{15}N(N0_3)$, $^{18}O(NO_3)$, $^{18}O(H_2O)$, $^{2}H(H_2O)$, $^{34}S(SO_4)$, $^{18}O(SO_4)$) to identify and quantify denitrification processes; and
- Nitrate attenuation potential in riparian/hyporheic zones with regard to typical Irish subsoils.

4.3.6 Recommendations

4.3.6.1 Recommendations for the Pathways Project

- Application of stable isotope techniques to identify and to quantify denitrification processes along relevant pathways; and
- Investigation of the attenuation potential in riparian/hyporheic zones with regard to typical Irish subsoils and catchment settings.

4.3.6.2 Recommendations for future research

- Distribution of DOC in confined and unconfined aquifers and its bioavailability as part of assessing key processes driving denitrification;
- Occurrence of denitrification across the fracture/ weathered matrix/matrix sub-zones to evaluate denitrification zones within fractured bedrock aquifers;
- Assessment of whether small-scale studies of denitrification in fracture networks can be scaled up to regional aquifer/catchment scale; and
- Influence of pore size (including pore size exclusion and bioavailability of porous matrix organic carbon) on the efficacy of denitrification processes.

4.4 Summary

Table 4.10 gives an overview of the knowledge and data gaps in relation to both nitrogen and phosphorus in order to provide focus for fieldwork investigation.

Table 4.10. Summary of availability of data and knowledge.

Sufficient literature/data available on:		Phosphorus	Nitrogen
Source – application in Ireland		✓	✓
Irish land use and variations		o	✓
Irish groundwater monitoring data		o	✓
Irish surface water monitoring data		✓	✓
Irish monitoring methodologies		✓	✓
Irish analytical methodologies		✓	o
Scale		x	o
Mobility	Ireland	✓	✓
	UK	✓	✓
	Europe	✓	✓
	International	✓	✓
Attenuation	Ireland	x	o
	UK	o	o
	Europe	o	o
	International	o	o
Pathways	Ireland	o	✓
	UK	✓	✓
	Europe	✓	✓
	International	✓	✓
Contaminant transport models	Ireland	o	o
	UK	✓	o
	Europe	✓	o
	International	✓	o
Ongoing research	Ireland	✓	✓
	UK	✓	✓
	Europe	✓	✓
	International	✓	✓
Catchment management tool	Ireland	x	o
	UK	o	✓
	Europe	o	✓
	International	o	✓

✓ Sufficient data to populate catchment management tool.
o Some data available to populate catchment management tool.
x Insufficient data available to populate catchment management tool.

5 Sources of Pathogens, Pesticides and Sediment

5.1 Introduction

In Ireland, past research has predominantly focused on the impact of nutrients on water quality and aquatic biota. In this chapter, pathogens, pesticides and sediments are considered as additional potential contaminants of concern and their source, fate and transport mechanisms in the hydrological cycle are considered. As in Chapter 4, Chapter 5 aims to highlight relevant completed and current/ongoing research that has been undertaken related to hydrological pathways and attenuation processes. Particular emphasis is placed on the current knowledge and data gaps. Given that research on pathogens, pesticides and sediment is limited in Ireland, serious consideration is given to assessing whether there are sufficient data available to effectively model each contaminant within the CMT. Recommendations for further research are presented, both within and beyond the scope of the Pathways Project.

5.2 Pathogens

One of the objectives of the WFD is "*to provide for sufficient supply of good quality surface water and groundwater as a need for sustainable balanced and equitable water use*" (WFD Ireland, 2006). Although the Directive does not explicitly identify pathogenic (disease-causing) micro-organisms as contaminants of concern, the WFD's requirement for the incorporation with existing standards and objectives indirectly implicates microbiological standards in groundwater and surface water in protected areas through the EU Drinking Water (No. 2) Regulations, 2007, the EU Bathing Water Directive for surface waters used for recreational purposes, and food standards relating to shellfish. These directives aim to protect public health from chemical and microbiological pollutants. EPA drinking water quality and bathing water quality reports for 2008 reveal that microbiological contaminants pose the greatest risk to human health in both categories, with all freshwater bathing water quality exceedances having poor microbiological quality (EPA, 2009; Page et al., 2009). Similarly, almost all issues related to drinking water safety are related to poor microbiological quality that may impact public health. Coffey et al. (2007) summarised the incidences of water-borne illness in Ireland from 1998 to 2005, during which the number of identified water-borne disease outbreaks rose from 10 to 22; all aetiological (disease-causing) agents were identified as micro-organisms. The authors noted that the incidences of disease were suspected to grossly underestimate the true extent of pathogen contamination in Irish fresh waters. This suggestion is supported by the EPA report for drinking water quality in Ireland for 2007–2008, which notes that almost all water supplies (public and private) that failed to meet water quality standards did so because of their microbiological quality (Page et al., 2009). This issue may be addressed by further levels of water treatment. However, this approach runs contrary to Article 7.3 of the WFD which requires Member States to aim to reduce purification treatment (European Commission, 2006). To tackle this issue the EPA recommends following the World Health Organisation (WHO) risk assessment protocol, which includes the identification of all risks to water quality in a catchment as a means of reducing levels of pathogens in water supplies. Such assessment and associated management of the risk of waters becoming contaminated by pathogens require an understanding of the impacts of the various sources of pathogenic micro-organisms in the environment and the controls on their attenuation along pathways connecting sources with receptors (EPA, 2008).

5.2.1 Pathogenic micro-organisms in the environment

Micro-organisms (bacteria, protozoa, and viruses) occur widely in the natural environment. Most pose no threat to human health and may perform vital functions necessary to maintain healthy ecosystems. However, a subset displays potential to impact human health – pathogens. These may occur naturally in the wider environment or, more commonly, they may be introduced into the hydrological cycle in microbiologically contaminated water, either deliberately or unintentionally, as a consequence of human activity. Diseases and illness caused by the ingestion of contaminated water, which serves as a passive carrier for infectious agents, are known as water-borne diseases (Maier et al., 1999). As the outbreak of cryptosporidiosis in Galway in 2007 demonstrated, water-borne disease resulting from contamination with pathogenic micro-organisms has considerable potential to impact Irish public health (see EPA, 2008). Pathogenic micro-organisms identified by Coffey et al. (2007) as disease-causing agents in Ireland fall into the following three categories:

1. **Bacteria:** Unicellular prokaryotic micro-organisms. Most bacteria are of 0.5–1.0 µm in diameter, and 1–2 µm in length (Maier et al., 1999). Pathogenic bacteria identified as relevant in the Irish context include *Escherichia coli* O157:H7, *Campylobacter* and *Salmonella* species.

2. **Protozoa:** Unicellular eukaryotic organisms. Pathogenic protozoa include the parasites *Giardia lamblia* and *Cryptosporidium* spp. (Crypto), both of which are capable of forming cysts that permit them to survive stressful conditions, including water treatment, better than bacteria. Crypto cysts have dimensions of between 1 and 10 µm, with *Giardia* cysts being 7–15 µm (ICAIR, 1984). Incidences of *Giardia* contamination related to water-borne disease have yet to be conclusively demonstrated in Ireland. In contrast, Crypto occurrence in Irish water supplies has been responsible for a number of water-borne disease outbreaks, where the source of contamination has been attributed to diffuse agricultural pollution.

3. **Viruses:** Obligate intracellular parasites. Pathogenic viruses of relevance to the Irish context include Rotavirus and Norovirus. Although the largest viruses have sizes comparable to the smallest bacteria, in general they are significantly smaller (tens of nanometres). This has led to speculation about their greater mobility in the subsurface (Robertson and Edberg, 1997). The species-specific nature of many pathogenic viruses suggests that the principal threat to human health derives from enteric viruses from human sources (sewage), rather than from livestock and/or wildlife.

The survival of enteric micro-organisms (micro-organisms hosted in the gut of warm-blooded animals), once voided from host organisms, can be a crucial factor in determining their impact. Prolonged survival will not only determine persistence at source, but also in aquatic receptors (surface water and groundwater). Generally, conditions are unfavourable to enteric micro-organism survival outside the host organism and micro-organism levels decrease with time. Nonetheless, John and Rose (2005) noted that inactivation rates (rates at which pathogens lose their ability to cause infection) have proved highly variable and the influences on inactivation rates are difficult to define. These recently published data have suggested that guideline times of 30–90 days for the elimination of pathogens from water supplies may underestimate their persistence in the wider environment. Smith and Perdek (2004) present data indicating that pathogenic bacteria may survive for up to 1 year in soil. This is in line with findings of ongoing research in Irish soils (Fiona Brennan, Teagasc, personal communication, 2009). The results have significant implications for the protection of those water supplies where inadequate levels of treatment currently exist, such as private supplies and group schemes, as identified by the 2007–2008 EPA drinking water report (Page et al., 2009); these may require significant increases in the size of well-head protection zones surrounding groundwater sources if appropriate treatment measures cannot be undertaken following abstraction (van der Wielen et al., 2006). In other words, if the time taken for pathogens to die off is longer than the time taken to reach a receptor, the receptor may be at risk of microbiological contamination.

5.2.2 Monitoring

Water quality monitoring, carried out by collecting water samples at defined locations at regular intervals, provides an important means of evaluating the impact of pathogens on water quality and, by inference, the extent of contamination. Difficulties associated with analysis and detection of pathogens have led to the development of an analytical protocol to investigate for the presence of other micro-organisms indicative of contamination by pathogens. These faecal indicator organisms (FIOs) should provide a conservative indicator of the presence of pathogens in a sample. In other words, pathogens may not be present where indicator micro-organisms have been detected. However, their absence should indicate the absence of pathogens (Pachepsky et al., 2006). Table 5.1 summarises the principal ideal criteria for indicator micro-organisms:

Widely used indicators of bacterial contamination (in order of preference) of water supplies employed across the EU include:

- Total viable counts (TVCs) at 22°C and 37°C as indicators of total numbers of bacteria in a sample. Under the EPA's Drinking Water Quality Monitoring Policy, significant increases in TVCs require further investigation/more frequent monitoring.

- Faecal coliforms as indicators of faecal contamination. This suite of micro-organisms includes *E. coli*; these organisms are widely accepted as strong indicators of bacterial contamination.

- Faecal streptococci are taken as a secondary indicator of faecal contamination. If faecal streptococci are detected in conjunction with coliforms, the coliforms are regarded as faecal in origin.

- *Clostridium perfringens* is an indicator of faecal contamination, which, if detected in the absence of the above two indicators, may be regarded as an indicator of intermittent contamination.

Levels of the above indicators vary by host species, as illustrated in Table 5.2.

The use of indicator micro-organisms in water quality monitoring in Ireland has focused on bacterial indicators. A pitfall of this approach, which has become increasingly apparent in recent years, has been the limited ability of the method to indicate the presence of other micro-organism types that may persist for longer in the environment, notably viruses and cyst-forming protozoa. Limited work exists on the occurrence of

Table 5.1. Criteria for an ideal indicator micro-organism (adapted from Maier et al., 1999).

- The organism should be useful for all types of water
- The organism should be present wherever enteric pathogens are present
- The organism should have a reasonably longer survival time than the hardiest enteric pathogens
- The organism should not grow in water
- The testing method should be easy to perform
- The density of the indicator should have the same direct relationship to the degree of faecal pollution
- The organism should be a member of the intestinal microflora of warm-blooded animals.

Table 5.2. Average concentrations of indicator micro-organisms per gram of animal faeces (after Geldreich, 1978).

Species	Faecal coliforms	Faecal streptococci	*Clostridium perfringens*
Humans – raw sewage	13,000,000	3,000,000	1,580
Cow	230,000	1,300,000	200
Pig	3,300,000	84,000,000	3,980
Sheep	16,000,000	38,000,000	199,000
Horse	12,600	6,300,000	<1
Chicken	1,300,000	3,400,000	250

either micro-organism type in Ireland. These studies have largely been localised focused investigations rather than longer-term monitoring programmes. The EPA monitors drinking water for the cyst-forming *C. perfringens* as an indicator of the possible presence of Crypto contamination. However, recent findings suggest that the relationship between the occurrences of both micro-organisms is inconclusive and that monitoring should be abandoned, leaving turbidity as the principal surrogate indicative of Crypto contamination in surface waters. In other words, the pathways capable of transporting sediment are assumed to be the principal routes for Crypto dissemination. The occurrence and transmission of Crypto in groundwater have received scant attention in the scientific literature, although at least one case of Crypto-contaminated groundwater discharging from a spring has been acknowledged in Ireland. Nonetheless, Crypto is not routinely monitored in EPA countrywide water quality monitoring. Despite these shortcomings, existing water quality monitoring data sets provide a means of assessing the extent of microbiological contamination in RBDs and of indicating potential sources of contamination. Groundwater monitoring data have already shed considerable light on pathogen occurrence in Irish aquifers by investigating relationships between contaminant detection, geological setting and meteorological conditions at the time of sampling (see Section 5.2.4). A similar approach may be applied to surface water quality monitoring. In both cases, if chemical, physical and biological monitoring can be reconciled with source data they can provide an insight into pathogen transport and attenuation processes.

5.2.3 Environmental water-borne pathogens in the Irish context – sources

5.2.3.1 Naturally occurring pathogens – soil and wildlife

Some pathogenic species occur naturally in the environment; these may be present in a soil's microbiological flora, e.g. *Clostridium botulinum* and *Lysteria monocytogenes* (Bultman et al., 2005), or in surface water (Rusin et al., 1997). Many species such as *Legionella* are widespread and capable of causing severe infection, or even death, at sufficiently high concentrations. As a corollary to this, wildlife, including wildfowl, is capable of contributing large concentrations of enteric micro-organisms to surface water (Jones et al., 2002). Similarly, incidences of pathogens such as Crypto in rodents may pose a threat to human health (e.g. Harter et al., 2000). Thus, the occurrence of pathogens is not restricted to environments impacted by human activity. At the catchment scale, Ferguson et al. (2009) identified wildlife as a significant contributor to background coliform levels. However, in the Irish context, an overview of water-borne disease outbreaks completed by Coffey et al. (2007) failed to identify wildlife sources as disease-causing micro-organisms.

5.2.3.2 Rural contamination – point sources

Intensification of agriculture in Europe and North America during the post-war period has led to greater contamination of rural water supplies in many areas. In areas where livestock rearing is the principal economic activity, microbiologically contaminated wastes still account for the main source of water contamination (Hooda et al., 2000).

Point sources of pathogen contamination are a consistent feature of livestock-rearing activities. In traditional agricultural practice, some species have been specifically retained in confined areas or close to farmyards permanently, e.g. pigs and poultry. Others have been housed for more limited periods on a daily to annual basis. For example, dairy cattle may be left out to pasture but must be brought to milking parlours regularly. Furthermore, depending on meteorological conditions, cattle may need to be housed indoors during winter periods (Kiely, 1998). Edwards et al. (2008) have demonstrated the considerable potential of these areas and associated farmyards to impact the microbiological quality of water during both wet and dry periods. High concentrations of animals can generate large volumes of pathogen-bearing waste. These sources have considerable pollution potential yet must be disposed of.

Table 5.3 provides an indication of the amounts of wastes generated by each category of livestock. Wastes generated by agricultural point sources, such as intensive animal-rearing units, are often stored prior to disposal. Tymczyna et al. (2000) highlighted the potential of animal waste storage units to cause

Table 5.3. Typical masses of waste generated by livestock (source: Ferguson et al., 2009).

Animal	Country	Manure (kg/day/animal)
Cattle (Dairy)	United States	55
Cattle (Dairy)	Canada	50
Cattle (Beef)	United States	21
Cattle (Beef)	Canada	23
Calves	United States	5.6
Calves	Canada	5
Sheep	United States	1.1
Sheep	Australia	1
Pigs	United States	5.1
Pigs	Canada	5
Poultry	Netherlands	0.088
Poultry	Canada	0.11

contamination. However, pathogen and FIO levels are often significantly lower in solid stored manure than in its fresh equivalent. Elevated temperatures associated with traditional storage methods using solid manure stockpiles can inactivate a considerable proportion of pathogens in relatively short periods (Nicholson et al., 2005). On the other hand, more recent practices of storing manure in liquid form prior to land application significantly reduce inactivation rates (Unc and Goss, 2004). In a related vein, Krapac et al. (2002) have demonstrated the potential for unlined storage pits to contaminate groundwater, particularly where they may bypass shallower soil layers of the unsaturated zone, which could otherwise further attenuate waste, thus enhancing the possibility of pathogenic contaminants entering groundwater (Armstrong et al., 2004). Furthermore, features such as improperly abandoned wells may effectively provide a fast route for contaminants at the ground surface to reach the water table (Simpson, 2004), while poorly constructed operational wells may also act as conduits that permit pathogens to enter groundwater. Indeed, in this case, pathogens may be able to reach groundwater with little or no interaction with potentially attenuating soils. Wright (1999) estimates that there are over 200,000 wells in Ireland in various states of repair. These are mainly located in rural areas and provide considerable potential to inadvertently cause groundwater contamination (Misstear and Hynds, 2007).

5.2.3.3 Sewage – non-reticulated supplies

Human faecal waste must be disposed of to the environment. In rural Ireland, this is typically achieved by unsewered systems that are intended to store and inactivate micro-organisms, before effluent discharges to groundwater. ESBI (2008) estimates that there are over 400,000 unsewered systems in Ireland, the vast majority of which are septic systems. This study indicated that significant numbers of these systems are located in unsuitable areas and/or is not appropriately maintained.

Although extensive information exists concerning incidences of contamination by on-site sewage treatment facilities, information on source concentrations of pathogens and indicator micro-organisms discharging from septic tanks, and investigations into the degree of attenuation experienced by them, is more limited. Like livestock wastes, protozoan and bacterial pathogens have been noted in human sewage. Hagerdorn et al. (1978) have shown that total coliform levels in septic tank effluent may reach 10^8 cfu/100 ml. Similarly, Gaut et al. (2008) noted that the presence of septic tanks near groundwater supplies elevated the risk of groundwater contamination by Crypto. Despite findings concerning septic-tank-derived bacteria and protozoa impacting groundwater, Ferguson et al. (2003a) claim that viruses pose the greatest microbiological threat to groundwater quality. Furthermore, in contrast to livestock, where species barriers may prevent viruses derived from one animal from infecting another, human-derived viruses can pose a threat to public health, even at very low levels. Indeed, Yates and Yates (1988) reported that the majority of groundwater health complaints in the United States could be linked to septic tank effluent. No comparable systematic investigation has been carried out in Ireland. Consequently, impacts in the Irish context are largely underdetermined due in part to under-reporting of water-borne disease outbreaks (Coffey et al., 2007). In the wider context, preliminary studies on levels by Breathnach (undated) in samples of Irish groundwaters from karst sources failed to detect viruses. However, high levels of contaminant variability in the microbiological and chemical quality of karst groundwater have been reported by Thorn and Coxon (1992). The lack of targeted analyses completed to date, coupled with the widespread distribution of (domestic sewage) hazards and potentially rapid pathways for contaminant delivery, suggests that enteric virus impacts to groundwater and surface water quality are extensive across Ireland, yet remain largely undetected.

5.2.3.4 Rural contamination – diffuse sources

In a review of pathogen transfer from grasslands to receiving waters, Oliver et al. (2005) note that losses from manure deposited by livestock constitute the principal source of both FIOs and pathogens. This has been corroborated by other studies by Vinten et al. (2004) and Ferguson et al. (2003a). Crowther et al. (2002) indicate that this risk of microbiological contamination of water by manures is highest immediately after deposition. However, because of the ability of micro-organisms to survive for limited periods in stressful conditions, manures form a diminishing hazard after they have been deposited. Pathogen and FIO survival (and thus the rate at which the hazard diminishes) depends on a range of factors including temperature, moisture content and exposure to UV light (Unc and Goss, 2004).

At the catchment scale, the impacts of grazing livestock on water quality are a function of a number of issues (Ferguson et al., 2008).

- **Stocking density:** Stocking density determines the volume of manure generated and its areal coverage. Moreover, high stocking densities can pose a disproportionate risk to public health as they elevate the risk of transmission of infection to stock and in wildlife.

- **Length of grazing season:** Prolonged, or even year-round, grazing in humid climates can result in extended periods when fresh manure is applied to grassland. Schulte et al. (2006) noted that milder climatic conditions result in a longer grazing season. Furthermore, application of manure to wet soils during prolonged wet periods increases the possibility of entrainment into surface runoff, or to drain water. Moreover, the low temperatures, moist conditions and lower levels of sunlight during the period from late autumn to early spring may prolong micro-organism survival at the ground surface.

- **Land-use practice:** Investigations by Hafez et al. (1969) noted that manure deposited by cattle was not uniformly distributed in pastures. Grazing cattle with unrestricted access to water courses spent 5–30 times more time in riparian zones than in open pasture (Belsky et al., 1999). This results in disproportionate deposition of manure in riparian areas and, even more critically, directly into watercourses. A recently completed study has demonstrated that cattle are up to 50 times more likely to defecate while crossing water than on dry land (Davies-Colley et al., 2004). Tiedemann et al. (1987) noted that this feature may overprint the effects of stocking density or grazing season, because the source of micro-organisms is directly deposited in the receptor. Given the high concentrations of FIOs, and possibly pathogens, in manure, access by livestock, even over a short stretch of river, displays considerable potential to cause gross microbiological contamination. Removal of pathogens under these circumstances depends on in-stream processes such as disinfection by natural light and predation. Micro-organism association with SS provides an additional attenuation mechanism, although this may prolong survival, with subsequent release associated with gradual desorption or re-suspension during ensuing hydrological events (Pachepsky et al., 2006).

Apart from the impacts of grazing cattle and sheep, land application of wastes from livestock-rearing units (LRUs) is the other principal source of diffuse microbial contamination in rural settings. Intensification of agriculture in many areas has resulted in greater numbers of LRUs in the Irish countryside. Traditionally, wastes generated by LRUs have been applied to land as fertiliser. Liquefied manure/slurry should be stored and applied during drier periods. However, limited storage facilities and high manure production rates often require rapid disposal to land, even when hydrological conditions are unsuitable (Smith and Perdek, 2004). As with pasturing, application to land under wet conditions significantly enhances the risk of runoff and impacts the microbiological quality of watercourses.

Methods of manure application and the condition of the ground receiving manure/slurry will determine associated micro-organism mobility; for example, band spreading on tilled ground increases pathogen survival as it limits manure exposure to UV light (Jones, 1986). Evidence for the relative impact of spreading on grass-covered and tilled soils on surface water quality suggests that pathogens and FIOs may survive marginally longer on grassland (Nicholson et al., 2005). Oliver et al. (2005) note that micro-organisms in infiltrated effluent enjoy greater protection from sunlight and desiccation than those on tilled soils. Infiltration, particularly in finer-grained soils, may be considerably aided by macropores. On the other hand, tillage can destroy these features. These points suggest that application to tilled land may preferentially promote pathogen delivery to watercourses by surface runoff, often in association with sediment (see Sections 5.2.4 and 5.4). However, as with pasture, the impact depends on how and when incompletely treated manure-based fertilisers (containing viable pathogens) may be applied (Jørgensen et al., 1998).

In catchments where both pasture and land spreading are practised, little information exists on the relative contributions of manure derived from each source. This is complicated by similar characteristics of different waste sources and the complex processes influencing micro-organism fate and transport. However, modelling studies by Vinten et al. (2004) in Scotland indicated that grazing represented a greater threat to drain water quality than slurry application, but that pathogens associated with drains only delivered a small proportion of the total enteric micro-organism load to watercourses.

Recent advances in molecular biology and microbiology display considerable potential for further constraining the source of microbiological contamination using microbial source tracking (Graves et al., 2007). On the other hand, Stapleton et al. (2007) noted that quantitative source apportionment was not yet possible. However, significant progress is currently being made in this area and quantifiable tools may be available in the near future (Vincent O'Flaherty, National University of Ireland, Galway, personal communication, 2009).

