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Modelling the Response of Freshwaters to Catchment-Scale Phosphorus Loading and Mitigation in the Irish Ecoregion

Sheila Greene

A thesis submitted to the University of Dublin, Trinity College
for the Degree of Doctor of Philosophy

October 2012

Department of Geography



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Summary

Freshwater eutrophication, caused by over-enrichment by P as a result of anthropogenic activity, is increasing worldwide. In response, POMs that seek to reduce and reverse eutrophication and its effects through the mitigation of inputs of P have been implemented at national and international levels. Current European legislation requires effective mitigation of P loss from catchments containing freshwaters classified as below good status or at