5.2.3.5 Forestry

With the exception of inputs from wildlife, the absence of pathogen-bearing source materials associated with forestry suggests that it does not constitute a hazard to the microbiological quality of water. The application of sewage sludge to forestry, as practised in Great Britain and elsewhere, is not carried out in Ireland (Mary Kelly-Quinn, University College Dublin, personal communication, 2009).

5.2.4 Processes controlling pathogen mobility in the environment

High concentrations of pathogens may be released to the environment from the sources listed in Section 5.2.3. In a review of microbial sources in drinking water catchments, Ferguson et al. (2009) noted that Crypto levels in calf faeces could reach 2.5×10^4 oocysts/g, while Rao et al. (1989) reported hepatitis A levels of 2.5×10^8 pfu/ml in domestic wastewater (cited in Maier et al., 1999). These high levels contrast with the very low concentrations of 10 oocysts of Crypto needed to initiate infection in a population, or one virus (Westwood and Sattar, 1976). Consequently small amounts of pathogen-bearing waste may be capable of rendering large volumes of water unfit for human consumption. As a corollary to this point, the generally low levels of pathogens encountered in the wider environment imply that natural attenuation processes act to reduce pathogen levels, between the time they first enter the environment and the time they reach a receptor. Attenuation processes operating along connecting pathways play a crucial role in lower pathogen levels.

Considerable effort has been devoted to characterising pathogen mobility in the environment over the past 20–30 years, at scales ranging from the laboratory (column and batch) level, through field test sites measuring tens to hundreds of metres, up to the catchments measuring hundreds of square kilometres. Pachepsky et al. (2006) noted that smaller-scale laboratory studies provide conclusive proof of the fundamental mechanisms controlling micro-organism mobility by exerting high degrees of control, while field-scale studies provide an insight into those mechanisms that are most important for micro-organism transport and survival in the natural environment. This in turn indicates possible directions for lumping mechanisms in coarse-scale models. Table 5.4 summarises crucial findings from these studies.

The principal outcomes of these studies from the perspective of the current review are as follows:

- The extent of impacts to water quality by pathogens is predominantly a function of the time taken to transport micro-organisms from sources to receptors coupled to the survival characteristics of micro-organisms of concern in the environment. Pathogens may be attenuated along pathways by dilution, predation, adsorption to solids, and inactivation.

- Adsorption to solids may impede mobility in the environment should the solids be fixed. However, solids may also be mobile as suspended solids in the near surface and at the ground surface. Bonding to mobile sediment may alter micro-organism mobility/survival.

- Micro-organism survival when attached to solids may be greater than, equal to, or less than when freely suspended. The literature suggests that associations with organic matter tend to prolong pathogen survival.

- The degree of adsorption to solids depends on micro-organism type, water chemistry and conditions on the adsorbing surface.

- Batch and column studies have demonstrated that adsorption is time dependent, with the process being modelled as occurring at a constant (first-order) rate. In other words, all other things being equal, micro-organisms in contact with solids for longer periods will adsorb to a greater degree.

- Micro-organism mobility depends on hydrodynamics; fast-flowing systems will deliver greater numbers of micro-organisms to receptors. In porous systems, mobility thus depends strongly on texture, particularly in saturated soils and subsoils. At the ground surface, this will depend on whether soil conditions promote surface runoff, and whether contaminated runoff forms a continuous layer in connection with the receiving water body (Ferguson et al., 2007). This significantly promotes travel times relative to subsurface pathways.

- Greater levels of interaction between micro-organisms and solids in the subsurface present greater opportunities for adsorption and attenuation. In contrast, interactions are more limited at the surface. Consequently, greater levels of attenuation may be anticipated by micro-organisms following subsurface pathways (interflow and groundwater flow – shallow and deep).

- Attached micro-organisms may desorb from fixed surfaces. Consequently, pathogen-bound particles in deposited sediments may contribute to the pathogen concentration of surface water over prolonged periods.

- Changes in chemical conditions (e.g. drop in the ionic strength of water) may alter desorption rates, while increases in the physical energy of systems may bring pathogens back into the water column to impact water, even though sources may no longer be present at the ground surface across the catchment.

- No data could be found in the literature dealing with pathogen attenuation in interflow, although studies of virus transport through columns of unsaturated sand demonstrated that the presence of the air–water interface at low levels of soil saturation can promote adsorption/inactivation.

The implications of these findings for pathogen content of water bodies are as follows:

- Overland flow passing over areas containing pathogens is capable of supplying high concentrations of pathogens to surface water in short periods of time corresponding closely to periods of high discharge.

- Overall, this leads to periods of high pathogen concentrations and fluxes associated with high energy hydrological events followed by

Table 5.4. Summary of critical findings of potential relevance to investigating pathogen fate and transport at the catchment scale (modified from Ferguson et al., 2003a).

Laboratory studies/topic	Authors	Finding	Relevance to Pathways Project
Soil moisture and inactivation	Jenkins et al. (1999)	• Increase in inactivation rate with declining water potential	• Septics and unsaturated soil
	Anderson (1986)	• Lower micro-organism inactivation rates in association with faecal matter	• Pathogens and faecal indicator organisms survive longer in manure than in water
	Thompson and Yates (1999)	• Viruses inactivated at the air–water interface	• Underscores the importance of the vadose zone for removing pathogens
	Gagliardi and Karns (2000)	• Bacteria survive within pockets of soil moisture	• Bacteria may persist in partially dried soil
Temperature, sunlight, pH	Crane and Moore (1986)	• Prolonged survival of bacteria at low temperatures	• Bacteria present a greater hazard to water quality in wintertime
	Walker et al. (2001)	• High temperatures (>25°C) enhance Crypto inactivation	• Ditto Crypto
	Jenkins et al. (1999)	• Freeze–thaw cycles decrease infectivity	• Very low temperatures may aid inactivation
	Davies and Evison (1991)	• UV lethal to pathogens and faecal indicator organisms	• Exposure to light may continue to attenuation in surface water
	Sattar et al. (1999)	• UV enhances oocyst inactivation	• Ditto Crypto
	Hekman et al. (1995)	• Extreme pH decreases bacterial viability but not viruses	• Viruses may be more persistent in acid environments, e.g. those associated with peatlands
Nutrients	Jenkins et al. (1999)	• Ammonia in manure enhances oocyst inactivation	• Ammonia in manure may attenuate Crypto
	Gerba (1984)	• Humic acids can block virus deposition sites	• Areas of naturally high organic matter levels are at greater risk of pathogen contamination
	Lim and Flint (1989)	• Increase of nitrogen in water enhanced *Escherichia coli* survival	• Faecal indicator organisms may survive longer in areas of intensive agriculture
Adsorption/ Desorption	Jewett et al. (1995)	• pH has little effect on bacteria between 5.5 and 7	• pH of most soils
	Ferguson et al. (2003b)	• Little information available on Crypto adsorption to soils	• High levels of uncertainty in heterogeneous soils
	Ferguson et al. (2003b)	• Little information available on soil faecal matter adsorption to soils	• High levels of uncertainty in heterogeneous soils
	Goyal and Gerba (1979)	• Adsorption specific to virus types	• Adsorption of an indicator virus may not be representative of other virus types
	Grant et al. (1993)	• Inactivation rates of viruses while sorbed may differ from those in suspension	• Pathogens may be preferentially preserved in sediments
	Loveland et al. (1996)	• Fate determined by attachment, release and inactivation rates	• Provides basis for equations feeding into catchment management tool
	Formentin et al. (1997)	• Adsorbed viruses do not lose capacity to infect	• Pathogens bonded to sediment may cause illness

Table 5.4 *contd.*

Laboratory studies/topic	Authors	Finding	Relevance to Pathways Project
	Wellings et al. (1976)	• Large proportion of viruses associated with solids after secondary treatment	• Viruses may bond and be transported with organic matter
	Ferguson et al. (2009)	• Sediments can act as virus reservoirs; also likely for Crypto	• Micro-organisms observed in surface water samples may be derived from sediments in rivers
		• Adsorption depends on solid type	• Different soils will display different pathogen attenuation capacities
Filtration	Martin et al. (1992)	• Abiotic aspects of bacterial behaviour predicted by filtration theory	• Provides a predictive framework for understanding the impacts of soil texture on pathogen mobility
Hydrology	Khatiwada and Polprasert (1999)	• Hydraulic retention time among most important factors for attenuation in soils	• Travel time critical in determining degrees of attenuation
	Currieo et al. (2001)	• Strong correlation between heavy rainfall and water-borne disease in the US	• Provides hydrological basis for scrutinising available faecal indicator organisms monitoring data
	Ferguson (1994)	• Strong correlation between heavy rainfall and Crypto in Sydney	• Ditto Currieo et al. (2001)
	Ferguson et al. (2009)	• Rainfall important for mobilising pathogens	• Ditto Currieo et al. (2001)
		• Slope influences oocyst transport	• Topography can influence risk of pathogen contamination
	Ogden et al. (2001)	• Risk of pollution highest immediately after manure application	• Characterisation of source conditions essential for understanding pathogen response
	Poletika et al. (1995)	• Macropores play important role in transport	• Critical for understanding subsurface mobility, particularly in fine-grained soils/subsoils
	Natsch et al. (1996)	• Bacteria rapidly transported by preferential flow to deep layers after heavy rain	• Explains pathogen contents in areas where aquifers are covered with fine-grained sediment
	Evans and Owens (1972)	• Faecal bacteria can pass rapidly through soils to drains	• Soils provide incomplete protection from filtration
	Wellings et al. (1976)	• Pathogens may desorb in soil during rainfall	• Pathogens observed in sample may have been present in the environment for prolonged periods of time
	Davies et al. (1995)	• Microbial survival often longer in sediment than in water	• River beds can be a source of pathogens that may be re-mobilised during high-energy hydrological events, or dredging
	McMurry et al. (1998)	• Tilled soil blocks retained faecal contamination longer than sod-covered blocks	• Tilled areas may act as a reservoir for pathogens for a prolonged period after organic fertiliser application
	Ferguson (1994)	• Smaller micro-organism size leads to greater mobility	• Viruses may impact water quality more than bacteria
	Natsch et al. (1996)	• More bacteria at depth in untilled fields	• Macropores can promote mobility in pasture

Table 5.4 *contd.*

Laboratory studies/topic	Authors	Finding	Relevance to Pathways Project
	Bitton and Marschall (1980)	• Soil protects from inactivation by sunlight and filters bacteria	• Subsurface application of organic wastes can promote pathogen survival
	Mawdsley et al. (1995)	• Transport of oocysts greater through clayey soils than sandy but mainly transported through runoff	• Surface runoff principal risk to pathogen content of water quality
Field experiments	Keswick et al. (1982)	• Viruses survive longer in groundwater than surface water	• Viruses may pose a prolonged threat to public health
	Bales et al. (1993)	• Viruses can travel in groundwater for long periods and remain infective	• Viruses may migrate from sources to groundwater supplies
	DeBorde et al. (1998)	• Prolonged survival implied setback distances inadequate	
	DeBorde et al. (1998)	• Virus adsorption in field significantly reduces concentrations in groundwater	• Subsurface acts to attenuate viruses
	Taylor et al. (2006)	• pH critical in determining adsorption rate in field	• Hydrochemical conditions are critical for understanding pathogen behaviour in the environment
Scale issues	Ferguson (1994)	• Batch studies of limited relevance to field studies. Only large-scale studies can demonstrate role of macropore and relative importance compared with overland flow	• Verification of processes needed at catchment scale
	Pachepsky et al. (2006)	• Field studies demonstrate environmental relevance	

significantly lower fluxes during slower lower-energy periods (Smith et al., 2005). Where pressures are identical, pathogen levels in areas experiencing limited surface runoff can be anticipated to be lower than those of poorly drained areas where delivery to watercourses may be by drains or overland flow.

- Because of filtration processes, pathogen contents in groundwater may be anticipated to be considerably lower than those in surface runoff, except in extreme cases such as karst conduit systems, or where poor monitoring of well construction permits contaminated effluent to reach groundwater via the well annulus.

The challenge of understanding pathogen impacts at the catchment level is further complicated by scale as parameters derived at the smaller field scale or in the laboratory may not be applicable at the catchment level. Pachepsky et al. (2006) noted that attenuation parameters applied at the laboratory scale may require empirical adjustment for application to field- and catchment-scale studies as part of the lumping process. On the other hand, pathogen mobility models are typically superimposed on hydrological models developed from physical data alone (see Section 5.2.6). As noted in Chapter 2, these models are often highly empirical and may have a range of possible solutions. Thus, inappropriate weighting of pathways may partially explain the discrepancy of scale. Integration of hydrological and hydrochemical data to better understand flow responses displays considerable potential for resolving this issue.

Physical processes rather than chemical or biological factors are dominant in determining the pathogen and FIO contents in surface waters in areas prone to frequent overland flow. Oliver et al. (2005) cite a number of studies that note that surface waters have significantly higher FIO and pathogen loads during hydrological events, which in turn points to the rapid delivery of contaminants. However, Mawdsley et al. (1995) observed that the type of subsoil layering in a catchment, in conjunction with topography, may be critical in determining how micro-organisms partition into runoff.

To the best of the authors' knowledge, no systematic investigations studying pathogen fate and transport in Irish RBDs have been completed. Perhaps the most comprehensive studies have been associated with recent cryptosporidiosis outbreaks in drinking water supplies. These have been associated with periods where manure application from infected livestock has coincided with heavy rainfall events. Pathogen input to surface waters under these circumstances has been attributed to overland flow. However, the evidence to support these conclusions has been partially circumstantial and based on analogy with similar outbreaks elsewhere. Moreover, systematic investigations of the origin of pathogen levels (and FIOs) in bathing water and drinking water have not been completed. A limited body of work completed in the UK, with particular focus on bathing water quality, has implicated surface runoff from farms as the principal pathogen source, although direct deposition of manure has been noted in areas where livestock have direct access to watercourses. Similarly, cases where fresh manure entering drains adjacent to roads/pathways routinely used by cattle pose a significant threat to surface water quality, given the possibility of rapid transfer of contaminants to surface watercourses, while experiencing very limited attenuation (Steve Fletcher, formerly of Environment Agency of England and Wales, personal communication, 2009). The role of septic tanks as a potential contributor in the UK has received less attention, largely due to their lower importance as a means of wastewater disposal compared with the Republic of Ireland. Similarly, the bulk of rural domestic wastewater discharges to reticulated sewers in Northern Ireland, and thus a lower relative contribution from on-site sewage treatment may be anticipated.

Pachepsky et al. (2006) noted that studies of contaminants with comparable environmental behaviour to micro-organisms may provide a means to better understand their mobility. The authors proposed using organic phosphorus. Given the greater understanding of phosphorus mobility in the Irish context (see Section 4.2), the approach displays some merit for further investigation. Similarly more detailed investigations at the catchment scale may permit the potential of using more easily measured surrogates, such as electrical conductivity and turbidity, in estimating pathogen content of waters, thus providing a more detailed insight into pathogen fate and transport.

In terms of FIO and pathogen impacts to groundwater, numerous studies have demonstrated that septic tank effluent can impact groundwater quality. Craun (1979) and DeBorde et al. (1998) have shown that although micro-organism concentrations decline significantly while percolating through the soil adjacent to septic tanks, effluent containing indicator bacteria and viruses has been demonstrated to reach the water table and thus contaminate groundwater. Beal et al. (2005) noted that most of this attenuation occurred in the unsaturated zone immediately below the infiltration area. Conversely, the absence of this interval significantly elevates the risk of microbiological contamination of groundwater. This issue is of particular concern in Ireland in those areas where septic tanks are located in poorly drained subsoils, where the water table is close to the surface. Similarly, septic systems in many of these areas are suspected to experience surcharging where infiltration rates are insufficiently high and effluent discharges to the land surface. Where this occurs greater opportunities for effluent (and micro-organisms) to impact the wider environment arise. Given the higher frequency of overland flow in poorly drained areas, it is feasible that pathogens contained in surcharged effluent may contribute significantly to pathogen fluxes in surface water during higher energy hydrological events. This process may be greatly assisted by the reduced frequency of SMDs in surcharging systems, which increases the possibility of delivery of exfiltrated effluent to surface water by overland flow, even during moderate hydrological events that would not stimulate comparable hydrological responses in surrounding areas whose upper soil layers remained unaffected by the effluent. On the other hand, limited studies completed by QUB during a prolonged wet period in summer 2009 in a catchment underlain by poorly drained glacial till soils failed to detect this process (Alison Orr, Queen's University Belfast, personal communication, 2009).

In a more general sense, the processes influencing the fate and transport of pathogens and FIOs in Irish groundwater remain little studied. Interrogation by Dorrian (2009) of the EPA's database of the results of microbiological analyses of groundwater samples, collected from 203 monitoring points, showed that samples from 18 points consistently exceeded detection limits. On the other hand, faecal coliforms were never detected at 59 locations. Of the remaining monitoring points, 46 sites regularly had intermittent levels in excess of 100 cfu/ml, while 25 sampling points displayed intermittent levels of extreme contamination (>1,000 cfu/100 ml). The remaining 55 points had intermittent levels, but these did not regularly exceed 100 cfu/ml. Of those wells displaying intermittent contamination, 46% displayed statistically significant relationships between faecal coliform levels and rainfall, reflecting both the persistence of contamination sources within the borehole catchment and the presence of flow paths to deliver contaminants to groundwater before they can be fully inactivated. More detailed analyses of the most contaminated points were in hydrogeological units typically characterised as having low effective porosities and elevated travel times (see Chapter 2). This revealed that of the 100 most contaminated points, 46 were located in karstified aquifers, while 35 were located in locally productive bedrock units. The remaining 19 occurred in regionally productive fissured bedrock or sand and gravel units. Conversely, groundwater samples collected from some of the aquifers in each of these categories have had consistently low levels of FIOs. The data suggest that the contamination hazards from wildlife may be low, if distribution across the country is assumed reasonably even.

Kay et al. (2008) employed a comparable approach to investigate FIO levels in surface water and to develop pathogen export coefficients with associated confidence intervals for a range of catchments with differing land uses. Access to similar data sets for Irish surface water quality are anticipated in the near future, where they may provide a means for developing hypotheses concerning pathogen and FIO fate and transport in catchments on an RBD scale following a comparable approach. Moreover, investigation of these data on a more detailed site-specific basis may provide an improved basis for better understanding of underlying mechanisms contributing to microbiological contamination within a catchment. The utility of the data will depend strongly on the size of data sets and the availability of complementary information concerning hydrological conditions at the time of sampling.

5.2.5 CSAs for pathogens

Little has been published on the identification of CSAs for microbiological contaminants, apart from the development of empirical observations. However, reconciling conceptual models of hydrological processes with topographic, hydrological and water quality information may provide a means of focusing on candidate areas for further investigation.

The presence of a continuous layer of surface water connecting a pathogen source to a watercourse greatly facilitates overland flow and thus the delivery of pathogens. Consequently, those areas experiencing overland flow would prove to be more susceptible to sporadic high inputs of micro-organisms. This could include those areas with low hydraulic conductivity soils and areas where the water table rises to the surface during wet periods, giving rise to saturation-excess overland flow (see Section 2.1). In the latter category, this could include waterlogged riparian zones where high levels of manure may have accumulated from watering cattle. These areas would thus be considered potential CSAs.

5.2.6 Modelling pathogens at catchment scale

Modelling levels of pathogens and FIOs at the catchment scale presents a number of challenges above those for modelling system hydrology or conventional non-reactive contaminant transport. As noted, it is difficult to confidently identify which processes, amongst those identified at smaller scales, are of relevance at the catchment level. This has led to a number of alternative approaches to modelling pathogen concentrations in surface water. These range from generic statistical approaches (Dorner et al., 2004; Kay et al., 2008) to empirical techniques (e.g.

Vinten et al., 2004), to process-based approaches using spatially distributed data (e.g. Ferguson et al., 2009). As with conventional modelling, generic statistical models, although providing broad relationships, can only be used with a low level of confidence. Similarly, empirical models, although valuable for predicting behaviour in individual catchments, are of limited use in characterising pathogen fate and transport elsewhere. Conversely, distributed models show significant potential for incorporating the spatial heterogeneity widely encountered in Irish RBDs with observed pathogen levels. The current project proposes developing a series of equations to simulate pathogen fate and transport that can be integrated into a catchment-scale distributed model. The high levels of heterogeneity anticipated will require assumptions to be made concerning the influence of variable chemical and physical conditions on pathogen/FIO mobility.

Ferguson et al. (2003a) note that development of appropriate conceptual models of pathogen fate and transport is an essential first stage in identifying appropriate assumptions. Of the limited number of published studies addressing the modelling of pathogen fate and transport at the catchment scale, those pathways operating during high-energy hydrological events have been regarded as the predominant means of micro-organism mobilisation and transport, i.e. surface runoff and drain discharge. In addition, some authors have incorporated direct deposition into channels, mobilisation of pathogen/FIO-bearing sediment during high flow, and inputs from wastewater treatment plants. This latter issue has been regarded as the easiest to address from characterisation and remediation points of view.

Studies by Haydon and Deletic (2007) emphasise the overriding importance of understanding physical processes before considering attenuation of FIOs. However, due to assumed predominant delivery of micro-organisms to surface water by overland flow/drain flow, catchment-scale models have omitted inputs from deeper subsurface pathways, largely as a consequence of modelling objectives to satisfy bathing water standards; the relative contribution of water from these deeper pathways is considered negligible from a bathing water quality perspective. The investigation completed as part of this review has demonstrated that the impacts to groundwater used for drinking water are significant and need to be addressed as part of the WFD. Moreover, the study of Sinclair et al. (2009) of pathogen levels in surface waters in Nova Scotia demonstrated that baseflow levels could contribute up to 35% of the total bacterial load, suggesting that assumptions concerning the dominance of overland flow may be oversimplistic. In addition, integration of physical and water quality data to provide an improved understanding of hydrological mechanisms shows considerable promise in resolving this issue. This in turn promises to provide a more effective series of equations, which may be integrated into a hydrological modelling platform, to be developed in the latter part of this study. On the other hand, modelling will require detailed source characterisation. Preliminary investigations suggest that unregulated direct discharge of domestic sewage effluent to watercourses may constitute a significant component of nutrient and pathogen fluxes in catchments where soils have low infiltration capacity and OWTSs such as septic tanks are inefficient/ineffective in removing contaminants (Valerie McCarthy, Dundalk Institute of Technology, personal communication, 2009).

The requirement to consider the impacts of pathogens on both surface water and groundwater presents the dilemma of whether modelling the impacts to the two receptors should be coupled, or considered as two separate models. The issue has not been comprehensively addressed in the international modelling literature, given the focus on either groundwater or surface water, but not both. The reported role of surface and near-surface processes in dominating global pathogen fluxes would suggest that the issue is not of relevance to Ireland. However, the impact of on-site sewage systems (associated with diffuse settlement) that discharge to groundwater and possibly directly to surface water, on the microbiological quality of water bodies has yet to be assessed in the Irish context. The results of ongoing studies in County Monaghan promise to shed more light on this topic.

5.2.7 Recommendations

Development of tools to manage the pathogen content of surface waters has received considerable attention from the international research community over the past 20 years. Despite the persistence of considerable ambiguities concerning pathogen fate and transport, the predictive power of these methods provides a firm basis for improving the understanding of the fundamentals influencing pathogen levels in water at the catchment scale, identifying their CSAs and appropriately adapting monitoring programmes. A large body of FIO monitoring data already exists for Irish groundwater and surface waters. Combination of these data sets, coupled with existing hydrological, chemical, geological and land-use databases, provides scope for improving the general understanding of the relationship between FIO/pathogen levels in water and controllable parameters such as land use. More detailed evaluation of the results of monitoring data for specific catchments, coupled with detailed water quality sampling/flow monitoring during hydrological events, will permit the confidence with which generic monitoring data can be used to be established. Moreover, detailed characterisation of water quality data, when viewed in conjunction with spatially variable physical data sets, such as land use, and detailed topography provides a means of identifying those areas where pathogen inputs to surface watercourses are likely to be most significant and where programmes of measures may have most impact. The following areas of investigation are anticipated to help achieve these goal.

- Compilation and integration of surface water quality monitoring data with land-use data, meteorological data and stream/river discharge data to investigate the possibility of developing catchment export coefficients following the approach comparable to that of Kay et al. (2008).

- Detailed field investigations in selected study catchments to investigate variations in FIO levels and other water quality parameters during high-energy hydrological events. The results of these data will be compared with predicted levels determined using catchment export coefficients developed elsewhere (Scotland, Wales) to determine the degree of confidence with which export coefficients can be used as a baseline for predicting conditions in RBDs, and further data acquisition efforts may be optimised to improve confidence in predicted levels. The proposed approach is also anticipated to provide a better understanding of contaminant transport/ attenuation mechanisms.

- Assessment of the interrelationship between FIO levels and those of other constituents of concern may be used to evaluate proposed relationships with other more easily/widely measured water quality parameters, e.g. phosphorus (Pachepsky et al., 2006). This may in turn provide an improved insight into pathogen mobility on a wider and/or longer-term basis.

- More detailed investigation of groundwater monitoring data from any potential contaminated monitoring points within selected type catchments to better understand the root causes of pathogen levels observed. This may be coupled with well-head sanitary surveys and, where possible, spatial variation in contaminant levels between measurement/monitoring points, compared with surface responses to evaluate how representative the data are of catchment-wide conditions.

- Analysis of spatial distribution of pathogen levels in water within type catchments, combined with water quality data and topographic/hydrological data to identify potential CSAs.

- Investigation of the feasibility/benefit of pathogen transport models coupling attenuation in the subsurface with surface processes as a means of simultaneously understanding impacts on both groundwater and surface water. This will require further evaluation of modelling data requirements to assess its feasibility within the framework of the Pathways Project.

5.3 Pesticides

One of the major aims of the WFD is for enhanced protection and improvement of water quality through specific measures for the progressive reduction of discharges, emissions and losses of priority substances. Thirty-three substances have been identified by the European Council to be of particular concern due to their toxicity and persistence in the environment. This list includes a number of pesticides used widely in agriculture and horticulture. Pesticides can be toxic to plants and animals and are used extensively in agriculture to control or destroy unwanted plants (herbicides), animals (insecticides, molluscicides, etc.), and fungi (fungicides). There are approximately 400 active ingredients licensed for use in the EU, in addition to those listed as priority substances, with varying toxicity for aquatic plants and wildlife. In addition, pesticide degradation products can be more toxic than parent compounds (Goody et al., 2002).

The loss of pesticides to receiving waters depends on the application rate and factors controlling the degradation and mobility of the active ingredient. The use of pesticides is closely related to cropping patterns (SNIFFER, 2006). Many pesticides are considered to be persistent organic pollutants and have a long half-life in soil, sediment, water and air. Pesticides have a wide range of chemical and physical properties and these different properties govern the fate and transport of the pesticide when applied to land (Gevao and Jones, 2002).

5.3.1 Sources

5.3.1.1 Forestry

Forestry covers approximately 10% of the Republic of Ireland, accounting for 669,167 ha, of which 57% are state owned and 43% privately owned. Both herbicides and insecticides are used in forestry practice and are regulated by the Pesticide Control Service of the Department of Agriculture, Fisheries and Food (DAFF), and by the Forest Stewardship Council (WRBD, 2006).

Pesticide application is dictated by stages of tree growth. For example, insecticides are predominantly applied to protect deciduous trees prior to planting when the plant bundles are pre-dipped in insecticide in order to reduce the requirement for spray application. Further insecticide is applied post-planting to the tree stem (area prone to attack by weevils) of young trees (WRBD, 2006). Furthermore herbicides are applied to forestry containing broadleaf trees in the initial years after planting to control weed growth (WRBD, 2006).

The most common herbicide applied in forestry practice is glyphosate. Table 5.5 shows the predominant insecticides and herbicides used in forestry based on data collected by Coillte in 2006.

Following glyphosate, atrazine is the most widely used herbicide in forestry and (along with chlorpyrifos, isoproturon, simazine and trifluralin as listed on the priority hazardous substance list) has been withdrawn from the market since July 2007 largely due to its persistence in the environment.

5.3.1.2 Agriculture

Pesticide application in agriculture is largely dependent on crop type, with arable land receiving greater loads per hectare in comparison to grassland. The type and quantity of pesticides applied to land varies from year to year, as it is dependent on cropping rotation. Moreover, farmers routinely change the active ingredient applied in order to avoid insects and weeds building a resistance against the active ingredient. This practice complicates the characterisation of pesticide loads when considering the usage of pesticides from year to year. Field-scale information is required to determine pesticide type and

Table 5.5. Coillte pesticide usage by type (modified from WRBD, 2006).

Type	Active ingredient	Amount of active ingredient (g/l)
Insecticide	Alpha-cypermethrin	240
Insecticide	Carbosulfan	10% (applied as solid)
Herbicide	Asulam	400
Herbicide	Atrazine	500
Herbicide	Glyphosate	864
Herbicide	Imazpyr	250
Herbicide	Triclopyr	240

usage weight at a catchment scale (Bloomfield et al., 2006).

Pesticide usage services data

The first national survey of pesticide use in the Republic of Ireland focused on use of plant protection products on grassland and fodder crops harvested during the calendar year 2003. The survey, undertaken by the Pesticide Control Service, was based on a sample of 679 holdings, stratified by region and size and was representative of grassland and the main fodder crops (maize, fodder beet, arable silage, swedes/turnips and kale/rape). The data collected were then calculated to provide estimates of national pesticide use (DAF, 2006).

A second national survey of pesticide usage was based on a sample of 236 holdings, stratified by region and size and chosen to be representative of the main arable crops (barley, wheat, oats, oilseed rape, peas, beans, potatoes, sugar beet, linseed, lupins, set-aside and non-food crops).

Table 5.6 summarises the information presented in the usage reports (DAF, 2006, 2007) for use of active ingredients in relation to arable and grassland land use (SWRBD/RPS, 2008). The dominance of grassland agriculture belies the fact that areas under arable cultivation receive disproportionate pesticide loads.

Timescale for application of pesticides

In relation to arable crops, over 80% of the yearly pesticide application occurs between the beginning of April and the end of September, with May being the month with the highest amount of pesticide applied in 2004 (DAF, 2007). In 2003, over 80% of the total pesticides used on grass and fodder crops were applied between the beginning of May and the end of September, with the greatest application occurring in June (DAF, 2006).

5.3.2 *Pesticide mobility in the environment*

Pesticides entering the soil system are subject to a variety of transport and degradation processes. The overall dissipation of a pesticide from soil cannot be attributed to any one process alone, as there are a number of attenuation mechanisms that act to reduce concentrations. In addition, there are hundreds of pesticides currently on the market, all with varying physico–chemical characteristics. The following processes must be considered when assessing the primary transport pathway for each individual active ingredient (Gevao and Jones, 2002; Bloomfield et al.,

Table 5.6. Total pesticide application (kg) to arable crops (2004) and grassland (2003) (modified from SWRBD/RPS, 2008).

Active substance	Arable (2004)	Grassland (2003)	Total (kg)
Glyphosate	116,731	93,056	209,787
Mancozeb	157,295	508	157,803
Isoproturon	107,852	349	108,301
Mecoprop	8,992	21,761	30,753
Atrazine		24,152	24,152
2,4-D (2,4-Dichlorophenoxyacetic acid)		23,458	23,458
Dimethoate	17,592	458	18,050
Simazine	5,576	269	5,845
Chlorpyrifos	3,852	337	4,189
Cypermethrin	2,274	73	2,347
Trifluralin		653	653
Linuron	190	45	235

2006; Hollis et al., 2006; Centofanti et al., 2007; Reichenberger et al., 2007):

- Chemical properties – molecular size, water solubility, ionisability, lipophilicity, polarisability, volatility, adsorption/desorption;
- Abiotic degradation – chemical hydrolysis, photolysis, dehydrohalogenation, oxidation–reduction;
- Biotic degradation – dependent on microbial community and redox conditions;
- Soil properties such as infiltration characteristics, hydraulic conductivity/permeability of soil, pore size distribution, soil organic matter content, ion exchange capacity, soil moisture content, soil temperature, pH and oxygen status;
- Plant uptake; and
- Climatic factors such as rainfall events, and photolysis (a chemical reaction in which pesticide molecules are broken down by photons, e.g. sunlight).

In relation to pesticides, the predominant transport pathways have been associated with surface water runoff (overland flow), leaching through soil to groundwater, preferential flow paths, such as macropores, and tile drain transport, and transport in groundwater (Reichenberger et al., 2008).

5.3.2.1 Overland flow

Transport of pesticides by overland flow (or runoff) includes dissolved, suspended particulate and sediment-absorbed pesticides transported by water as a result of application or atmospheric deposition to land (Leonard, 1990; Muller et al., 2006; Barriuso et al., 2008).

The nature and extent of overland flow of pesticides are governed by the following (Leonard, 1990; FOCUS, 2006):

- Physico–chemical properties of the applied pesticide;
- Application rate;
- Time of application in relation to rainfall events;
- Method of application; and
- Active ingredient and formulation applied.

Field experiments have shown that major pesticide losses to surface water occur within 14 days of a rainfall event and are predominantly associated with events where surface runoff has been generated (Muller et al., 2006). Surface runoff may be infiltration excess runoff (Hortonain runoff) and saturation excess runoff. Surface water begins as laminar sheet flow and after a certain travel length may channelise, with the flow becoming turbulent and capable of suspending sediment (see Section 2.1). Sediment may be derived from in-channel erosion or directly from the land surface as raindrop-stripping soil erosion occurs. In the latter case, pesticides lost in runoff or overland flow may be transported as dissolved runoff or absorbed to eroded soil particles. Runoff is considered to be the predominant loss mechanism for transport of pesticides from a field. However, overall loss of pesticides due to erosion is considered to be small in comparison with total runoff as the amount of eroded soil transported from a field is small in comparison with runoff volume (Reichenberger et al., 2007; Leonard, 1990). However, for highly sorbed pesticides (sorption coefficient (K_{oc}) greater than 1,000 l/kg), loss of pesticide via erosion may be the predominant loss mechanism (Reichenberger et al., 2007). Furthermore, sorption to particles is dependent on the portioning coefficient, the concentration of pesticide absorbed to soil and remaining dissolved in soil water. Moreover, this parameter determines that, when rainfall replaces pre-event soil water which has been in equilibrium with the soil, there is a potential for desorption of pesticide from the soil into the event water (Gevao and Jones, 2002; Bloomfield et al., 2006; Blanchoud et al., 2007).

Molecular transformation processes may occur during overland flow of pesticides. The predominant transformation process for pesticides at the ground surface is biotic degradation (microbes breaking down a pesticide molecule into smaller parts or transformation products) and each pesticide is quoted with a half-life value (DT_{50}). This value is the time taken for 50% of the pesticide concentration to be removed. Degradation of some pesticides may result in the formation of metabolites with aquatic toxicity similar to or, in some cases, more toxic than the parent compound (Johnston et al., 2000; Bloomfield et al., 2006).

5.3.2.2 Interflow/Infiltration

Leaching to groundwater

Pesticides with higher persistence (higher DT_{50}) and weaker sorption properties (low K_{oc} value) are more readily leached to the subsurface and therefore have a higher probability of migrating to groundwater (Stenemo and Jarvis, 2007). Migration of pesticides from soil to groundwater is predominately by leaching, where leaching is defined by Gevao and Jones (2002) as "*a fundamental soil process whereby constituents, dissolved or suspended are lost from the soil profile by the action of percolating liquid water*". Without percolating water pesticides are more likely to remain above the water table where they may degrade. Numerous studies demonstrate increased concentration of pesticides detected in groundwater after rainfall events (Gevao and Jones, 2002; Baran et al., 2008; Bloomfield et al., 2006; Morvan et al., 2006; Blenkinsop et al., 2008; Nolan et al., 2008). Conversely, in highly stratified units with significant permeability reductions below the upper layers, temporary saturation may give rise to lateral transport of contaminants above the water table resulting in rapid delivery of infiltrated pesticides to aquatic receptors. This possible significance has yet to be investigated. However, this and drain flow may account for elevated fluxes attributed to preferential flow (see below).

Groundwater ubiquity score

The mobility of pesticides may be calculated using the Groundwater Ubiquity Score (GUS) index (Gustafson, 1993), using the following equation:

$$\mathrm{GUS} = \log(DT_{50}) \times (4 - \log(K_{oc})) \qquad \text{Eqn 5.1}$$

where DT_{50} is the half-life of the pesticide in question and K_{oc} is the water–soil coefficient (Freundlich partition coefficient).

The GUS score[2] only considers the properties of the pesticide and does not incorporate soil properties or changes in mobility in relation to absence or presence of percolating water.

Preferential flow

Until quite recently traditionally movement of pesticides to water has been considered to be by soil matrix flow. However, matrix flow cannot account for the rapid appearance of pesticides in surface and groundwater after application (Stone and Wilson, 2006; Jarvis, 2007; Kordell et al., 2008). Preferential flow can occur in virtually all types of soils and is caused by heterogeneities at various scales, e.g. worm burrows, desiccation cracks and gravel lenses. However, to date very little is known about the relative significance of finger flow, heterogeneous flow and macropore flow in determining the subsurface mobility of pesticides. As water moves along preferential pathways, such as macropores, degradation is likely to be limited relative to matrix flow due to limited opportunities to interact with fixed solid surfaces (Jarvis and Dubus, 2006). Tile drains are also considered to be a form of preferential flow, and degradation of pesticides is limited, given bypass of the soil matrix (Stone and Wilson, 2006). In the soil, fast water flow and pesticide transport are commonly observed, with high breakthrough concentrations attributed to preferential flow (Branger et al., 2009; Jarvis et al., 2009; Lindahl et al., 2009). Numerous models have been produced to consider preferential flow of pesticides to water, including MACRO, PEARL (FOCUS, 2006; FOOTPRINT, 2009) and PESTDRAIN (Branger et al., 2009).

5.3.2.3 Groundwater flow

The variables that determine the susceptibility of groundwater to pollution by pesticides due to direct recharge include climate and land use, as well as soil and hydrogeological conditions and contaminant-specific vulnerability. The transport processes responsible for pesticides have been discussed in Section 5.3.2.2, where mobility is strongly determined by soil moisture content/saturation, which in turn determines soil water potential. In a similar vein,

2. The GUS is used to calculate the intrinsic mobility of pesticides. A score of >2.8 indicates a pesticide with high mobility and greater potential for migration to groundwater, while a GUS score of <1.8 indicates a less mobile contaminant and therefore less likely to leach to groundwater. As demonstrated by ERBD (2008b) there is a significant range in the GUS score for active ingredients applied in Ireland indicative of a significant range in mobility to Irish groundwater

groundwater pesticides may be transported by advective transport which depends on hydraulic gradients, hydraulic conductivity and effective porosity. Transport by hydrodynamic dispersion results in mixing and dilution of pesticides along groundwater flow paths, while diffusion is a function of concentration gradients and molecular weight (Movan et al., 2006; Baran et al., 2008). In addition, advection–dispersion processes, and chemical and biological reactions may result in attenuation along flow paths. Studies have shown that microbial degradation can be the predominant attenuation mechanism for pesticide degradation in groundwater and can result in the formation of toxic degradation products (Goody et al., 2002). Water supply wells, springs and groundwater contribution to rivers (baseflow) are all considered as groundwater receptors. As with pathogens (Section 5.2), existing studies suggest that relative to surface water, groundwater is usually considered a minor pesticide receptor in terms of total pesticide losses. This is attributed to physical, chemical and biological attenuation processes in soil and dilution and dispersion in the saturated zone (Worrall and Besien, 2005; Bloomfield et al., 2006). However, given the local importance of groundwater as water supply, the potential of pesticides to impact public health cannot be ignored, particularly in those aquifer types where attenuation levels may be small due to low effective porosities and short travel times.

5.3.3 Monitoring for pesticides in Ireland

5.3.3.1 Drinking water

Under the Drinking Water Directive there are two general parametric values for pesticides – one for total pesticides of 0.5 µg/l and the other for individual pesticides of 0.1 µg/l (referred to as the Drinking Water Standard (DWS)), while there are also some specific pesticides parametric values in the EU Drinking Water (No. 2) Regulations, 2007. Local authorities provide data for the total pesticide parametric value (i.e. by adding the results of analyses of any pesticides together) and also report all individual pesticides detected above the limit of detection to the EPA. For the 2007–2008 reporting period, 1,481 samples were analysed for pesticides in 1,003 water supplies, of which 1,257 samples showed no traces of pesticides. Of the remaining 224 samples where pesticides were detected, four reported total concentrations in excess of the total parametric value of 0.5 µg/l. These exceedances occurred in drinking water supplies in East Meath, Jarretstown and Navan–Mid-Meath supplies (all Meath County Council), as well as one private group water scheme. In addition, in 11 supplies the individual pesticide values detected were greater than the individual pesticide parametric value of 0.1 µg/l (EPA, 2009a).

5.3.3.2 Surface water

As part of the WFD requirement, the dangerous substances monitoring surveillance network is currently sampling surface waters for 69 compounds, including a suite of pesticides (Ciaran O'Donnell, EPA, personal communication, 2009). An Environmental Data Exchange Network (EDEN) is currently under development to house these monitoring data. For the purpose of this report, the EPA provided a partial data set for review. The database provided contained monitoring data, including pesticides from 152 monitoring locations dating from July 2007 to January 2009. Based on the partial data set, the most commonly detected pesticides were simazine, atrazine, mecoprop and glyphosate with less frequent findings of 2,4-D (2,4-dichlorophenoxyacetic acid), diuron and isoproturon. Isoproturon was detected in the River Nanny, County Meath, and the River White, Coneyburrow Bridge, County Louth, at concentrations of 1.2 and 4.6 µg/l, respectively, and was the only pesticide found to exceed the proposed EPA surface water maximum admissible concentrations (1 µg/l) (EPA, 2007a). However, sampling at many locations is suspected to have been completed during low flow periods, and/or a considerable period after pesticide application. Given the elevated mobility of pesticides during high-energy rainfall events, these findings significantly underestimate fluxes to aquatic receptors. Indeed, the findings may reflect low-level pesticide desorption from river sediment rather than more distal delivery. The importance of this mechanism has been recently demonstrated in Donegal, where residues of glyphosate were not encountered in conventional monitoring, but required specific specialised sampling protocols employing semi-permeable membrane samplers (Ray Thomas, Northern Ireland Environment Agency, personal communication, 2009).

5.3.3.3 Groundwater

The EPA commenced collecting groundwater samples for pesticide analysis in July 2007. For the purposes of this report, the groundwater monitoring data from July 2007 to July 2008 were reviewed (Sherry, 2009). The review suggests that a greater percentage of pesticide detections is found in areas of high to low to extreme vulnerability than in areas of low or moderate vulnerability.

In addition, the review indicates that pesticide exceedances of 0.1 µg/l (Daughter Groundwater Directive and Drinking Water Directive) are more likely to occur in groundwater at monitoring points where there has been a rainfall event within 5 days prior to sampling (Sherry, 2009).

Mecoprop, MCPA (2-methyl-4-chlorophenoxyacetic acid) and glyphosate accounted for five, three and two of the 10 DWS exceedances in groundwater, respectively. There was only one exceedance of the DWS reported for Northern Ireland, which was for atrazine. In addition, 74 pesticides were detected but below the DWS in 74 samples. Of the 74 samples, 51 (70%) contained MCPA and/or mecoprop, while, in Northern Ireland, mecoprop and/or MCPA was detected in 53% of samples containing pesticides (Sherry, 2009).

5.3.3.4 Analytical considerations

Studies on the impacts of pesticides often prove difficult to evaluate due to the increasingly diverse range of products on the market. The environmental mobility of compounds is difficult to evaluate due to high analytical costs and the limited availability of analytical protocols (Hayes et al*.,* 2006). The development and application of methodologies for determining pesticides and their transformation products in soil and water is a challenging task, as a result of the varying chemical characteristics of individual pesticides. The main issues in relation to analysis of pesticides are summarised as follows (Andreu and Picó, 2004):

- The concentration of analytes in soil and water samples can be extremely low, resulting in the need for corresponding extremely highly sensitive analytical methods that are adequate for detection and quantification of these pesticide species at such levels;

- There are hundreds of pesticides currently available, covering a wide range of solubilities, from the insoluble to the soluble, with the latter considered the most hazardous compounds which can be transported to the water environment via leaching or runoff processes;

- The strong binding of the analytes to sediment which requires special extraction techniques prior to analysis; and

- The degradation products formed can contribute to a complex blend of substances. For example, one study reported that 28 different metabolites of trifluralin were formed in soils. As standards were available for only trifluralin and six of its metabolites, the other degradation products were identified from tandem mass spectrometry (MS/MS) data, but could not be quantified, pointing out yet another issue with information and standards available to consider degradation (Lerch et al., 2003).

As a result, chemical characterisation of pesticides and degradation products in soil demands state-of-the-art techniques for sampling and sample preparation, analyte separation, detection and quantification. The current approach often is to use classical methodologies with newly reported improvements that are quite aggressive to analytes, but well established, and achieve a high sample throughput. Much research is still required on the analysis of pesticides in soil and water. This particular field of research is in constant flux as new degradation products are being identified. Analytical developments need to be made constantly to determine pesticides and the increasing amounts of toxic degradation products released into soils and water. Analysis is generally carried out by gas chromatography or liquid chromatography coupled to different detectors, especially to mass spectrometers. However, alternative and/or complementary methods, using capillary electrophoresis, biosensors and bioassays are emerging recently which may improve detection limits and analytical sensitivity (Andreu and Picó, 2004).

5.3.4 Data availability

Table 5.7 provides a summary of the past and current research and data available on pesticides. This section focuses on the most relevant ongoing research in Ireland and in Europe.

5.3.4.1 Most relevant ongoing European studies

FOOTPRINT Project

The overall aim of the FOOTPRINT Project is to develop a set of three computer tools that enable the identification of the dominant pathways and sources of pesticide contamination in the agricultural landscape. This can allow estimations of levels of pesticide concentrations in surface water and groundwater in order to make scientifically based assessments of how the implementation of risk reduction strategies is likely to reduce pesticide contamination of water resources. The FOOTPRINT Project is scheduled to be completed by October 2010 and a suite of three pesticide risk assessment and management tools will be available free of charge. A brief description of these three tools follows:

- *Tool 1 – FOOT-FS*

  FOOT-FS (FS: farm scale) is mainly targeted at farmers and organisations, such as Teagasc, that provide advice to farmers. The main aim of the FOOT-FS tool is to identify the pathways and those areas that most contribute to contamination of water resources by pesticides at the farm scale and provide site-specific management recommendations to minimise transfers of pesticides in the local agricultural landscape (http://www.eu-footprint.org/FOOT_FS.html).

- *Tool 2 – FOOT-CRS*

  FOOT-CRS (CRS: catchment and regional scales) is primarily targeted at local authorities and RBD managers and those involved in implementing the WFD and/or limiting the contamination of water resources by pesticides.

  This tool, which is based on the same decision rules as those implemented in FOOT-FS, will be made available as an add-on to the ArcGIS software. The main objectives of the tool are to identify those areas that most contribute to pollution of waters by pesticide CSAs, thus enabling managers to define and optimise monitoring and action plans at a catchment scale. This tool facilitates estimates of pesticide concentrations in edge-of-field surface water bodies, surface water resource abstraction points and local groundwater to be calculated from simulated pesticide inputs by diffuse sources and point sources while considering the size and discharge of the water body, the water volumes associated with runoff and drainage inputs and the presence of bed sediment (http://www.eu-footprint.org/FOOT_CRS.html).

- *Tool 3 – FOOT-NES*

  FOOT-NES (NES: national and European scales) is predominantly targeted at EU and Member State policy and decision makers, and pesticide registration authorities such as the Pesticide Control Service (PCS). The objectives of the FOOT-NES tool are to identify those large areas that are most at risk of pesticide contamination and to assess the probability of pesticide concentrations exceeding legislative or ecotoxicologically based thresholds at the Member State and EU levels. FOOT-NES, as with FOOT-CRS, has been developed as an ArcGIS add-on. FOOT-NES includes an automated parameterisation system to support higher-tier modelling applications within the context of pesticide registration (http://www.eu-footprint.org/FOOT_NES.html).

- *Additional FOOTPRINT Tools*

  In addition, the FOOTPRINT Pesticide Properties Database (FOOTPRINT PPDB) is a comprehensive relational database of pesticide physico–chemical and ecotoxicological data and holds chemical and physical data which can influence the fate and transport of pesticides in the environment and ecotoxicological data for a range of taxa for all EU Annex 1 listed pesticides and selected metabolites.

INTERACT Project

INTERACT is an ongoing project focused on measuring the ecological impacts of pesticides cost-effectively. Researchers involved in the project have developed a system called the SPEcies At Risk (SPEAR) system which could provide an accurate and cost-effective means of assessing the effects of

Table 5.7. Summary of completed and ongoing research and monitoring relevant to pesticides.

	Project	Area of focus	Time frame
Ireland			
SWRBD/TNO	Screening Monitoring Programme	Surface water, groundwater	2005–2006
WRBD	Measures and standards Forests and water Priority action Relevant pollutant and general component candidate for surface water in Ireland	Forestry and surface water	2006
EPA	Surveillance network dangerous substances monitoring (to include a suite of pesticides)	Surface water	2007–2010
EPA	Groundwater Monitoring Network	Groundwater	2007–Ongoing
EPA/Local authorities	Drinking Water Monitoring Network	Drinking water	Ongoing
ERBD/CDM	Risk to groundwater from diffuse mobile organics	Groundwater	2008–Completed
Teagasc, TCD, UCD – Stimulus Funding DAFF	Assessment of the vulnerability of groundwater to pesticide inputs from Irish agriculture	Groundwater	2008–2011 Ongoing
DCU (EPA STRIVE)	Priority Pollutants	Wastewater	Ongoing
DCU (NI Water)	Development of analytical methods for pesticides in drinking water	Drinking water	Ongoing
United Kingdom			
SNIFFER	Provision of a Screening Tool to Identify and Characterise Diffuse Pollution Pressures: Phase II	Surface water and base of soil profile	2006–Completed
NIEA	WFD-GW-7 Chemical diffuse source pressures – pesticides	Groundwater	2008–Completed
Scotland	Nitrogen and Pesticide Project in Aberdeenshire	Surface water	Ongoing
Environment Agency	Prediction of Pesticide Pollution in the Environment (POPPIE)	Surface water (rivers)	1995–2000 Completed
DEFRA	Agriculture and Water: A Diffuse Pollution Review (http://www.defra.gov.uk/farm/environment/water/csf/reports/pdf/dwpa01-e.pdf)	Surface water	2002–Completed
Europe			
EU[1]	FOCUS (http://focus.jrc.ec.europa.eu/)	Surface water/ groundwater	1995–2006
EU[1]	AquaTerra (Subproject BASIN) (http://www.eu-aquaterra.de/aquaterra/)	Soils, surface and groundwater	
EU[1]	FOOTPRINT (http://www.eu-footprint.org/home.html)	Surface water/ groundwater	2006–June 2009
EU[1]	Pesticides in European Groundwaters (PEGASE)	Groundwater	2000–2004

SWRBD, South Western River Basin District; WRBD, Western River Basin District; EPA, Environmental Protection Agency; ERBD, Eastern River Basin District; TCD, Trinity College Dublin; UCD, University College Dublin; DAFF, Department of Agriculture, Fisheries and Food; DCU, Dublin City University; STRIVE, Science, Technology, Research and Innovation for the Environment; NI, Northern Ireland; SNIFFER, Scottish & Northern Ireland Forum for Environmental Research; NIEA, Northern Ireland Environment Agency; DEFRA, Department for Environment, Food and Rural Affairs; EU, European Union.
[1]Denotes UK involvement.

pesticides in streams and may prove useful in implementing the WFD. The SPEAR system assesses the impacts of stressors on freshwater invertebrates that are at risk and $SPEAR_{pesticides}$ specifically examines the effects of pesticides. In order to be cost-effective, $SPEAR_{pesticides}$ was modified to assess impacts at the family level rather than species at risk. The fieldwork component of the project monitored aquatic biota in 48 small sites on streams in Finland, France and Germany. The level of pesticide-related toxicity was calculated using $SPEAR_{pesticides}$ for these sites at both family and species levels. The researchers then compared the results for individual species with the overall family result. Results indicated that variation in $SPEAR_{pesticides}$ values at both the family and species level was explained by pesticide toxicity. The SPEAR system is understood to be a good indicator of the ecological impact of pesticides, as results revealed that only five species had SPEAR values that were significantly different between the species and the family levels. These species comprised only 1.8% of the overall number of species and were all considered 'not at risk' at the species level but 'at risk' at the family level. The research also demonstrated that $SPEAR_{pesticides}$ values were not influenced by the region where the monitoring took place, suggesting that $SPEAR_{pesticides}$ could be used throughout Europe (Beketov et al., 2009).

5.3.4.2 Ongoing Irish research

In Ireland, the most relevant research project in relation to pesticides and diffuse pollution is entitled *Assessment of the Vulnerability of Groundwater to Pesticide Inputs from Irish Agriculture* and is financially supported through the Research Stimulus Fund administered by DAFF and led by University College Dublin (UCD) with project partners Trinity College Dublin (TCD) and Teagasc. The project duration is from January 2008 to 2011 (Sarah MacManus, Teagasc, personal communication, 2009).

Although currently there are no results to report, the project objectives are as follows:

- To rank pesticides of environmental and toxicological concern;
- To assess pesticide mobility in a number of Irish soil types and under varying environmental conditions;
- To assess adsorption and desorption of pesticides in Irish soils;
- To compare model predictions from the MACRO model with observed trial data, thus acting as a validation stage for the model for Irish conditions;
- To create meaningful, spatially related vulnerability maps of groundwater with regard to the risk of pesticide contamination;
- To develop farm, catchment and regional risk management plans to minimise pesticide contamination in high risk areas; and
- To ensure that the techniques developed in this project will offer an opportunity for transfer of skills to other policy makers and stakeholders and national research capacity.

In addition, the EPA STRIVE Priority Pollutant Project focuses on pesticides (led by Dublin City University (DCU)). However, this project is not directly applicable to the Pathways research as it focuses on establishing suitable suites of analysis for point sources. A further pesticide study, also undertaken in DCU, and funded by NI Water, is investigating the development of suitable analytical methodologies for pesticides in drinking water (Fiona O'Regan, DCU, personal communication, 2009).

5.3.5 Knowledge gaps

In relation to source information for pesticides, there is currently very limited information available for use within a CMT. Unlike nitrogen and phosphorus, it has proven very difficult to estimate the export coefficient for pesticide to a catchment, given insufficient access available to pesticide usage databases and source information. It is understood that DAFF holds such a database, but considers it confidential. As noted previously, application of pesticides varies from field to field and year to year. Without information relating to farm-scale use and application, it will prove difficult to determine the export coefficient for various active ingredients and degradation products at catchment scale.

Furthermore, there are very limited data available for Ireland in relation to mobility and attenuation of pesticides. Although significant research has been conducted internationally on pesticide fate and transport in soils and water, there is a need for such research to be undertaken in Ireland to consider climate and the heterogeneous geological conditions. Given the variety of active ingredients applied to land in Ireland, the impacts of a mixture/cocktail of pesticides on attenuation processes should be considered. Consideration should also be given to establishing monitoring programmes capable of analysing degradation products that are sometimes as toxic to the environment as the parent active ingredient.

In a similar vein, monitoring data are limited in relation to pesticides in Irish groundwater and surface water. Currently there are pesticide data for drinking water, limited data from the dangerous substances surveillance monitoring programme in surface waters, and EPA groundwater monitoring network data. International research demonstrates that rainfall events and pesticide detection in surface and groundwater are linked (Muller et al., 2007; Blenkinsop et al., 2008; Nolan et al., 2008) and this is also noted in a review of the available groundwater monitoring data for Ireland (Sherry, 2009). In order to investigate pesticide impact in Ireland, rainfall event monitoring should be based around hydrological events, particularly in the period shortly following application. Moreover, appropriately adapted sampling protocols need considerations, e.g. the diffusion membrane samplers, along with developing methods for analysing degradation products.

The analytical methodologies used to analyse pesticides should also be reviewed as there appears to be a move away from gas chromatography towards alternative analytical methods in order to improve analytical precision and accuracy. Currently, the DWS for pesticides is 0.1 µg/l, which is considered very low in terms of analytical detections. Bloomfield et al. (2006) highlighted that as advances in analytical methods continue it is evident that the impact of pesticides in the environment is greater than originally thought.

In relation to development of a CMT for pesticides, the FOOTPRINT tool is scheduled to be available free of charge from October 2010. This tool focuses solely on pesticides and is a culmination of 20 years' research. However, before this can be considered, co-operation from DAFF, Teagasc and farmers should be sought. Without this co-operation it will be very difficult to obtain source (farm-scale) information to populate the CMT. Emphasis should be placed on validation of the FOOTPRINT model for Ireland as opposed to development of a new CMT to consider pesticides.

5.3.6 Recommendations

Therefore, based on the availability of data, pesticides cannot be considered to be contaminants of concern within the Pathways Project as the limited amount of existing data, ongoing research being completed elsewhere and complex analytical requirements would consume a disproportionate amount of project resources with poor to no projected benefit.

A suitable CMT (FOOTPRINT) has been identified within this report for pesticides but significant additional research and monitoring are required before this tool can be applied to Ireland. Recommendations for future research projects, outside the scope of the Pathways Project, include the following:

- Development of suitable analytical suites to include degradation products;
- More targeted monitoring of both surface water and groundwater;
- Further investigation of the impact of rainfall events on contaminant transport to water bodies;
- Additional research on the fate and transport of pesticides in Ireland, validating the information within the FOOTPRINT database;
- Co-operation and involvement from DAFF, Teagasc and farmers to develop a farm-scale usage database made available to researchers and regulators; and
- Use and validation of the FOOTPRINT model as the preferred CMT for pesticides in Ireland.

Based on recommendations from the Pathways Steering Committee, the ecological impact of pesticides on aquatic biota should be considered in one study catchment. The INTERACT project may be a suitable system to apply in the catchments and should be considered in the ecological component of the Pathways Project. An understanding of the ecological impact of pesticides may then be coupled with the FOOTPRINT model to provide a useful tool for assessing pesticides in relation to the WFD in the future.

5.4 Sediment

Sediment is a generic term used to describe any particulate matter that can be transported by fluid flow, and which is eventually deposited. The term encompasses all particles ranging from clay (<2 µm) to cobbles (60–256 mm) and greater. However, for the purposes of this study, it is the fine-grained sediment (i.e. clay, silt and fine sand) that is of most interest. Fine-grained sediments have greater surface area per unit mass than the coarser fractions and therefore have a greater capacity to adsorb. Fine-grained material is also relatively easily brought into suspension at a range of flow conditions and thus has greater environmental mobility than coarser material. The latter is mainly mobile as bedload or suspended load during high-energy hydrological events.

The relationships between flow and erosion, transportation and sedimentation are described by the Hjulstrøm Curve (Fig. 5.1). The curve shows that particles of a size just less than 1 mm require the least energy to erode, as they are fine sands that do not coagulate. Clays require a higher velocity to produce the energy required to split the very small clay particles that have coagulated. Larger particles such as pebbles are eroded at higher velocities, and very large objects such as boulders require the highest velocities to erode. When the velocity drops below the *line of critical velocity*, particles will be deposited or transported instead of being eroded, depending on the river's energy.

Particulates in water can be characterised into three broad groups: total dissolved solids, total suspended solids (TSS) and settleable solids (Table 5.8). Correlations can often be made between the sediment content and other properties of water which are more easily or cheaply measured. These are summarised in Table 5.8 from various sources.

Fine-grained sediment is an important diffuse source pollutant because it plays a major role as a vector for sorbed metals, nutrients, pesticides and other organic substances. Moreover, it can have significant impacts on aquatic ecosystems in its own right, for example

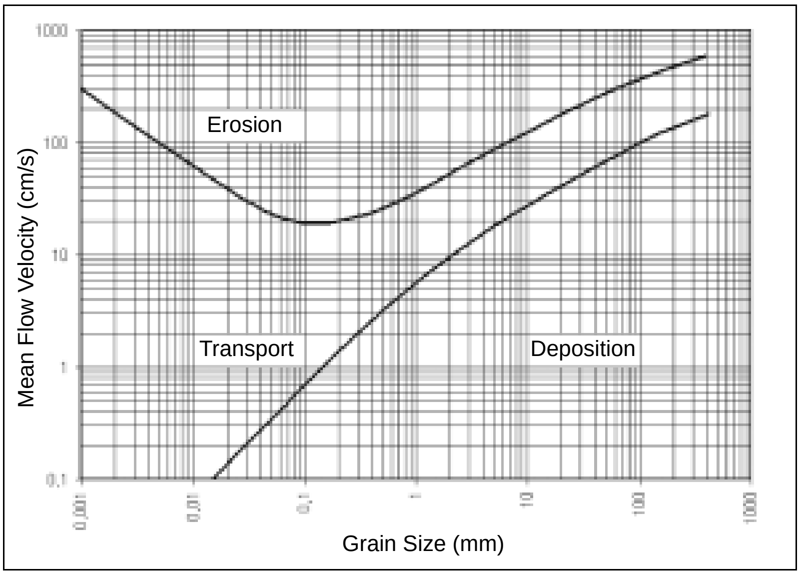

Figure 5.1. The Hjulstrøm Curve showing the relationships between flow and particulate erosion, transportation and sedimentation (downloaded and adapted from http://en.wikipedia.org/wiki/File:Hjulstr%C3%B6ms_ diagram_en.PNG).

Table 5.8. Operational definitions of particulates measured in waters (summarised from http://www.wikipedia.com unless otherwise stated).

Particulate matter	Operational definition	Correlations
Colloidal material (Macleod et al., 2007)	Suspended sediment in the range 1 nm to 1 µm	Usually just amalgamated into TDS
Total dissolved solids (TDS)	Suspended sediment (including colloidal material) passing through a 2-µm filter	Approx. = electrical conductivity. A conversion factor can often be applied
Total suspended solids (TSS or SS)	Suspended sediment not passing through a 2-µm filter	Can generate site-specific correlations with turbidity. Direct TSS measurements are more accurate but more expensive and are therefore less common
Settleable solids	Sediment of any size that will not remain suspended or dissolved in a holding tank not subject to motion	Does not include TDS or TSS

deposited silt can cover salmonid spawning habitats and prevent critical aeration of the river bed, while SS can reduce light penetration through the water column thereby affecting benthic organisms and visibility for fish (Walling and Collins, 2008).

Erosion and deposition of sediment in the landscape and stream migration sediment transfer processes are natural dynamic geomorphological processes that continuously deliver sediment into the environment. However, they can be greatly accelerated by anthropogenic activities, particularly forestry and agricultural practices. Delivery mechanisms may be gradual, as in the weathering of exposed bedrock, subsoils or soils, or may be more episodic, for example landslides, or bank and bed erosion in river/stream beds in response to extreme hydrological events.

Sediment sources are widespread and are temporally and spatially variable, contributing different fluxes to streams and rivers under different hydraulic conditions (Edwards and Withers, 2007). It is, therefore, important in assessing sediment fluxes in waterways that the source of the sediment and the transport mechanism be correctly identified, so that appropriate conceptual models can be developed and effective mitigation measures, if required, may be specifically targeted.

5.4.1 Sources

5.4.1.1 Bank and bed erosion

Bank erosion is a significant contributor of SS to streams, as well as nutrients and other contaminants where they are in particulate form. In the River Bush Catchment in Northern Ireland, bank erosion was found to be highest (e.g. mean 38.1 mm from the bank face per storm at one site) in regions of the catchment with the least cohesive bank materials during high flow conditions. Preferential transport of fine sand, silt and clay-sized material (<0.250 mm) was observed. Livestock poaching was found to exacerbate damage to banks at a localised scale and led to selective patches of bare land being susceptible to further erosion. Drainage maintenance work, forest clear-fell and dieback of macrophyte beds were also shown to influence the quantity of sediment transported through the study channels (Evans and Gibson, 2004).

A Danish study found that bank erosion contributed 50–75% of the TSS export in one study year (Laubel et al., 1999). Laubel et al. (2000) found in another Danish study of 26 small first-order streams that the median delivery of sediment to streams by bank erosion was 0.010 m^3/m of stream reach on one side only, but the mean value was more than double that at 0.023 m^3/m, emphasising the importance of single events for contributing large sediment loads to the overall total loss. They also found that the bank erosion rate was significantly higher in sandy soils than in loamy soils.

Channel bed erosion and remobilisation of sediment that has temporarily fallen out of suspension are also important sources of sediment in a river. As can be seen from the Hjulstrøm Curve in Fig. 5.1, it takes considerably less energy to deposit a particle than it does to erode or transport it. As the flows fluctuate, so too will the amount of sediment in suspension. During low flow periods or in pools or lakes, sediment accumulates on the channel bed, and it is not remobilised until the flows increase again sufficiently. In this way, sediment slowly progresses down the length of a stream channel until it reaches the outflow. The proportion of sediment that is intercepted and stored during transport and delivery frequently exceeds the proportion exported (Walling and Collins, 2008).

5.4.1.2 Agriculture

Agricultural activities contribute sediment to the landscape through damage to the soil by inappropriately timed or ill-suited land use, usually in wet weather (Harrod and Theurer, 2002). Activities may deliver sediment directly, for example in manures and slurries (see Section 5.2), or may modify the landscape in such a way that soil erosion is promoted.

Some examples of agricultural sources of sediment and their typical delivery mechanisms are listed in Table 5.9.

Bilotta et al. (2008) reported that while there has been a distinct research focus on soil erosion on lowland arable land and upland areas, lowland intensively managed grassland can also contribute significantly to sediment-related water quality problems. They found that during individual rainfall events, 1-ha grassland lysimeters yielded up to 15 kg of SS, with concentrations in runoff waters of up to 400 mg/l. Comparable yields were reported from arable land in Sweden by Alström and Åkerman (1992). Higher yields were reported from arable land in Denmark of between 71 and 88 kg/ha/year (Kronvang et al., 1997), and in the UK of between 75 kg/ha/year and 650 kg/ha/year (Withers et al., 2006).

Table 5.9. Agricultural sources of sediment and their sediment delivery mechanisms (compiled from Harrod and Theurer, 2002).

Source	Delivery mechanism
Cultivation, preparation of soil for planting	Exposure to precipitation of bare soil which is more vulnerable to erosion and promotes overland flow. Seed beds perpendicular to contours are of particular concern
Animal access to stream banks	Increased bank erosion. Direct delivery of manures
Compaction by heavy machinery, often in concentrated areas at farm gates, roads, farmyards, feeding racks, etc.	Reduces porosity and permeability and increases likelihood of overland flow
Out-wintering animals and intensive outdoor rearing units such as piggeries	Poaching and generation of muddy nutrient waters in heavy soils which can be rapidly transported to nearby watercourses
Land spreading of manures or other farmyard wastewater in wet weather	Direct application of sediment and nutrients to land surface, with a high risk of overland flow due to a precipitation event. Risk is increased where buffer zones around watercourses and riparian strips are not maintained
Farmyard runoff	Can become a point source of sediment and nutrient-rich runoff if not adequately managed
Land drainage	Provides fresh surfaces for new sediment erosion and facilitates easy access for sediment and nutrients to watercourses. Ancillary drainage treatments within fields may create preferential flow pathways
Overgrazing, often in upland areas (also applies to areas used for walking or other leisure activities)	Degradation of vegetation and exposure of soil to the elements resulting in increased overland flow
Modification of hydrological regime with major land-use change (e.g. forestry harvesting)	Increased discharge and bank erosion, or decreased discharge and additional sedimentation
Quarrying and mining of gravels from streams	Generation of turbid waters and release of previously stored sediment

There are a number of research papers, guidance documents and best practice codes available for the agricultural sector for use in Irish conditions. While many are focused on management of nutrients (e.g. DAFF and DoE, 1996; Tunney et al., 2000; EU, 2005; Ryan, D. et al., 2006), as the nutrients are often sorbed to SS, many of the recommendations are also appropriate for management of sediment.

5.4.1.3 Forestry

Ground preparation, planting and harvesting during forestry operations are the key times at which soil erosion and the subsequent delivery of sediment to watercourses is likely to occur. The principal sources of soil erosion are cultivation techniques, forest road development, river/stream crossings and soil loosened by heavy machinery. The forestry industry has produced a series of guidelines detailing best practice techniques for reducing sediment transport and delivery to streams (Forest Service, 2000). These include:

- Use of buffer zones, cut-off drains, brash mats and sediment traps;
- Maintenance of intact riparian zones;
- Construction and maintenance of appropriate forest roads and river crossings such as bridges rather than fords;
- Selection of appropriate cultivation techniques such as ripping or mounding instead of ploughing; and
- Timing of operations using heavy machinery to avoid wet weather.

It has been stated that it is poor practice that leads to water quality issues and not the forestry itself (Crowley, 2004). There is some support for this statement in the literature (refer to Section 5.3.1) as there appears to be a range of in-stream responses to forestry operations reported.

5.4.1.4 Urban

Runoff in urban environments responds quickly to rainfall events and can rapidly deliver sediment to streams as there is typically little infiltration through the made ground. In an urban area study in Massachusetts, Solo-Gabriele and Perkins (1997) compared stream flow hydrographs with time series plots of SS concentrations and used hydrograph separation to identify different sources of sediment. They found that peak SS concentrations reached more than 85 mg/l, while during non-storm conditions concentrations were relatively constant, between 3 mg/l and 7 mg/l. At flows greater than 0.4 m^3/s, the constant sediment contribution was attributed to groundwater inputs, plus the contribution from channel erosion. At flows less than 0.4 m^3/s, the sediment was deposited. The study showed that sediment transport was associated with three distinct components in the hydrograph:

1. Quick storm flow (storm sewer flows, direct precipitation into the channel and direct runoff close to the channel);
2. Slow storm flow (interflow, groundwater associated with the raising of the water table due to storm water infiltration and waters from upstream source areas affected by the routing response); and
3. Long-term baseflow (influenced by seasonal climatic changes and large-scale abstraction).

Rainfall also influenced sediment transport, as did the storage effects of large reservoirs which contributed seasonal effects such as algal growth and deposition of particulates.

A study in the Bradford Beck Catchment in west Yorkshire, UK, found that for individual storms, the sediment yields from an urban sub-catchment were generally higher than those from a rural system, although the annual yields were comparable (Goodwin et al., 2003). In the urban setting, the peak flow events were dominated by the impact of the combined sewer overflows discharging, which delivered higher peak sediment concentrations than in the rural areas where sediment transport was supply limited.

Sediment transfer in urban areas is generally well studied in the field of storm water runoff management and as it is not a focus for this study it is not considered further.

5.4.2 Controls on mobility

Based on all the research carried out for this literature review, it appears that the two main pathways for delivery of sediment from the land surface to streams are overland flow and drain flow, including subsurface field drain flow. However, sediment transport via streams and rivers is also an important pathway through a landscape, which needs to be considered as it presents challenges when conceptualising sediment transfer using data from discrete sampling points. As sediment transfer can influence the mobility of other contaminants, a brief discussion on that topic is included at the end of this section.

5.4.2.1 Overland flow

Overland flow is a common delivery mechanism for sediment and other associated contaminants to aquatic receptors and can be broadly considered in terms of three processes:

1. Sheet erosion;
2. Rill erosion; and
3. Gully erosion.

Sheet erosion is often widespread, diffuse, turbid surface flow that doesn't cut channels, while rill and gully erosion concentrate the sediment into distinct channels or larger gullies (Harrod and Theurer, 2002). This may give rise to preferential contaminant transport pathways across the ground surface, not only for sediment, but also for other contaminants of concern in this study.

A study in Denmark (Kronvang et al., 2000) found that rill erosion was significantly higher on winter cereal and ploughed fields, compared with grassland fields and untreated stubble, and was also very temporally variable over the 6 years of the study. A large proportion of the fields was found to have no rill erosion at all. They calculated the average annual soil loss from fields to be 0.3 m^3/ha, 44% of which was due to rill erosion. The average annual losses of associated nitrogen and phosphorus were estimated as 0.24–10 kg N/ha and 0.17–0.45 kg P/ha, respectively.

Buffer zones are a widely selected tool used by most management and regulatory bodies to minimise the effects that forest operations, such as clear-felling, might have on aquatic habitats (Giller et al., 2002). They are strips of land vegetated by trees and other vegetation bordering watercourses, often of designated size and deliberately left unharvested or deliberately planted. Research has found that in general they are effective in preventing the input of sediment and soil into streams, but that the presence of a buffer strip alone does not always prevent an input of sediment into a stream, particularly if there is even a single direct link between a clear-fell area and the stream, such as a runoff channel, a bank collapse or a crossing point for machinery (Giller et al., 2002).

5.4.2.2 Drain flow and subsurface field drain flow

The term drain flow can be used to describe (a) artificial drains and channels around a field boundary that deliver overland flow to the nearest natural stream channel, and (b) subsurface field drains within a field, such as tile drainage, that deliver infiltrating water to nearby drains or natural stream channels. Both types of drains are important sources of sediment.

Walling et al. (2008) used source fingerprinting techniques in seven sub-catchments in the UK to provide information on the relative contributions of surface and channel/subsurface pathways[3] to the SS and PP concentrations. They found that channel/subsurface flow contributed 40–55% of the SS flux in the Wye Catchment and 1–41% in the Avon Catchment, and contributed 21–43% and 1–54% of PP, respectively.

The significant contribution that subsurface field drains make to stream flow and sediment flux is well documented. Russell et al. (2001) demonstrated that field drains (tile and mole drains) in two small agricultural catchments that were extensively drained accounted for 27–55% of the total SS load. Bank erosion in the same catchments contributed 10% or less, and surface sources accounted for 34–65%.

Kronvang et al. (1997) found that subsurface tile drains were an important pathway for the transfer of sediment and PP to streams via preferential flow from the topsoil, particularly during storm events. They found that in a

3. Channel and subsurface pathways in this study referred to actively eroding channel margins, ditch and gully systems and incised tracks that cut into the underlying subsoil and regolith.

small agricultural catchment that was 50% drained, the drainage water accounted for an average of 25% (range 3–69%) of SS losses during 17 single storm events. On an annual basis this amounted to 11–15% of the total catchment export of SS.

In contrast, however, results from the GrasP (Grassland sediment and colloid Phosphorus) project at a site in Devon (see Section 5.4.3.2 for further discussion on the project) suggest that subsurface drainage causes a reduction, by as much as 50%, in the total quantity of SS and TP transferred from 1 ha of intensively managed grassland plots (Bilotta et al., 2007).

5.4.2.3 Sediment transport via watercourses

The link between (a) upstream erosion and sediment mobilisation and (b) downstream sediment yield and contaminant transfer is not clear-cut. This is because there is usually sediment retention, with both long-term and short-term sediment storage at intermediate locations in the landscape, such as at the foot of slopes, the river channel and the flood plain (Walling and Collins, 2008). This presents challenges in assessing sediment flux through a catchment when the number of monitoring points is limited.

In the River Bush study in Northern Ireland (Evans and Gibson, 2004), temporal and spatial variations were found in fine sediment (<5 mm) transported through the river channel in suspension (median value range of 0.025–0.625 kg/m/week) and along the bed (median value range of 0.025–6.15 kg/m/week). The large range of sediment flux in results indicated that some parts of the river experienced a relatively high sediment load in comparison with other reaches. At some sites, sediment load was limited by sediment transport factors, while at others sediment source availability was the controlling factor.

A study in Denmark (Kronvang et al., 2002) looked at the loss of SS from eight small agricultural catchments (average 9.5 km^2) and found that there was a significant linear relationship between annual mean SS loss and annual mean runoff. Total phosphorus loss was also linked to sediment loss. The study's results indicated that new active source areas and hydrological pathways become important with increasing precipitation in the catchment. The findings are consistent with those hypothesised by Doody et al. (2006) from expanding CSAs for phosphorus (see Section 4.2), further reflecting possible associations between sediment and PP.

This linear relationship between SS and flow in small catchments is in contrast to the variabilities found in the much larger River Bush Catchment (340 m^2) and highlights the problems of upscaling and the importance of understanding sediment transport processes at the whole catchment scale.

5.4.2.4 Sediment control on the mobility of other contaminants

Sediment can be a vector for a wide array of contaminants and, therefore, the processes controlling sediment transport can also control the mobility of other contaminants. Sediment deposition can be an important mechanism for the removal of contaminants from the water column, while sediment re-suspension and transport can play an important role in the mobilisation of contaminants through an aquatic ecosystem (see Sections 4.2, 5.2 and 5.3). In addition to the sorption and transport of contaminants, biotic and abiotic processes associated with sediments can be also important in transforming pollutants. A number of different processes are available for the sorption, transport, transformation and re-release of pollutants which depend on the geological nature of the sediment, the microbial community structure and activity, and the chemical composition of the water (Baldwin et al., 2002). Once pollutants enter waterways, they can be become attached to sediment particles and be transported a long distance downstream before the sediments are deposited and the pollutants are re-released.

The links between sediment and phosphorus transport, in particular, have been extensively studied. Jarvie et al. (2008) found that in livestock-dominated headwater streams TP loss was dominated by PP and was linked to different processes at low flows and high flows (during storm events):

- Low flow conditions
  In-stream sediment precipitation/deposition, e.g. direct deposition of pathogens and nutrients in manure, with sorption/co-precipitation of phosphate and/or localised in-channel mobilisation

of sediment (by cattle or channel clearing operations);

- Storm events;
  Sediment erosion and transportation associated with near-surface runoff.

In a Danish study of 26 small first-order streams, Laubel et al. (2000) found that, on average, PP constituted 62% of the TP export from sandy and loamy soils, and the majority of that PP was derived from bank erosion. Using some assumptions and data for nutrients in bank materials, they were able to estimate the nutrient losses arising from bank erosion to be of the order of 0.4–1.1 kg/ha for nitrogen and 0.1–0.4 kg/ha for phosphorus. Surface runoff was found to contribute significantly in wet years.

5.4.3 Studies to date

The impacts of forest operations on sediment transfer are widely recognised and there is, therefore, a significant body of research in this area, including research specific to Ireland. Studies in the literature on transport of sediment from agricultural activities appear to be mainly focused on transport of sediment-associated nutrients from cultivated areas, although there is some recent research in the UK into grassland areas (see the GrasP project described in Section 5.4.3.2). This emphasises the important linkages between sediment and nutrient transfer. Some examples of the more relevant studies are provided below.

5.4.3.1 Ireland

Forestry research in Ireland has looked at the impacts of clear-felling on sediment transport levels and found a range of variable results. Cummins and Farrell (2003b) found that there were no impacts of clear-felling on SS in drains from a forestry site at Cloosh, western Ireland. Gallagher et al. (2000), however, monitored 16 clear-fell sites in the south-west of the country, before and after felling, and found that levels of SS in stream water increased at 10 of the 16 sites during storm events. They found that increases were generally short term during the clear-fell operations. Where they were more long term, they were associated with large post-felling flood events which washed soil from the site into the stream. Increases in soil and sediment on the stream bed originating from the clear-fell site were found in seven out of the 16 sites.

Rodgers et al. (2007) found that in baseflow conditions, clear-felling and extraction had no impact on SS levels, but that daily peak concentrations doubled during the winter immediately following a late summer harvest. In the 12 months following the harvest, the net SS rate from the harvested catchment was 272 kg/ha/year, compared with a net rate from the undisturbed forest catchment of 172 kg/ha/year.

The impacts of forestry on aquatic ecology and water quality are not ubiquitous. They are very much catchment specific and are heavily dependent on whether, and how well, the best practice forestry guidelines have been followed (Giller and O'Halloran, 2004).

Studies into sediment transport in agricultural areas in Ireland are mainly focused on the links with phosphorus transport. Douglas et al. (2007), for instance, looked at the magnitude of phosphorus and sediment transfers at three different scales in the Oona Catchment (field, 0.15 km^2; farm, 0.62 km^2; and landscape, 84.5 km^2) and found that phosphorus transfer increased with scale, with the higher transfers at landscape scale related to soluble inputs between storms. Despite being a grassland catchment, more than 50% of the phosphorus fraction transferred was found to be in particulate form and was strongly correlated with SS, manganese and iron, during both storm and non-storm periods. They concluded that soluble phosphorus may be entrained to equilibrium by manganese- and iron-rich suspended sediment from multiple sources, including stream bank and bed sediments.

5.4.3.2 UK

In addition to the studies already discussed above, there are a number of other projects of relevance under way in the UK. The MOPS projects (http://www.lec.lancs.ac.uk/cswm/mops/po.php) are looking at measuring the effectiveness of mitigation measures, such as farm ponds and constructed wetlands, for reducing phosphorus and sediment losses from agricultural lands. The project website acknowledges that much of the diffuse pollution loss may not occur in runoff over the field surface, but may be transferred to the stream through the soil or field drains. Ongoing research is concentrating on mitigation measures on the land surface as there are not as yet practical in-field measures for reducing subsurface losses.

The major GrasP project, currently under way in the UK, is looking at how intensive grassland management influences sediment and colloidal phosphorus losses (refer to Table 5.8 for definitions) to surface waters at the plot, field and catchment scales (Macleod et al., 2007). Experimental field-scale lysimeters have been established for two drained and two undrained hydrologically isolated plots. Flow quantity and quality have been measured along the surface pathway (0–0.3 m bgl), and the subsurface drainage pathway (0.85 m bgl), in response to hydrological events (Bilotta et al., 2007). Natural and artificial tracing techniques are also being employed to look at the transport of particulate, dissolved and colloidal slurry phases (Old et al., 2007). Results show that a lack of understanding of the link between hydrology and sediment dynamics limits further insights into phosphorus transfer dynamics. The difficulties with upscaling from the plot to catchment scale were also highlighted (Kreuger et al., 2007).

The River Bush Integrated Monitoring Project was initiated as a pilot monitoring study for Northern Irish catchments, to measure both fine and coarse sediment loads, with a view to recommending improved management strategies, particularly with respect to addressing fine sediment content and oxygen concentrations in the river for the protection of salmonid spawning habitats (Evans and Gibson, 2004).

The Flood Risk Management Research Consortium in the UK is conducting research into flood science and flood engineering and one of its key areas of interest is looking at the role of sediment dynamics on flood management (http://www.floodrisk.org.uk). During Phase One of the research programme, the group looked at, amongst other things, how river sediment dynamics and morphological changes affect flooding. A sediment toolbox of approaches was developed for looking at sediment at a broad scale. Field studies and modelling were carried out to assess the role of sediment dynamics in estimating flood risk and predicting sediment-associated contamination. Field studies in Wales found that sediment yields are significantly increased in agriculturally improved upland areas. This research is ongoing and while it is obviously focused towards flood risk management, there are elements of the work that will be applicable to the Pathways Project research.

5.4.3.3 Europe

There have been a number of studies in Denmark (discussed above) that have looked at characterising and quantifying sediment transfer along the various hydrological pathways. While these studies have been relatively successful in quantifying and modelling sediment transfer in Denmark, some further work would be required to determine whether the results were transferable for modelling purposes here.

The EU has developed a Thematic Strategy on Soil Protection and a proposal for a Soil Framework Directive. Assessment and management of soil erosion processes are a priority of the directive (http://ec.europa.eu/environment/soil/three_en.htm). The objective of the thematic strategy is to protect soil by reducing degradation. Erosion and compaction (which leads to erosion) are listed as two of the major threats.

Various projects at the European level have been funded to look at different aspects of the issue of soil erosion, just four of which include:

1. SoCo Project – Sustainable Agriculture and Soil Conservation, http://soco.jrc.ec.europa.eu/index.html;

2. SOWAP Project – Soil and Surface Water Protection using conservation tillage in northern and central Europe, http://www.sowap.org/;

3. Soil Erosion and Global Change (COST Action 623), http://soilerosion.net/cost623/annex.html; and

4. On- and Off-Site Impacts of Runoff and Erosion (COST Action 634), http://soilerosion.net/cost634/.

A major publication entitled *Soil Erosion in Europe* (Boardman and Poesen, 2006), the culmination of the first COST Action project, includes area-specific soil erosion rates and soil erosion risk maps.

5.4.3.4 International

Sediment is seen as the single greatest polluter of water in the USA (Nicholls, 2006). Consequently, there is a range of both research and management programmes currently under way, many of which focus on the development of modelling tools. Of particular note, the Agricultural Research Service of the Department of Agriculture in the US has been developing new technology and modelling tools for estimating sediment yield from catchments (http://www.ars.usda.gov). Similarly, the United States Geological Survey (USGS) has developed a watershed model called SPARROW (SPAtially Referenced Regression On Watershed Attributes), which provides managers with predictions that allow them to quantify, locate and assess sediment sources and the factors that affect the fate and transport of sediments (Brakebill, 2009).

At smaller scales (~300 km^2), a fingerprinting approach is being developed by the USGS to identify CSAs and retention areas for sediment and nutrients, especially phosphorus (Gellis, 2009). This approach compares physical and chemical properties of the transported suspended sediment with those of potential sediment sources within the catchment. Sources have even been determined for individual storm events.

In a related programme, the USGS is also promoting the use of the sediment budget approach (refer to Section 5.4.3.6) to help water resource managers understand the linkages between source areas, depositional sites and sediment export. Based on this approach, mitigation measures can then be specifically targeted in areas of highest erosion where they will have most effect (Gellis, 2009).

5.4.3.5 Data availability

In rivers, electrical conductivity is widely monitored as part of the EPA's monitoring programme under the WFD during regular water sampling. Turbidity is not routinely measured but TSS is monitored directly under specific sub-programmes as shown in Table 5.10.

Table 5.10. Total suspended solids sampling regime.

Sampling sub-programme	No. of sites	Frequency
Freshwater Fish Directive	112	Monthly
Mine sites (point sources)	13	Quarterly
Special forestry subnet	13	Monthly

Just two of the 34 designated salmonid rivers were reported as having recorded TSS parameter exceedances >25 mg/l in the period 2004–2006, the River Maine (average 48 mg/l) and the River Swilly (average 54 mg/l).

No continuous measurement of sediment levels or their surrogates are currently undertaken by the EPA. Potential benefits can be derived, however, from such data in better characterising sediment/discharge relationships and their impact on aquatic ecosystems.

In groundwater and lakes, conductivity and turbidity are both routinely monitored across most sites under the WFD, while TSS is not directly measured.

As TSS is one of the major environmental concerns in forestry operations, data have also been collected as part of various specific forestry research projects (e.g. in the Srahrevagh Catchment in County Mayo; Rodgers et al., 2008).

5.4.3.6 Methods of determining sediment fluxes

Various methods can be used to conceptualise and assess the sediment transfer through a catchment. A catchment sediment budget approach has been recommended by Walling and Collins (2008) to conceptualise sediment transport through a catchment. The approach identifies and attempts to quantify the key sediment sources, sinks and outputs from a system within a mass balance framework and is useful for highlighting CSAs.

Rare earth element oxides have been used to trace sediment CSAs in the UK by Stevens and Quinton (2008) and have been described as a quick and cheap method of identifying sources of eroded sediments with potential for use for determining erosion rates. The source fingerprinting techniques used by Walling et al. (2008) provided information on the relative contributions of surface and channel/subsurface pathways to the suspended sediment and PP concentrations in the Wye and Avon Rivers. Recent completion of the Tellus geochemical survey of Northern Ireland has highlighted the significant levels of geochemical heterogeneity across the province, and the potential for the application of comparable techniques to those discussed above to Irish RBDs, assuming that similar levels of heterogeneity apply across the rest of Ireland (http://www.bgs.ac.uk/gsni/tellus/map_viewer/application/soils_as.html).

Withers et al. (2007) have developed a simple laboratory soil test that quantifies dispersed particles and associated phosphorus in the same suspension. Test results correlated well with the amounts of suspended sediment, total phosphorus and dissolved phosphorus in overland flow generated by indoor simulated rainfall. The test can be used to help identify the comparative risk of sediment and phosphorus mobilisation from CSAs connected via both surface and subsurface pathways.

5.4.4 Conceptual model based on above findings

Based on the knowledge gained from the current literature review, which will be improved with further reading as the project progresses, the key points of the preliminary conceptual model for sediment transfer are as follows:

- Sediment is derived from natural geomorphological processes but natural fluxes can be greatly exacerbated by agricultural, forestry and urban activities.

- Sediment is primarily transported from land to watercourses via overland flow into drains or natural channels, and through preferential flow paths into subsurface drainage, rivers and groundwater. Bank and bed erosion are important in-stream sources.

- Sediment is a vector for transporting sorbed particulates, including nutrients, pathogens and pesticides. Sediment therefore has potential to be used as a proxy for other contaminants in monitoring programmes.

- Sediment loads in a stream may be transport or source limited, and are often temporally and spatially variable.

- Understanding sediment transport from the land surface to discrete sampling points in watercourses is complicated by the presence of different sources and sinks of sediment within the catchment, some derived from natural geomorphological processes, some artificially derived.

- Between discrete sampling points, the watercourses themselves also need to be considered as pathways. Sediment sources and sinks in the channel banks, beds and flood plains can provide additional sediment and contaminants to a system, or significantly increase the retention time, depending on the flow and geomorphological conditions. Sediment transport and delivery mechanisms are an important factor in interpreting sediment monitoring data.

- Linear relationships between flow and sediment are more likely to exist in smaller catchments than in larger ones. This is possibly due to the added complexities of temporal and spatial variability in geomorphological processes along the length of a larger river. This highlights the difficulties with upscaling.

- Sediment in watercourses impacts on the aquatic ecosystems by reducing water quality and degrading habitats. It also results in increased filtration costs at drinking water supplies.

5.4.5 Knowledge gaps

The impacts of forestry operations on stream water quality and the transport of PP associated with sediment at the field scale appear to be the most well-studied areas of sediment transfer processes in Ireland. Some of the key knowledge gaps appear to include the following:

- Understanding the sources and sinks within a catchment and the sediment transfer processes, including stream and bank erosion, and how they relate to sediment monitoring results at discrete monitoring points;

- The relationships in specific catchments between sediments and nutrients, pathogens and pesticides;
- There are only limited high-resolution temporal data concerning sediment fluxes in Irish rivers, principally using surrogate measurements such as turbidity; and
- Upscaling sediment and associated nutrient transfer understanding from field, farm and sub-catchment scales to catchment and basin scales.

5.4.6 Recommendations

The following are the recommendations for work to be carried out by the Pathways team:

- Carry out geomorphological surveys in the study catchments selected for further investigation to identify major sediment sources and sinks, and the impacts of hydrological changes on sediment transfer. Generate a catchment sediment budget if possible. These data can then be used in modelling contaminant transfer throughout the study catchments.
- Look at relationships between sediment and flow, preferably at different scales, and between sediment and other contaminants of interest, i.e. pesticides, nutrients and pathogens. These relationships can be used in the models underpinning the CMT.
- Carry out high-resolution temporal monitoring of sediment fluxes to better understand sediment mobilisation and transportation mechanisms such that these can be incorporated into the contaminant modelling components of the CMT.
- Propose sediment delivery and transport hypotheses using values from the literature. Conduct further sampling and consider sediment fingerprinting and transport modelling to test the hypotheses. This understanding will then inform the contaminant transport and attenuation components of the CMT.

The findings of this review suggest that it may be worth considering focusing in on sediment in comparison with some of the other contaminants of interest, as many of the latter are often associated with sediment and it is likely that understanding sediment transport will be important for understanding and modelling transport of other contaminant groups.

5.5 Summary

Table 5.11 provides an overview of the knowledge and data gaps in relation to pathogens, pesticides and sediment. Data availability for pesticides is considered insufficient to populate a CMT. The project team therefore recommends that FIOs, sediment and nutrients are investigated as part of the Pathways Project. Substantial additional research will be required before there will be enough data available for modelling and CMT development for pesticides. The additional research required is beyond the scope and resources available to the Pathways Project team.

Table 5.11. Summary of availability of data and knowledge.

Sufficient literature/data available on:		Sediment	Pathogens	Pesticides
Source – application in Ireland		n/a	o	x
Irish land use and variations		o	o	x
Irish groundwater monitoring data		✓	✓	o
Irish surface water monitoring data		o	o	o/x
Irish monitoring methodologies		✓	o	x
Irish analytical methodologies		o	✓	x
Scale		o	x	x
Mobility	Ireland	o	o	x
	UK	✓	✓	✓
	Europe	✓	✓	✓
	International	✓	✓	✓
Attenuation	Ireland	x	x	x
	UK	o	o	x
	Europe	✓	o	✓
	International	✓	o	✓
Pathways	Ireland	x	x	x
	UK	✓	o	x
	Europe	✓	o	o
	International	✓	o	o
Contaminant transport models	Ireland	x	x	x
	UK	x	o	x
	Europe	o	o	✓
	International	✓	✓	✓
Ongoing research	Ireland	✓	o	x
	UK	✓	✓	✓
	Europe	✓	✓	✓
	International	✓	✓	✓
Catchment management tool	Ireland	x	x	x
	UK	?	o	✓
	Europe	?	o	✓
	International	✓	o	✓

✓ Sufficient data to populate catchment management tool.
o Some data available to populate catchment management tool.
x Insufficient data available to populate catchment management tool.

6 Receptors – Irish Water Quality

6.1 Introduction

The WFD's requirement to consider water bodies in a holistic manner represents a significant departure from previous concepts of water management, which viewed water bodies as isolated entities (Pollard and Huxham, 1998), and the links between water occurring in different parts of the hydrological cycle and how transport and exchange mechanisms impact receptors must now also be considered. This chapter aims to highlight the receptors present in RBDs and how they are used to assess status. This includes an overview of biological indicators used in the assessment of potential impact of anthropogenic inputs on fresh waters and some of the metrics routinely applied. Metrics are defined as "*measurable parts or processes of a biological system shown to change in value along a gradient of human influence*" (Karr and Chu, 1999). Specific reference is made to those metrics used in Ireland and in particular metrics that have been inter-calibrated for the WFD. Given that most of the metrics involve some comparison with type-specific conditions, an outline of river and lake types is included. This is followed by some consideration of the impacts of certain pressures on aquatic biota. This chapter is not intended to be an exhaustive review, but rather to highlight some of the key issues and emerging knowledge gaps.

6.2 Receptors of Concern

6.2.1 Surface water

The WFD states that surface water bodies, which include rivers, lakes, transitional waters (estuaries and lagoons), coastal waters, and artificial and heavily modified water bodies, must be assigned a status based on their chemical and ecological status. The ecological status of natural surface waters falls into one of five classes: High, Good, Moderate, Poor, or Bad, while artificial or heavily modified surface waters are subject to a different set of standards that focus on ecological potential rather than ecological status; these are classified as either Good Ecological Potential (GEP) (equivalent to Good Status) or less than Good Ecological Potential (equivalent to Moderate Ecological Status). Biological and physico–chemical quality elements are combined on the 'one out, all out' principle, that is if either biological or physico–chemical status is poor, then the overall status for the water body is poor (SWSG, 2008a).

6.2.1.1 Natural surface water ecological status

The surface water ecological classification for natural waters is a combination of the following three factors (ERBD, 2008b):

1. *Biology*

   Surface water biology classification systems describe the extent to which pollutants associated with human activity have altered the ecological communities present in water bodies by comparing the condition of aquatic animals and plants with undisturbed or pristine conditions. The organisms presented in Table 6.1 are widely used as bio-indicators to assess the impact of pollutants on aquatic ecosystems for rivers and lakes and will be discussed in more detail in Section 6.3 onwards.

Table 6.1. Ecological communities in river and lakes (ERBD, 2008b).

Animals	• Fish • Aquatic invertebrates (e.g. insects, crustaceans, molluscs, worms)
Plants	• Diatoms (microscopic plant organisms) • Macrophytes (larger aquatic plants) • Filamentous algae • Phytoplankton (a microscopic plant containing the green pigment chlorophyll) in lakes and deep rivers

2. *Supporting water quality conditions (general conditions and specific pollutants)*

   In addition to the use of biological classification systems to determine ecological status, the general physico–chemical status of waters is assessed by measuring oxygen, nutrients, transparency, temperature, acid status and salinity. Water is also analysed for concentrations of specific chemical pollutants, including metals, pesticides and hydrocarbon compounds, of local relevance in Ireland. The levels or concentrations of these physico–chemical parameters and specific pollutants are then compared with environmental quality standards set to protect aquatic health (ERBD, 2008b).

3. *Supporting hydrology and morphology (physical condition)*
   The third factor in determining the ecological status of a surface water body is the assessment of hydrological and morphological conditions to ensure that conditions are suitable to support aquatic ecosystems. Hydrological conditions are measured by recording river flow, lake level and tidal patterns, while morphological conditions are assessed by surveying channel, substrate and bed shape and physical conditions (ERBD, 2008b).

6.2.1.2 Surface water chemical status

The chemical status of natural surface waters is assessed as either Good or Fail. The majority of Irish waters have yet to have chemical status assigned. Concentrations of priority substances, which include metals, pesticides, hydrocarbons, volatiles and hormone-disrupting compounds, have been targeted for monitoring to determine the chemical status of surface waters by comparing with Environmental Quality Standards (EQSs), set to protect the ecological health of aquatic ecosystems in compliance with the Priority Substances Directive (ERBD, 2008b). Determination of the Irish EQSs for these priority substances is currently at the consultation stage and will be finalised in the near future (Ciaran O'Donnell, EPA, personal communication, 2009).

Table 6.2 provides a summary of the interim status of rivers, lakes, transitional and coastal waters in Ireland (SWSG, 2008a,b,c).

6.2.1.3 Artificial and heavily modified water bodies

The WFD defines Artificial Water Bodies (AWBs) as bodies of water created by human activity that cannot meet Good Ecological Status (GES). In a similar vein, Heavily Modified Water Bodies (HMWBs) are defined by the WFD as bodies of water which, as a result of physical alterations by human activity, are substantially changed in character and cannot, therefore, meet GES. HMWBs are distinct from AWBs in that they are changed or altered from their natural character. AWBs have been created by human activity where no water body previously existed (SWSG, 2008e). Instead of the GES used in the assessment of natural surface water bodies, the environmental objective for HMWBs and AWBs aim to achieve GEP by 2015. The approach to assessment of GEP is based on the draft UK Technical Advisory Group (TAG) guidance *Guidance on the Classification of Ecological Potential for Heavily Modified Water Bodies and Artificial Water Bodies* and involves an assessment of mitigation measures as an alternative approach for hydromorphological classification. The hydromorphological class is combined with the physico–chemical and biological class for the water body to determine the final ecological potential class (SWSG, 2008d,e).

6.2.2 Drinking water

Drinking water quality is not assigned a status as part of the WFD. In Ireland, 83.7% of drinking water from public supply originates from surface water (rivers and lakes), with 8.8% originating from groundwater and the remaining 7.5% from springs. Group water schemes and small private supplies are more reliant on groundwater or spring water. DWSs are set out in the

Table 6.2. Percentage of water bodies by status (interim) (SWSG, 2008a,b,c).

	High (%)	Good (%)	Moderate (%)	Poor (%)	Bad (%)	Unassigned (%)	Total (%)
Rivers[1]	11	35	35	17	2	1	100
Lakes	39.58	26.59	30.64	1.84	1.10	0.25	100
Transitional and coastal waters	14	10	33	–	–	43	100

[1]Values have been rounded up to the nearest whole number.

Drinking Water Regulations (2007). All monitoring results are assessed against these standards. Based on monitoring results for 2007 from 952 public water supplies, 830 public group water schemes, 588 private group water schemes and 888 small private supplies, the EPA (2008) concluded the following:

- *E. coli* was detected on at least one occasion in 52 public water supplies during 2007 (down from 77 in 2006), indicating that intermittent contamination of 5% of public water supplies occurred in 2007 (see Section 5.2);
- *E. coli* in private group schemes was detected 184 times in 2007 (246 in 2006), meaning that over 31% of private group water schemes were contaminated at least once during 2007;
- Overall compliance with the chemical standards is 99.1%;
- In terms of chemical quality, compliance with several indicator parameters, in particular aluminium and turbidity parametric values, remains poor; and
- Cryptosporidiosis is an issue in some water supplies, e.g. Galway City supply.

FIOs, such as *E. coli*, are not considered within the WFD. However, drinking water monitoring results are useful as they can be indicative of faecal contaminants and may also be associated with elevated nitrogen and phosphorus concentration due to wastewater treatment plants, malfunctioning septic tanks and livestock defecating near and in streams. These issues provide part of the motivation for further investigating the fate and transport of pathogenic micro-organisms within the framework of this project (see Section 5.2).

6.2.3 Groundwater

Classification of groundwater bodies differs from that undertaken for surface water bodies, in that the surface water status relates to ecological status. Groundwater status does not directly assess ecology, although the classification process takes account of the ecological needs of the relevant rivers and groundwater-dependent terrestrial ecosystems (GWDTEs); these depend on contributions from groundwater and also assesses the impact of pollution on the uses (or potential uses) of groundwater from the groundwater body, e.g. for drinking water supply. Groundwater status is determined by assessing chemical and quantitative status and may be classified as Good and Poor (GWG, 2008).

Groundwater classification is based on both the EU Working Group C *Guidance on Groundwater Status and Trends* (2008) and the UK TAG *Proposals for a Groundwater Classification System and its Application in Regulation* (2007). The guidance stipulates that, in order to determine groundwater status, a number of tests must be undertaken in relation to the quality and quantity of groundwater. These tests should be applied where there is risk that groundwater will not achieve both good chemical and quantitative status. Where no risks are identified, a water body can be classed as Good status without undertaking the more detailed investigations. If a groundwater body fails any of the classification tests, then the groundwater body is at Poor status (GWG, 2008). The four quantitative and five chemical tests applied by the EPA for groundwater bodies in the Republic of Ireland are summarised below (ERBD, 2008b).

Groundwater quantities are examined by the following tests (ERBD, 2008b):

1. Water balances of groundwater bodies;
2. Impacts to the natural flow conditions of rivers and streams;
3. Impacts to groundwater flow, discharges and levels within the catchment boundaries of groundwater-dependent wetlands; and
4. Saline intrusion in coastal settings.

Groundwater quality tests examine (ERBD, 2008b):

1. Water chemistry of the groundwater body;
2. Impacts on drinking water protected areas, including microbiological quality;
3. Impact on surface water quality;
4. Qualitative impacts on groundwater-dependent wetlands; and
5. Evidence of saline intrusion in coastal settings.

The thresholds set for quantity are intended to ensure the availability of groundwater resources to both humans and groundwater-dependent ecosystems. The thresholds set for quality relate to DWSs and trends in groundwater (ERBD, 2008b).

Table 6.3 outlines the number of water bodies in Ireland that fall under the classes of Good and Poor for chemical, quantitative and combined overall groundwater interim status (GWG, 2008).

Table 6.3. Numbers of groundwater bodies at each status (interim) (GWG, 2008).

Status	Chemical (quality)	Quantitative	Combined
Good	646	753	642
Poor	111	4	115
Total	757	757	757

6.2.3.1 GWDTEs

A number of Irish terrestrial ecosystems rely on groundwater to ensure ecological status. As part of the status assessment of groundwater, the Groundwater Working Group (GWG) highlighted GWDTEs as separate groundwater bodies in those cases where a risk was identified in the anticipation that such formal designation would raise the profile and visibility of GWDTEs in relation to the WFD and river basin management (ERBD, 2008b).

Kilroy et al. (2008) defined GWDTEs as terrestrial habitats/species that are dependent on groundwater to maintain the environmental supporting conditions required to sustain that habitat and/or species. For example, groundwater may provide a direct input to the habitat, such as in turloughs, fens and petrifying springs, or may have an indirect influence in maintaining high and stable water levels within the habitat, such as with raised bogs. Groundwater bodies can be affected by a range of pressures that can result in significant damage to GWDTEs depending on the susceptibility of the pathway and sensitivity of the receptor. To date, the main priority of work on groundwater-dependent wetlands under the WFD has been on GWDTEs within Special Areas of Conservation (SACs) designated under the European Habitats Directive (92/43/EEC). This is due largely as a result of Articles 5 and 6 of the WFD, which require a characterisation of the pressures and impacts on Europe's RBDs and the preparation of a Register of Protected Areas (RPA) including SACs (Kilroy et al., 2008).

The following list shows habitats under Annex I of the Habitats Directive that are GWDTEs of relevance in Ireland (Kilroy et al., 2008):

- Humid dune slacks;
- Machairs;
- Turloughs;
- Petrifying springs with tufa formation (Cratoneurion);
- Calcareous fens with *Cladium mariscus* and species of *Caricion davallianae*;
- Alkaline fens;
- Transition mires and quaking bogs;
- Active raised bogs (lagg and high bog);
- Degraded raised bogs still capable of natural regeneration;
- Blanket bog (if active bog) flushes;
- Bog woodland;
- Alluvial forests with *Alnus glutinosa* and *Fraxinus excelsior*;
- Rivers with muddy banks with *Chenopodion rubri* p.p. and *Bidention* p.p. vegetation; and
- Northern Atlantic wet heaths with *Erica tetralix* flushes.

Significant data gaps remain in assessing the status of GWDTEs, notably definition of threshold concentrations of contaminants causing adverse ecological reactions, and the sensitivity of GWDTEs to changes in physical hydrological conditions, e.g. water levels and flow rates.

6.2.4 Groundwater–surface water interface

The WFD outlines an approach in which interactions between groundwater bodies, GWDTEs and surface water bodies take on a central role (European Commission, 2000).

The groundwater–surface water interface can be divided into the following zones (Fig. 6.1):

- Riparian zone;
- Riparian wetland; and
- Hyporheic zone.

6.2.4.1 Riparian zone

The riparian zone is the area adjacent to a stream that is dependent on a variable moist regime. The difference between the riparian zone and a shallow permeable aquifer is the elevation of the water table during seasonal fluctuations. In a riparian zone, the water table is expected to reach the soil zone during the wetter months, whereas in a shallow aquifer the soil would rarely be saturated. Water, organic matter and nutrients are imported via surface water during flooding when the riparian zone is inundated (Naiman and Decamps, 1997).

The WFD requires two essential features of riparian areas to be evaluated under the following headings (Dahl et al., 2007):

1. Water requirements; and
2. Capability of maintaining high water quality of adjacent surface water bodies.

In the WFD, riparian water requirements (quantity) form part of the status assessment of the contributing groundwater body while the riparian water quality function forms part of the ecological status assessment of the adjacent stream or river. Assessment of ecological status of streams and rivers requires evaluation of biological, hydromorphological and physico–chemical elements of the stream and its riparian area if the structure and condition of the riparian area is relevant to achieve the environmental objectives of the stream (Dahl et al., 2007).

Riparian wetlands are areas associated with watercourses in which the water table is at or near the surface most of the year. The soils developed in these areas are anoxic due to long periods of constant saturation. Vegetation associated with these areas is adapted to wetland conditions (lack of soil oxygen) (Buss et al., 2005).

6.2.4.2 Hyporheic zone

The hyporheic zone is the water-saturated region below and adjacent to a surface water body, and is the interface between a surface water body and groundwater. This comprises the water-saturated alluvial sediments beneath and adjacent to streams. The direction of transfer between groundwater and surface water is governed by local hydraulic gradients and stream bed characteristics. Connectivity between

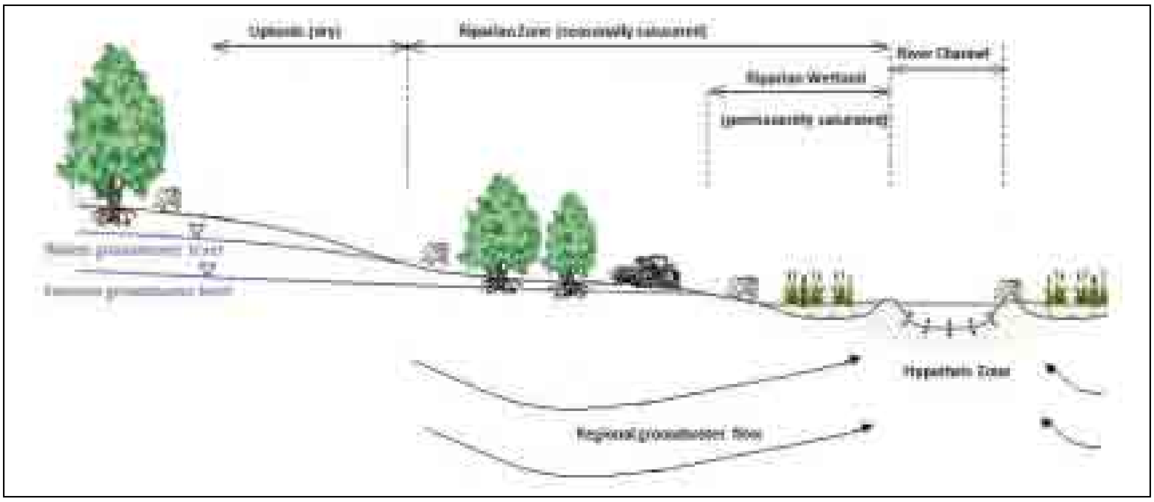

Figure 6.1. Zonation within a typical aquifer/river transition zone (modified from Buss et al., 2005).

groundwater and surface water creates a continuum of physico–chemical conditions from the surface stream vertically or laterally into the groundwater that can cause discontinuities in habitat availability and character (Kibichii et al., 2008a). Heterogeneous stream bed sediments may lead to complex flow patterns and the patterns of discharge/recharge can be very complex at fine spatial scales (<10 m) and over the course of a hydrological event (Malcolm et al., 2002). Hyporheic exchange increases hydrologic residence times and the volume of water in contact with sediment biota, thus enhancing biological reactions (see Chapter 4).

Water, nutrients, and organic matter occur in response to variations in discharge and bed topography and porosity. Nutrients are supplied to stream organisms by upwelling of subsurface water while downwelling stream water provides dissolved oxygen and organic matter to microbes and invertebrates in the hyporheic zone (Danielopol et al., 2006).

The hyporheic zone has the potential to enhance natural attenuation and is also a unique hypogean habitat. The geochemical conditions required for natural attenuation of certain priority pollutants, such as nitrate and halogenated ethenes (chemically reducing conditions), are the opposite of those conditions that typically enhance the biodiversity and ecological status of river systems (aerobic conditions). Consideration should be given to which ecological service, that is whether attenuation or enhancement of ecological habitat, is most valuable in a given catchment. In urban and other contaminated areas, the benefits provided by reductive natural attenuation processes in hyporheic sediments may be significant while in other catchments the benefits provided by a diverse and healthy hyporheic invertebrate community able to support fisheries and other higher faunal communities may outweigh the natural attenuation benefits. As river restoration continues, the relative benefit accrued by each ecological service may change, and river managers may need to consider this in long-term environmental restoration plans (Smith and Lerner, 2006).

The hyporheic zone ecotone is considered to support a rich diversity of aquatic invertebrates (Williams, 1989; Boulton et al., 1992; Storey and Williams, 2004). Moreover, it performs other important functions such as regulating the flow of water across the surface water–groundwater interface (e.g. Datry et al., 2007) and can transform the physico–chemical composition of that water (e.g. Pretty et al., 2006; Wagner and Beisser, 2006). Until recently little was known about hyporheic fauna in Ireland. The first detailed study was completed as a PhD study by Samuel Kibichii in UCD. The work focused on a relatively small number of sites yet produced some significant results. In terms of hydrochemistry the research highlighted vertical and lateral reductions in dissolved oxygen and concurrent increases in alkalinity, conductivity and the concentration of calcium (Kibichii et al., 2008a). A sampling protocol was tested (Kibichii et al., 2008b) and applied to capture hyporheic invertebrates below the stream bed, the exposed marginal gravel banks and at the terrestrial margin. Examination of spatial and temporal changes in the composition and abundance of the hyporheic invertebrates was concentrated on the Delour River, a third-order tributary of the Nore Catchment, which rises in the Slieve Bloom Mountains. Fieldwork was undertaken in March, May, August and September 2006 and samples were collected from two depths (0.2 m and 0.5 m) below the wetter stream channel, below the exposed marginal gravels and at the terrestrial margin. Some 86 taxa were encountered, mainly insect larvae but also some molluscs, worms, crustaceans, including typical groundwater species (e.g. *Niphargus* sp.). Multivariate analyses of the data highlighted four ‘spatial assemblages’. These are:

1. A ‘shallow sub-stream’ assemblage, dominated by insect larva and nymphs with a few micro-crustacean species, found in the upper 0.2-m depth below the wetted channel;

2. A shallow ‘ecotonal’ assemblage dominated by micro-crustaceans found in the hyporheic habitat 0.2 m below marginal gravels;

3. A ‘deep sub-stream’ assemblage with a mixture of insect larvae and micro-crustaceans found 0.5 m below the stream; and

4. A ‘marginal’ assemblage characterised by true groundwater specialists *Niphargus kochianus*

irlandicus and *Parastenocaris* sp. found 0.5 m below the exposed marginal gravel and at both depths sampled at the terrestrial margin.

The exact locations of these assemblages varied seasonally with the groundwater specialists moving closer to the stream in summer when the surface water was most likely dominated by groundwater seepage.

Kibichii (2009) also investigated the potential impact of surface water quality and condition of the riparian zone on the hyporheic communities. Some 14, third- to fourth-order tributaries of the Nore and Barrow Rivers were chosen on the basis of having good deposits of gravel forming the hyporheic habitat both within the wetted stream channel and on the exposed stream banks. Sites were chosen to represent the following conditions:

- Clean streams with intact riparian woodland;
- Clean streams without riparian woodland;
- Moderately polluted streams without riparian woodlands, particularly those accessed by livestock and people; and
- Moderately polluted streams with intact riparian woodland.

Results showed that there were reductions in invertebrate abundance and taxon richness in the hyporheic habitats of the polluted streams with and without riparian woodland, although substantially more at polluted stream sites without riparian woodland. Kibichii hypothesised that reduction in oxygen and sediment infilling of interstitial spaces may account for the results observed. For example the hyporheic habitats of polluted streams were characterised by low EPT (Ephemeroptera, Plecoptera, Trichoptera) taxa which are sensitive to low oxygen. Crustaceans too were virtually absent from hyporheic habitats below the exposed gravel at polluted sites where riparian zones were impacted while they were most abundant below the exposed gravel of clean and polluted streams with intact riparian woodland, therefore supporting the hypothesis that these hypogean taxa are more sensitive to physical disturbances than water quality. In conclusion the hyporheic zone may represent an important pathway for attenuation but that capacity may be determined by the functional role of the fauna inhabiting this zone, an area that requires further research.

Management practices associated with the groundwater–surface water interface area

Buffer strips have been proposed as an effective mitigation measure for decreasing phosphorus and sediment loss from soil to water. The effectiveness of buffer strips in retaining contaminants varies depending on site-specific factors such as buffer strip width (Table 6.4), slope, soil type, vegetation and site hydrology. The main retention mechanism in buffer strips is sedimentation and, as such, suspended sediment and PP are two of the main contaminants retained in the buffer strip.

Magette et al. (1989) found that TP and SS were reduced by 27% and 66%, respectively, in a 4.6-m-

Table 6.4. Performance of buffer zones for phosphorus retention (modified from Fogg et al., 2005).

Vegetation type	Buffer zone width (m)	Removal of total phosphorus (%)
Hardwood forest	20–40	23
Grass	4.6	57
Grass	9.1	74
Grass	4.6	41
Grass	9.2	53
Grass	26	78
Grass	1.5	8

long grass filter strip, and these figures increased to 46% for TP and 82% for SS in a 9.1-m-long grass filter strip. Hoffmann et al. (2009) reported that up to 128 kg P/ha/year can be retained in buffer strips through sedimentation, while the retention of soluble phosphorus can be as low as 0.5 kg P/ha/year. Abu-Zreig et al. (2003) found that TP decreased by 47–60% in a 5-m grass filter strip, depending on the volume of water, and this value increased to a maximum of 89% in a 15-m-long buffer strip. Yuan et al. (2009) concluded that buffer strips significantly reduced sediment in surface runoff from agricultural soils and suggested that sediment retention was maximised in 3-m-wide well-vegetated buffer strips receiving relatively shallow non-channelised flow from gently sloping source areas. Although the sediment trapping efficiency of buffer strips increases with the length, there is significant variation in this relationship (Fig. 6.2). Hoffmann et al. (2009) highlighted the need for further research on the long-term retention of phosphorus in buffer strips as up to 8 kg P/ha/year was released from some buffer strips identified in their study.

The implementation of buffer strips requires an assessment of their cost-effectiveness in the context of catchment-specific characteristics. Byrne et al. (2010) calculated the cost-effectiveness of implementing a buffer strip in the Lough Melvin Catchment in north-western Ireland and found that the implementation of a 1.5-m buffer strip in riparian zones in the catchment would cost €1,357/kg phosphorus removed and concluded that buffer strips were not a cost-effective measure for decreasing phosphorus loss from soil to water in that catchment. However, Haygarth et al. (2009) concluded that the cost-effectiveness of buffer strips was very high, ranging from £3 to £5/kg phosphorus saved. This highlights the need to consider both the cost-effectiveness and removal efficiency when considering buffer strips as a mitigation measure for sediment and phosphorus.

Buffer strips in the form of riparian and hyporheic zones have been attributed to the reduction of groundwater contaminants, including nitrogen, prior to entering a surface water body (Mayer et al., 2005). Numerous studies have shown a considerable ability of the riparian zones to remove nitrate concentration by up to 100% (Vought et al., 1995; Hutton et al., 2008; Sahu and Gu, 2009). Conversely, a study by Borin et al. (2005) found that the TN concentrations increased within the buffer strip; however, this increase may be attributed to remobilisation or mulch mineralisation. Although there have been a considerable number of studies carried out internationally regarding nitrogen attenuation in the riparian zone, there is a significant lack of research and information specifically focusing on the Irish context. Furthermore, there is a lack of literature discussing the attenuation capacities of the hyporheic zone as most of the research focuses on the riparian zone. In many cases, this may be because the hyporheic zone is considered to be part of the riparian zone.

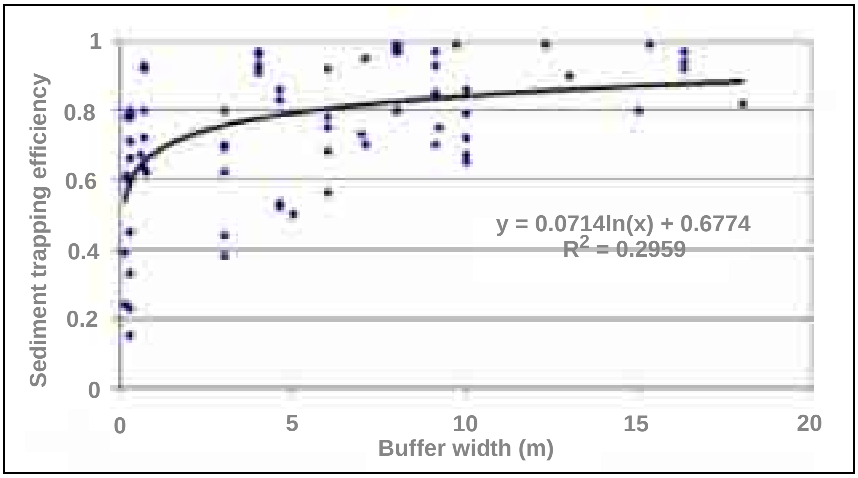

Figure 6.2. Variation in the sediment trapping efficiency with buffer strip width (Yuan et al., 2009).

6.2.5 Subterranean ecosystems

Subterranean waters may be separated into groundwater and hyporheic waters. Organisms are mostly restricted to the upper parts of subterranean ecosystems but in karst systems diverse stygofaunas may be found at depth, vertebrates can exist to a depth of several hundred metres in artesian aquifers and invertebrates have been reported at depths as great as 1 km. Different species are adapted to subterranean habitats to different degrees and there is a wide variety of ecological niches available within groundwater ecosystems, making groundwater ecosystems difficult to understand and study (Humphreys, 2009).

Large data gaps exist in international literature in relation to the following (Boulton et al., 1998):

- The structure of groundwater food webs;
- The tunnelling of energy through the underground and recycling of carbon and nutrients;
- The link between biodiversity and ecosystem functioning in relation to different scales;
- The self-purification potential of subsurface ecosystems and resistance; and
- The resilience towards anthropogenic impacts such as climatic change, among others, awaits detailed investigation.

The supplementation of the WFD with the Groundwater Directive means that there is now a legislative driver to promote an integrated approach to protect groundwater, both its good quality and quantity at different spatial scales. The directive has several positive aspects in that it emphasises the necessity to counteract negative trends in groundwater quality and quantity and it offers norms for the quality of the groundwater (especially for chemical parameters). However, it also has weaknesses, a major one being that it treats groundwater as a resource without recognising groundwater bodies as ecosystems (Danielopol et al., 2006). This issue remains to be firmly established and thus will not form a focal point of the Pathways Project. Moreover, there is currently an ongoing EPA STRIVE project in the University of Ulster researching the distribution, structure and functioning of subterranean fauna within Irish groundwater systems.

6.3 Biological Indicators of Physico–Chemical Pressures

The application of biological indicators in Europe to determine water quality dates back to the beginning of the 20th century with the development of the Saprobic System in Germany. Over the next seven decades, a number of index systems were developed based mainly on macroinvertebrates. One of the earliest was the Trent Biotic Index (Woodiwiss, 1964), which was later modified to produce a variety of index systems currently applied in some European countries, for example the UK (Wright, 1995), France (DePauw and VanHooren, 1983), and Belgium (Tuffery and Verneaux, 1968). The main problem with most of these index systems is that they were developed to detect the impact of point discharges of organic pollution, which was regarded as the main pollution problem in the early 20th century. More recently, schemes have been developed or adapted to assess the impact of diffuse pollutant sources.

Macroinvertebrates have been the principal biological groups used in the assessment of water quality. They satisfy the key requirements of a biological indicator in that they are:

- Widespread;
- Easy to sample;
- Show graded response to specific stressors;
- Applicable over a range of spatial and temporal scales;
- Cost-effective; and
- Scientifically and legally defensible.

However, the WFD poses new challenges, not least that it requires measurement of status to be based on several quality elements describing biological quality, general components (physico–chemical), specific relevant pollutants and hydromorphology (see Section 6.2.1.1). The descriptor parameters for each of these are set out in Annex V 1.1 of the WFD. In terms of the biological elements, the following must be addressed at the surveillance sites:

- Composition, abundance and biomass of phytoplankton;
- Composition, abundance and biomass of other aquatic flora (phytobenthos/macrophytes);
- Composition and abundance of benthic invertebrate fauna; and
- Composition, abundance and age structure of fish fauna (WFD 2000/60/EC).

All elements are to be examined in the surveillance programme for Irish rivers and lakes, with the exception of phytoplankton in rivers. Inter-calibrated metrics are not available for all elements. The following sections outline what metrics have been adopted for lakes and rivers in Ireland and what others are routinely applied.

6.3.1 Macroinvertebrates

A wide variety of macroinvertebrate metrics are in use across Europe and it is generally agreed that community composition and structure will show response to a wide variety of pressures (e.g. organic pollution, eutrophication, heavy metal contamination, thermal pollution, hydromorphological change). However, where there are multiple pressures it may not be possible to disentangle the effect of any individual pressure.

In Ireland, macroinvertebrates have formed the basis of river water quality assessment since the early 1970s. A Quality Rating (Q-value) System was devised in 1970 by Toner and was reported in the first national assessment of Irish rivers (Flanagan and Toner, 1972). The Q-value scale runs from Q1 to Q5 with intermediate scores possible, such as Q3–4. It is based on the proportions of five (A, most pollution sensitive, to E, most pollution tolerant) groups of organisms with differing pollution tolerances. The relationship between the Q-value and land-use pressures (catchment urbanisation and agricultural intensity, densities of humans and cattle) appears to be well supported (Donohue et al., 2006) and is related to various water quality variables such as the nutrients and biochemical oxygen demand (e.g. Clabby et al., 1992; McGarrigle, 2001). However, there appears to be wide scatter in the data and more refined assessment is probably required. The Q-value has nevertheless been successfully inter-calibrated with various other European macroinvertebrate index systems and Ecological Quality Ratio (EQR) boundaries have been set (Table 6.5). The

Table 6.5. Comparison between the Environmental Protection Agency Quality Rating System (Q-value), the corresponding Ecological Quality Ratio (EQR) values and the Water Framework Directive (WFD) Status classes defined by the inter-calibration exercise. The descriptions used in pre-WFD EPA water quality reports are also shown for comparison (from McGarrigle and Lucey, 2009).

Q-value	EQR	Boundary EQR	Historical description of water quality	WFD ecological status	WFD colour code
5	1		Satisfactory	High	Blue
4.5	0.9		Satisfactory	High	Blue
High–Good Boundary		0.85			
4	0.8		Satisfactory	Good	Green
Good–Moderate Boundary		0.75			
3.5	0.7		Slightly polluted	Moderate	Yellow
3	0.6		Moderately polluted	Poor	Orange
2.5	0.5		Moderately polluted	Poor	Orange
2	0.4		Seriously polluted	Bad	Red
1.5	0.3		Seriously polluted	Bad	Red
1	0.2		Seriously polluted	Bad	Red

EPA is currently developing an 'Auto-Q' computerised 'expert system' which will mimic the diagnostic procedure used in deriving a Q-value. The project is also examining the relationship between Q-values and other metrics generated by the ASTERICS assessment software (http://www.fliessgewaesser-bewertung.de) (see below).

The Small Streams Risk Score (SSRS) is a rapid assessment system developed for headwater streams in Ireland (EPA, 2005b). The SSRS system is considered to be an efficient indicator of risk from either point or diffuse pollution. It evaluates sites in terms of three risk categories – 'at risk', 'probably at risk' and 'probably not at risk' – based on the presence or absence of five macroinvertebrate indicator groups. These include the Ephemeroptera (Group 1), the Plecoptera (Group 2), the Trichoptera (Group 3), the Gastropoda, OLigochaeta and Diptera larvae (GOLD, Group 4) and *Asellus* species (Group 5) (EPA, 2005b).

A number of other macroinvertebrate metrics that are often applied to Irish data include the UK Biological Monitoring Working Party (BMWP) and the Average Score Per Taxon (ASPT) scores. The BMWP index ascribes a score to key macroinvertebrate families present in the sample, the sum of these scores giving an overall site BMWP score. The BMWP score is difficult to interpret unless an expected score has been determined from reference state. Values can range from less than 50 to greater than 200. To overcome this problem a modification of the BMWP score known as the ASPT was devised. The ASPT is calculated by dividing the BMWP score by the number of scoring taxa and, as such, is considered to be relatively independent of sample size, sampling technique or season (Pinder et al., 1987). A further issue with both the BMWP and ASPT scores is that they were developed for rivers in Great Britain where the distribution and pollution response of some of the macroinvertebrate taxa in the scheme may differ from those occurring in Irish rivers. Nevertheless, the ASPT in particular has been found to perform well in Irish headwater streams and may be more independent of seasonal factors than are Q-values (Callanan et al., 2008). More widely, Sandin and Hering (2004) also reported that the ASPT correlated well with the stress gradient in seven stream types across Europe.

Many of the biotic indices so far mentioned are based on a limited number of indicator taxa. Simple measures of total taxon richness and abundance are also routinely used to support conclusions drawn. Indeed, it is becoming increasingly common for those involved in bioassessment to use multiple metrics to improve confidence in the assessment. In this respect the project on the Development and Testing of an Integrated Assessment System for Ecological Quality of Rivers throughout Europe using Benthic Macroinvertebrates (AQEM) is of relevance. The project used a type- and stressor-specific approach to develop a multi-metric index complaint with WFD requirements. Numerous publications emerged from this project and a full listing is available at http://www.aqem.de/mains/publications.php. Among the many other outputs and products from AQEM is the ASTERICS assessment software (http://www.fliessgewaesser-bewertung.de) designed to assess the ecological quality of 28 European stream types based on macroinvertebrate taxa lists. This software calculates a wide range of European biotic indices as well as metrics relating to taxon richness, abundance and functional feeding groups. It is relatively straightforward to run. The only drawback is that the software was developed for specific European stream types which may not entirely match that expected in Ireland. Nevertheless, it provides a good exploratory tool. The follow-on STAR (STAndardisation of River Classifications) project builds on the AQEM results and considers several issues relating to WFD assessment such as the methods or biological quality elements best able to indicate certain stressors, methods appropriate to various scales, errors and uncertainty in assessment methods and indicators for early and late warnings (Furse et al., 2006).

While European metrics are available for riverine macroinvertebrates, no equivalent system exists for lakes and this also applies to Ireland. Donohue et al. (2009) have evaluated three metrics based on the response of littoral macroinvertebrates to eutrophication: (i) percentage TP-sensitive taxa, (ii) a TP score, and (iii) an indicator taxa metric. While these look promising their performance is likely to be altered in lakes with invasions of exotic species such as the zebra mussel *Dreissena polymorpha* (Atalah et al., 2010).

6.3.2 Phytobenthos

In terms of phytobenthos, most EU Member States have focused on the diatom component. This is mainly due to the fact that methods have been standardised (CEN, 2003a, 2004) and that the taxonomy is reasonably well described. A number of diatom metrics are available: the Trophic Diatom Index (TDI) in the UK (Kelly and Whitton, 1995), the German TDI (Coring et al., 1999), and the Trophienindex in Austria (Rott et al., 1999). These have been related to pressures, mainly eutrophication. The TDI is applied in Ireland and has been inter-calibrated. In lakes, phytoplankton biomass is measured in terms of chlorophyll; this metric has been inter-calibrated for some lake types.

6.3.3 Macrophytes

A multi-metric macrophyte index has been developed for Irish lakes based on responses to nutrient enrichment. The Free Index (Free et al., 2007) takes into account species composition and abundance at a minimum of four transects per lake. To date, no macrophyte index has been calibrated for Irish rivers. However, a number of candidate metrics are being examined. These include the Mean Trophic Rank (MTR) Index, LEAFPACS and the Canonical Correspondence Analysis-Based Assessment System (CBAS). The MTR was developed in the UK by Nigel Holmes in the 1990s (Holmes, 2010) to monitor eutrophication pressure and has been the subject of several studies since then (e.g. Demars and Harper, 1998). The LEAFPACS project is concerned with the development of a predictive macrophyte tool for assessment of status in lakes and rivers (Willby, 2004). All index systems take into account species cover and whether they favour nutrient-rich or oligotrophic conditions. The CBAS is based on calculated species optima and niche breadths in relation to oxygen, conductivity, pH, sediment and nitrate gradients, which are used to compile metrics (Dodkins et al., 2005a). The workshop on nutrient enrichment held in University College Cork in February 2009 highlighted the variable response of macrophytes to nutrient enrichment, especially at intermediate nutrient levels.

6.3.4 Fish

Until recently there has been no standardised monitoring of fish communities in Ireland and certainly none appropriate to WFD requirements. A recent WFD-related project investigated the relationship between river fish stocks, EPA Q-values, environmental factors and the degree of eutrophication (Kelly et al., 2007). This project illustrated a relationship between community composition and water quality as determined by Q-value. Sites surveyed with a Q-value <2 were dominated by non-salmonids and these formed <10% of the fish communities at sites with good water quality (≥Q4–5). Three metrics ((i) percentage composition of total salmonids, (ii) percentage composition of 1+ salmonids and older, and (iii) abundance of salmonids 1+ and older) successfully allocated sites into the five Q-value groups. The abundance of 1+ and older salmon also appears to be an effective metric for separating the High–Good and Good–Moderate boundaries for the WFD. Two predictive models were developed for sites with and without barriers. Although the relationships with water quality were reasonable, the models were limited in their ability to separate reference sites from those in the slight to moderate range. The extensive database generated in this project is being used for testing of an International Common Metric (ICM) (Jepsen and Pont, 2007). Surveillance monitoring of fish communities in Irish rivers was initiated in 2008 and covered 83 river sites. A further 100 sites were planned to be completed in 2009 using the standardised guidance for fish stock assessment in wadable rivers (CEN, 2003b).

Much the same story applies to lakes. A North–South Share project (http://www.nsshare.com) was initiated to address the lack of appropriate tools. A classification tool for lake fish communities was developed. It is reported to be a modified predictive multi-metric approach (Kelly et al., 2008). The tool apparently requires some expert input especially for lakes where non-native species occur.

6.3.5 Hydromorphology

Hydromorphological status considers the condition of the hydrological and geomorphological elements of waterbodies. In rivers, these elements can be affected by a range of land-use activities and anthropogenic inputs. A desk study undertaken to determine a methodology for monitoring the morphological condition of Irish rivers in terms of the WFD requirements was produced in 2005 (McGinnity et al., 2005). Since then an assessment technique known as the Rapid Hydromorphology Assessment Technique (RHAT) has been developed for Ireland (NIEA, 2009). The criteria that are scored include channel morphology and flow types, channel vegetation, substrate diversity and condition, barriers to continuity, bank structure stability, bank and bank top vegetation, riparian land cover and flood plain interaction. No assessment system for lakes is available yet. It is likely that a method being developed for UK lakes will be modified for use in Ireland. Research throughout Europe is addressing a knowledge gap on the relation between hydromorphology and ecology. Little has been published to date in this area.

6.4 Lake and River Types

The response of aquatic systems to stressors is dependent on their sensitivity to a particular input and this is in part determined by physico–chemical characteristics, the so-called type of river or lake. This is clearly recognised by the WFD, which requires assessment and reporting of 'ecological status' in terms of deviation from some expected natural state, referred to as the 'reference condition'. This must be defined for each 'type' of river. So some metrics will have to take into account typology in the setting of reference values. A typological classification of rivers and lakes has been carried out in Ireland. Kelly-Quinn et al. (2009) outline the approach adopted for the development of the lakes typology which resulted in the 13 types outlined in Table 6.6.

Dodkins et al. (2005b) present the approach adopted for developing the optimal typology for Irish rivers in detail. Twelve types were defined on the basis of geology and slope categories (Table 6.7). Each type carries a two-digit code, with the first digit indicating the geology of catchment and the second digit river slope. A map of the locations of each of the 12 river types is shown in Fig. 6.3 and a count of the number of typed river water bodies within each RBD is given in Table 6.8.

It is not necessary to consider typology in the assignment of Q-values. However, some of the other WFD metrics (e.g. Free Index) need to give some consideration to typology (viz. alkalinity).

6.5 Impacts of Contaminants of Concern on Aquatic Ecology

The following section concentrates on two key contaminants: nutrient enrichment and sedimentation. As mentioned earlier, this is not intended to be a literature review but rather highlights issues relevant to refining the scope of work for the present project.

6.5.1 Eutrophication

Eutrophication is considered to pose the highest threat to water quality in Ireland both from point and diffuse sources (see Chapters 4 and 5). A considerable body of information exists on the response of aquatic biota to nutrient enrichment. Nutrient inputs are often accompanied by organic material, particularly from point discharges, e.g. sewage effluent. Consequently, there appears to be a move towards considering both nutrient and organic matter inputs under the general term of organic enrichment. It is currently not possible to disentangle the effects of pure organic pollution from the effects of nutrient enrichment and processes governing the response of the biota are probably common to both. A plethora of publications outlines the effects of eutrophication on lake and river systems and specific components of both. Most confirm what is known about the typical response of the biological

Table 6.6. The overall typology for Irish lakes.

Parameters	Boundaries												
Altitude (m)	<200												>200
Alkalinity (mg $CaCO_3$/l)	<20				20–100				>100				
Depth (m)	<4		>4		<4		>4		<4		>4		
Area (ha)	<50	>50	<50	>50	<50	>50	<50	>50	<50	>50	<50	>50	
Type	1	2	3	4	5	6	7	8	9	10	11	12	13

$CaCO_3$, calcium carbonate.

Table 6.7. Details of geology and slope categories forming the 12-type[1] river typology (from Kelly-Quinn et al. (2005)).

Code	Catchment geology (% bedrock in upstream catchment by type)	Description	Hardness/Alkalinity
1	100% siliceous	Soft water	<35 mg $CaCO_3$/l
2	1–25% calcareous (mixed geology)	Medium hardness	35–100 mg $CaCO_3$/l
3	>25% calcareous	Hard water	>100 mg $CaCO_3$/l
Code	**Slope (m/m)**		
1	≤0.005	Low slope	
2	0.005–0.02	Medium slope	
3	0.02–0.04	High slope	
4	>0.04	Very high slope	

[1]The type codes have two-digit codes with the first digit indicating the geology of catchment and the second digit river slope.
$CaCO_3$, calcium carbonate.

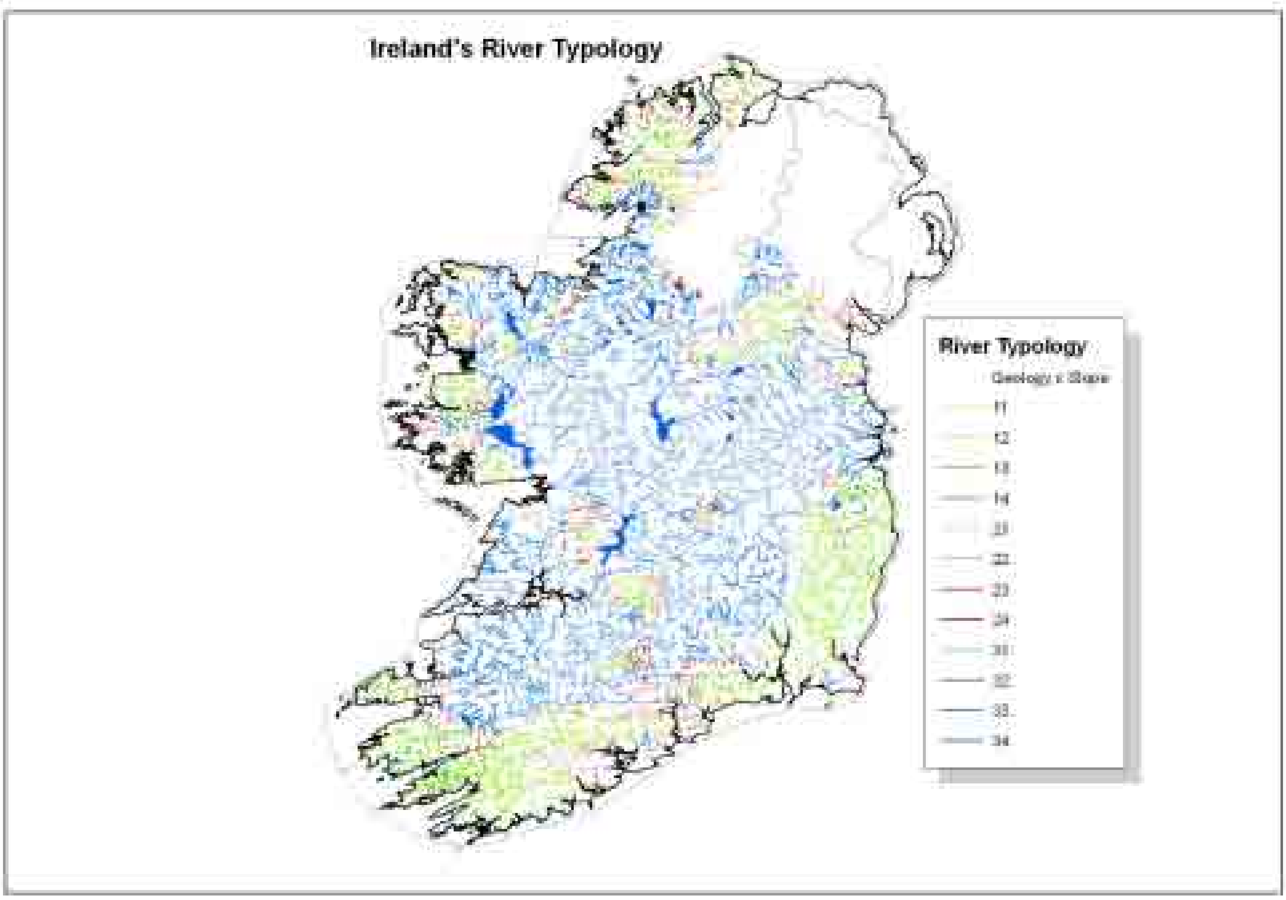

Figure 6.3. Distribution of the 12 river types in Ireland (Dodkins et al., 2005b).

Table 6.8. Number of typed river water bodies in each River Basin District (RBD) within the Republic of Ireland (see Table 6.7 for details of typology code).

RBD	Typology code											
	11	12	13	14	21	22	23	24	31	32	33	34
Eastern	34	51	23	28	5	15	1	0	122	47	0	0
Neagh Bann	9	8	0	4	1	11	2	0	22	10	0	0
North West	51	119	77	43	37	50	21	12	41	58	24	13
Shannon	8	35	8	15	15	23	10	3	491	187	33	8
South East	78	133	34	12	15	35	11	8	183	95	6	3
South West	51	237	116	124	23	54	15	9	52	60	5	2
Western	30	106	34	29	38	55	21	18	272	151	24	17
Totals	**261**	**689**	**292**	**255**	**134**	**243**	**81**	**50**	**1,183**	**608**	**92**	**43**

communities, such as an increase in primary production, be it in suspended or benthic algae, the knock-on effects on diel oxygen concentrations leading to oxygen deficits at specific times of the day or periods of the year and loss of pollution-sensitive taxa. Most recent efforts have focused on the likely effects of different concentrations and proportions of nitrogen and phosphorus, particularly at the level of the biofilm, which are likely to influence the overall response of the system (Marcarelli et al., 2009). The outputs of the EU STAR projects provide some useful information on assessments concerning the utility of higher taxonomic groups. According to Hering et al. (2006a), all biological groups respond to organic enrichment but the pattern differs among groups. They report that diatoms may be the most effective indicator of eutrophication, but that other groups – such as the macroinvertebrates – should be included in the assessment if other stresses are present. In fact, macroinvertebrates appear to a good general indicator of a range of stressors. Hering et al. (2006a) conclude that it is advisable to use more than one biological indicator group if pollution type is unknown or multiple stressors are suspected. Interestingly, the authors noted that the metrics used are based on species-level data and that if family-level data are used then only an indication of general degradation can be detected.

6.5.2 Sedimentation

Compared with eutrophication, significantly fewer publications deal directly with the effects of siltation on freshwater communities, despite its widely recognised impact (see Section 5.4). Siltation is identified as a pressure from a variety of land-use activities, such as agriculture, forestry and urbanisation, and is considered to have an effect on sensitive taxa in most biological groups, although there are limited published data to support this. Excessive sedimentation is considered to be a problem in over 45% of rivers and streams in the United States (Sutherland et al., 2002) and a considerable number of studies have documented effects on macroinvertebrates, fish and the condition of micro-habitats. No comparable figures are available for Europe. Most of the papers deal with the effects of silt on spawning gravels (e.g. Milan et al., 2000). There has been little consideration of sedimentation in an Irish context. McDonnell (2005) reported percentage fines (<2 mm) as having an effect on trout egg mortality. No Irish studies have addressed other biological groups. Hutton et al. (2008) assessed inputs of sediment from forestry activities and reported higher bedload sediment in association with felling in some catchments. No biological impacts were related to sedimentation.

Furthermore, there appears to be no standardised protocol for assessing the ecological impact of siltation. Some researchers measure percentage fine silt in bottom sediment, while others concentrate on SS or turbidity. Interestingly, Sutherland et al. (2002) noted that the difference in SS concentration between reference and disturbed streams was more consistent at baseflow than at storm flow. They therefore suggested that baseflow turbidity may be selected as an indicator of potential stream impairment. Some verification of the source of the sediment may allow assessment of attenuation measures and several papers cited in Section 5.4 have described various approached to sediment 'fingerprinting' (e.g. Collins and Walling, 2002).

6.6 Selection of Indicators and Metrics for Detecting and Assessing Stressor Impact – Some Considerations

Overall, most of the literature recommends that more than one biological group be used to assess status, especially if one attempts to link impact to a particular stressor. Challenges arise when one is dealing with more than one stressor and it appears to be practically impossible to disentangle the effects of one stressor from another. Multiple stressors may be additive, antagonistic (combined impact is less than the sum of individual effects) or synergistic (impact greater than the sum of the individual effects) and at present cannot be distinguished to predict the outcome for any combination of stressors (Folt et al., 1999). However, it appears that some prior knowledge of likely stressors may help the selection of appropriate indicators. Some indicators respond well to the primary or dominant stress (e.g. macroinvertebrates and diatoms respond to nutrient enrichment) but others may be better discriminators of the secondary stress (e.g. fish and hydromorphology) (Johnson et al., 2006). Although Hering et al. (2006b) suggest that fish are good indicators of hydromorphological pressure, it must be noted that they show high variation in density and population structure. This is related to habitat characteristics so, unless sites are carefully chosen or a high number of sites are used, natural habitat characteristics may be confounding factors. A further consideration worth noting is that many of the metrics and index systems described show clear responses at the extremes of the stress gradient but at intermediate values the responses are more varied. For this reason, a number of metrics should be applied in data analyses, preferably representing different organisational levels. Furthermore, there are a variety of classification techniques (e.g. similarity indices, Two Way Indicator Species Analysis – TWINSPAN) and ordination (e.g. Canonical Correspondence Analysis – CCA) which can be applied to whole community composition and structure to explore differences between sites. Some techniques (PERMANOVA) will highlight groups of taxa responsible for site differences which are often too subtle to be detected by standard metrics but may be biologically relevant.

6.7 Sources of Biological Data Sets

The EPA website allows access to current and historical Q-value data. The raw biological data collected for over 3,000 sites in the last 3 years are stored electronically and may be consulted on request. Earlier field data are being transferred to electronic databases but this will take a considerable amount of time to complete. The same situation applies to the lakes data – almost 300 sites on the monitoring programme are accessible; however, only the surveillance sites have the full suite of data (circa 76). Earlier data have not been incorporated into a unified database. Surveillance monitoring is carried out once in every 3 years, with more regular monitoring at some polluted sites – this limits the value of the data to the present research project. Furthermore, it is unlikely that the sites selected by the Pathways Project will coincide with the EPA monitoring sites but they should provide some indication of impact some distance from the project sites. Large macroinvertebrate databases are held by Kelly-Quinn for circa 50 reference headwater streams (Callanan, 2009), and other upland streams in Wicklow (AQUAFOR Project) and elsewhere in Ireland (FORWATER Project). The EPA RIVTYPE database has macroinvertebrate, macrophyte and phytobenthos data from 50 reference river sites. These databases may provide insight into community composition and structure in relatively clean water conditions and will be made available to the present project.

6.8 Knowledge Gaps Relevant to the Current Project

Nutrient enrichment/organic pollution remains a major stressor on freshwater systems in Ireland. We know that aquatic biota show a graded response to enrichment/organic pollution. However, in terms of knowledge gaps we do not know how biota respond to chronic (low or high concentrations) inputs or low and high acute inputs. Furthermore, it is not clear from the literature how long the impacts persist under these scenarios (this has implications for the recovery of sites to Good status). Most studies are based on once-off or two-season sampling and what goes on in-between is not certain. Responses are highly variable where moderate pollution has been detected and they may relate to the severity, duration and timing of pollution inputs. Dilution potential is obviously a factor and this is climate related which will become increasingly important with climate change.

Sedimentation remains an unquantified problem and often accompanies nutrient enrichment. There is a need to examine turbidity and bedload accumulation of fine sediments and in particular to estimate sediment fluxes. In Ireland, responses of macroinvertebrate and phytobenthos communities to elevated sediment are unknown.

Overall, efforts to understand biological responses to various stressors are curtailed by the scarcity of high-frequency hydrochemical and biological sampling data. The continuous monitoring/event-based sampling scheduled in this project would assist considerably in rectifying this matter.

6.8.1 Some considerations for the biological component of the research

Ecological research will firstly determine what impacts are present at sites influenced by the various attenuation pathways. The ideal would be to target sites that lie within catchments with varying pathway susceptibility. The main body of the ecological research to be completed in the framework of this project will provide assessment of temporal changes in community composition and structure in response to inputs. The final selection of indicators will depend on the pressures targeted and whether multiple stressors are an issue. At the very least, two biological groups will be selected and the analysis will involve the use of multiple metrics. The main objective is to reconcile the temporal changes in the biological indicators with the results of the event-based sampling. Anthropogenic stresses that impact on aquatic biota may not always be detected by routine hydrochemical sampling. The ecological monitoring will help validate whether the hydrochemical sampling undertaken in this project has detected the significant inputs. In a case where a biological impact is detected with no corresponding input of a contaminant, it may indicate that some pathways have been missed.

7 Summary of Knowledge Gaps and Recommendations

7.1 Introduction

This chapter aims to summarise knowledge gaps identified during the Pathway Project review process. Recommendations for further research are presented in relation to the Pathways Project and will be used to focus catchment-specific fieldwork plans once the final catchments are selected and agreed upon. Furthermore, recommendations on research beyond the scope of this project are also presented in order to assist the EPA in identifying possible future research projects.

7.2 Knowledge Gaps

7.2.1 Flow paths

The Pathways Project proposes to generally follow the conceptual model and terminology developed by the GWG, which was also adopted in the surface water and groundwater interactions study, as described in Section 3.5. One minor deviation is proposed at this stage – to use the term 'overland flow' to describe sheet flow on the surface and flow in the upper few millimetres of topsoil. A second aspect of the conceptual pathways model, namely field drainage, will require further consideration as the study progresses, given contrasting hydrochemical signatures in some drain waters compared with overland flow derived from the same area. Conversely, flows in field drains will often respond rapidly to rainfall events and may contain SS, similar to overland flow. However, studies also suggest that field drainage might be better placed within interflow (see Sections 4.1 and 5.1). The Pathways Project team will investigate whether the hydrological response of field drainage can be distinguished on a catchment scale using hydrochemical techniques from overland flow.

Based on the discussion of Irish hydrology and flow pathways in Chapter 3, the main data/knowledge gaps can be summarised as:

- Scarcity of reliable, long-term river gauging records for small catchments;
- An absence of long-term groundwater-level records from reliable monitoring points for the poorly productive aquifers;
- The paucity of field-based information concerning the interaction of groundwater and surface water in Ireland;
- The very small amount of work carried out in Ireland on the use of chemical tracers for hydrograph separation;
- There very few field data available on the quantification or the quality of interflow;
- The limited overland flow data available at the field scale (as opposed to stream flow measurements and flood event sampling, which have been assumed to be overland flow);
- The very limited understanding of the contribution of drains to overland flow and/or interflow; and
- The requirement for further data on the likely effects of climate change on Irish hydrology and, more specifically, on the flow contributions to receptors from different pathways.

7.2.2 Contaminants of concern

As outlined in Chapters 4 and 5, nutrients (phosphorus and nitrogen), sediments, pathogens and pesticides were considered during the review as potential contaminants of concern for consideration within the framework of the Pathways Project. The review process highlighted that phosphorus appears to have received most attention and had the greatest amount of data collected and associated research completed in the Irish context. This was followed by nitrogen, and then sediment. Nonetheless, there remain significant knowledge gaps, some of which will have to be addressed within this project. On the other hand, research completed in Ireland in relation to pathogens/FIOs has proved more limited, although there are substantial bodies of raw drinking water quality and groundwater quality monitoring data available for interpretation. Moreover, international literature suggests that a relationship may exist between the presence of nitrogen, phosphorus and sediment with pathogens from slurry spreading and septic tanks. Irish data and research concerning pesticide fate and transport have proved to be very limited. Currently, there is insufficient research or monitoring undertaken in Ireland to warrant considering pesticides further within a CMT without further fundamental studies being first completed.

In relation to nitrogen, phosphorus, pathogens and sediment, the knowledge gaps in Ireland are:

- Identification and delineation of CSAs;
- Issues associated with upscaling to catchment scale to permit incorporation into a CMT;
- Limited knowledge of contaminant attenuation processes;
- The role of preferential flow processes in understanding contaminant mobility; and
- The relationship with sediment transport and the mobility of the other contaminants of concern.

7.2.2.1 Pathogens

To date, no systematic investigations studying pathogen fate and transport in Irish RBDs have been completed and the processes influencing the fate and transport of pathogens and FIOs in Irish groundwater remain little studied. Furthermore, the requirement to consider the impacts of pathogens on both surface water and groundwater presents the dilemma of whether modelling the impacts on the two receptors should be coupled or considered as two separate models, given the demonstrated ability of FIOs (and by inference pathogens) to impact water quality in both domains. The issue has not been comprehensively addressed in the international modelling literature, given the focus on either groundwater or surface water, but not both.

7.2.2.2 Pesticides

Very limited data exist for pesticides in Ireland. Insufficient baseline information is available for Irish settings to consider incorporation of pesticides into a CMT. Given the substantial analytical and logistical issues associated with sampling/analysis of pesticides, it has proven very difficult to develop estimates of export coefficients for pesticides at the catchment scale, given the current very limited access to pesticide usage databases and source information. Moreover, there are very limited data available for Ireland in relation to mobility and attenuation of pesticides, while insufficient information exists to permit consideration of their transport and attenuation in heterogeneous Irish geological conditions. Overall, water quality monitoring data incorporating pesticides remain very limited. Moreover, currently there are no monitoring/analytical protocols addressing degradation products that are sometimes as toxic to the environment as the parent active ingredient.

7.2.2.3 Nitrogen

When considering the main knowledge gaps associated with nitrogen, it is immediately apparent that in groundwater the geochemical conditions that determine whether denitrification will take place are not well established beyond a broad appreciation that denitrification is unlikely to be significant under well-oxygenated conditions. Similarly, little is understood about the groundwater conditions that control the rate and extent of denitrification. Furthermore, the impact of septic tanks on catchment-scale nutrient budgets and the potential pathways followed by the effluent in low-permeability soils remains poorly characterised, even in the international literature.

7.2.2.4 Phosphorus

In relation to phosphorus, there are limited data available in Ireland to demonstrate the effectiveness of phosphorus mitigation measures at the catchment scale. Further research is required to elucidate the processes of phosphorus retention and release. In addition, there are growing concerns that septic tanks are having an impact on water quality; however, there are few studies that have demonstrated this impact with the exception of the ongoing study in Dundalk Institute of Technology (with involvement from the Pathways Project) focusing on the connectivity and associated contaminant fluxes from septic tanks to watercourses. Preliminary findings indicate the persistent presence of phosphorus in monitoring wells downgradient of septic tank discharge zones. In addition to attenuation processes, knowledge gaps on remobilisation of phosphorus during transport remain. A better understanding of the lag time between implementation of measures and subsequent changes in water quality is required. As mentioned previously, there exists a very limited understanding of the role of sediment in the mobilisation, attenuation and transport of phosphorus to water bodies. Furthermore, there is limited research available on the role of preferential flow channels in phosphorus export from soil and on phosphorus in groundwater bodies in Ireland.

7.2.2.5 Sediment

The main knowledge gaps associated with sediment relate to understanding the sources and sinks within a catchment and the sediment transfer processes, including in-stream mobilisation and bank erosion, and how they relate to sediment monitoring results at discrete monitoring points. Research on the relationships in specific catchments between sediments and nutrients, pathogens and pesticides is limited and there are only limited high-resolution temporal data concerning sediment fluxes in Irish rivers. These have been obtained principally using surrogate measurements such as turbidity. In addition, limited research or publications exist in relation to upscaling sediment and associated nutrient transfer from field, farm and sub-catchment scales to catchment and basin scales.

7.2.3 Ecology

Nutrient enrichment/organic pollution remains a major stressor on freshwater systems in Ireland. Although it is understood that aquatic biota show a graded response to enrichment/organic pollution, there is limited understanding of biota responses to chronic (low or high concentrations) inputs or low and high acute inputs. Furthermore, it is not clear from the literature how long the impacts persist under these scenarios (this has implications for the recovery of sites to Good status). Most studies are based on once-off or two-season sampling programmes. Processes operating in the intervening period remain uncertain. Responses are highly variable where moderate pollution has been detected and they may relate to the severity, duration and timing of pollution inputs. Dilution potential is obviously a factor and this is climate related which may become increasingly important with climate change and the predicted increase in extreme hydrological events. Similarly, the impact of increased sedimentation rates that often accompany nutrient enrichment remains unquantified. There is a need to examine turbidity and bedload accumulation of fine sediments and in particular to estimate sediment fluxes. Responses of macroinvertebrate and phytobenthos communities in Ireland to elevated sediment levels remain uncharacterised.

7.3 Recommendations for Further Research

7.3.1 Pathways research

This section is a summary of the recommendations for further research within the scope of the Pathways Project. These recommendations have been provided with a view to incorporating them into the catchment-specific fieldwork plans once the study catchments have been selected.

7.3.1.1 Recommendations for investigations of the relative importance of various flow paths

- Apply a range of physical hydrograph separation techniques to the available data and construct flow duration curves to gain insights into the contributions of the different flow pathways;

- Carry out event-based sampling and apply chemical hydrograph separation methods to improve conceptual models explaining the relative importance of hydrological processes and explaining hydrograph responses;

- Use shallow lysimeters and tensiometers to collect better information on interflow in a study catchment where the process is suspected to constitute a significant pathway;

- Use groundwater-level data and simple hydrogeological analytical equations to improve the reliability of hydrograph separation results; and

- Apply lumped parameter and possibly distributed or semi-distributed models to represent flow along the relevant pathways in the study catchments.

7.3.1.2 Recommendations to investigate contaminants of concern

Pathogens

- Compilation and integration of surface water quality monitoring data with land-use data, meteorological data and stream/river discharge data to investigate the possibility of developing catchment export coefficients for pathogens/FIOs;

- Comparison of samples taken during high-energy hydrological events with predicted levels determined using catchment export coefficients to determine the degree of confidence with which export coefficients can be used as a baseline for predicting conditions in RBDs, and further data acquisition efforts may be optimised to improve confidence in predicted levels;

- Assessing the interrelationship between FIO levels and those of other contaminants of concern considered in the Pathways Project to evaluate proposed relationships with other more easily/ widely measured water quality parameters;

- More detailed investigation of groundwater monitoring data from any potential contaminated monitoring points within selected type catchments to better understand the root causes of pathogen levels observed in groundwater;

- Analysis of spatial distribution of pathogen levels in water within type catchments, combined with water quality data and topographic/hydrological data to identify potential CSAs; and

- Investigation of the feasibility/benefit of pathogen transport models coupling attenuation in the subsurface with surface processes as a means of simultaneously understanding impacts on both groundwater and surface water.

Sediment

- Carry out geomorphological surveys in the study catchments selected for further investigation to identify major sediment sources and sinks, and the impacts of hydrological changes on sediment transfer, with a view to generating a catchment sediment budget if possible;

- Look at relationships between sediment and flow rates, preferably at different scales;

- Investigate relationships between sediment and other contaminants of interest, i.e. nutrients and pathogens;

- Carry out high-resolution temporal monitoring of sediment fluxes, possibly at a number of locations within type catchments to better understand sediment mobilisation and transportation mechanisms;

- Propose sediment delivery and transport hypotheses, using values from the literature and consider sediment fingerprinting and transport modelling to test the hypotheses; and

- Compare sediment with other contaminants of concern.

Phosphorus

- Although studies to date in Ireland have demonstrated that dissolved phosphorus is often the dominant phosphorus fraction exported to water bodies from surrounding land uses, further research is required on the role of sediment in the mobilisation, attenuation, and transport of phosphorus to water bodies;

- Further research is required into the role of septic tanks in supplying diffuse phosphorus to watercourses at catchment scale; and

- Limited data are available on phosphorus in groundwater in Ireland and increased monitoring of these water bodies is required.

Nitrogen

- Application of geochemical techniques to identify and to quantify denitrification processes along relevant pathways;

- Further research is required into the role of septic tanks in supplying diffuse nitrogen to watercourses at catchment scale;

- Evaluation of the mobility of nitrogen species along near-surface (interflow) pathways; and

- Limited information exists concerning the relative abundance of nitrogen species impacting aquatic receptors along different pathways during hydrological events, and how these responses compare with those of phosphorus.

Pesticides

- Further study of pesticides should not be considered within the Pathways Project framework in view of the limited data available in Ireland.

7.3.1.3 Ecological research

Ecological research will firstly determine what impacts are present at sites influenced by the various attenuation pathways. The ideal would be to target sites that lie within catchments with varying pathway susceptibility.

The main body of the ecological research to be completed will provide assessment of temporal changes in community composition and structure in response to inputs. The final selection of indicators will depend on the pressures targeted and whether multiple stressors are an issue. At the very least, two biological groups will be selected and the analysis will involve the use of multiple metrics. The main objective is to reconcile the temporal changes in the biological indicators with the results of the event-based sampling. Anthropogenic stresses that impact on aquatic biota may not always be detected by routine hydrochemical sampling. The ecological monitoring will help validate whether the hydrochemical sampling undertaken in this project has detected the significant inputs. Detection of biological impact with no corresponding input of a contaminant may indicate that pathways have not been considered or are missing.

7.3.2 Additional research

Recommendations for potential research considered beyond the scope of the Pathways Project include the following:

- Further characterisation of interflow across a range of hydrological scenarios;
- Investigation into the likely effects of climate change on the flow contributions to receptors from different pathways;
- Development of suitable analytical suites for monitoring of pesticides incorporating degradation products and/or surrogates and additional research on the fate and transport of pesticides in Ireland, validating the information within the FOOTPRINT database for use within the FOOTPRINT CMT;
- Reappraisal of water quality monitoring strategies leading to more targeted monitoring of both surface water and groundwater;
- An increased understanding of biogeochemical soil processes and their buffering capacity would provide an insight into the potential of soils to mitigate against diffuse pollution of watercourses;
- In Ireland, limited research has been carried out on the role of preferential flow channels on nutrient export from soil to water and hence this warrants further research; and
- Determination of the occurrence of denitrification across the fractured/weathered matrix/matrix sub-zones and assessment of whether small-scale studies of denitrification in fracture networks can be scaled up to regional aquifer/catchment scale.

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Acronyms

2,4-D	2,4-Dichlorophenoxyacetic acid
AE	Actual evapotranspiration
ASPT	Average Score Per Taxon
AWB	Artificial Water Body
BFI	Baseflow index
bgl	Below ground level
BMWP	Biological Monitoring Working Party
CBAS	Correspondence Analysis-Based Assessment System
CKBF	Time constant for baseflow
CMT	Catchment management tool
CSA	Critical source area
DAFF	Department of Agriculture, Fisheries and Food
DCU	Dublin City University
DIN	Dissolved inorganic nitrogen
DNRA	Dissimilatory nitrate reduction to ammonium
DOC	Dissolved organic carbon
DoE	Department of the Environment
DoEHLG	Department of the Environment, Heritage and Local Government
DPS	Degree of phosphorus saturation
DRP	Dissolved reactive phosphorus
DT_{50}	Half-life value
DWS	Drinking Water Standard
EDEN	Environmental Data Exchange Network
EMMA	End Member Mixing Analysis
EPA	Environmental Protection Agency
EPT	Ephemeroptera, Plecoptera, Trichoptera
EQR	Ecological Quality Ratio
EQS	Environmental Quality Standard
ESB	Electricity Supply Board
ESBI	ESB International
EU	European Union
FDC	Frequency duration curve

FIO	Faecal indicator organism
f_{OC}	Fraction of organic carbon
GEP	Good Ecological Potential
GES	Good Ecological Status
GIS	Geographic Information System
GMWL	Global Meteoric Water Line
GSI	Geological Survey of Ireland
GUI	Graphical user interface
GUS	Groundwater Ubiquity Score
GWDTE	Groundwater-dependent terrestrial ecosystem
GWG	Groundwater Working Group
HMWB	Heavily Modified Water Body
HOST	Hydrology of Soil Types
ICM	International Common Metric
IFI	Irish Fertiliser Industry
IWDDS	Interactive Web Data Delivery System
K_{oc}	Sorption coefficient
LRU	Livestock-rearing unit
MCPA	2-Methyl-4-chlorophenoxyacetic acid
MOPS	Mitigation of Phosphorus and Sediment
MRC	Master Recession Curve
MTR	Mean Trophic Rank
N	Nitrogen
NH_4	Ammonia
NO_2	Nitrite
NO_3	Nitrate
OD	Ordnance datum
OPW	Office of Public Works
OWTS	On-site wastewater treatment system
P	Phosphorus
PE	Potential evapotranspiration
Pn	Net precipitation
PP	Particulate phosphorus
QIF	Interflow contribution
QOF	Overland flow

QUB	Queen's University Belfast
RBD	River Basin District
RBMP	River Basin Management Plan
RHAT	Rapid Hydromorphology Assessment Technique
RPA	Register of Protected Areas
SAC	Special Area of Conservation
SAC^{254}	Spectral absorbance capacity at 254 nm
SMD	Soil moisture deficit
SNIFFER	Scottish & Northern Ireland Forum for Environmental Research
SOM	Solid organic matter
SPARROW	SPAtially Referenced Regression On Watershed Attributes
SPEAR	SPEcies At Risk
SRP	Soluble reactive phosphorus
SS	Suspended solids
SSRS	Small Streams Risk Score
STP	Soil test phosphorus
STRIVE	Science, Technology, Research and Innovation for the Environment
TAG	Technical Advisory Group
TCD	Trinity College Dublin
TDI	Trophic Diatom Index
TDP	Total dissolved phosphorus
TMDL	Total maximum daily load
TN	Total nitrogen
TP	Total phosphorus
TRP	Total reactive phosphorus
TSS	Total suspended solids
TVC	Total viable count
UCD	University College Dublin
USGS	United States Geological Survey
UV	Ultraviolet
VSA	Variable source area
WFD	Water Framework Directive
WHO	World Health Organisation

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomh-nithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail.
- Scardadh dramhuisce

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.

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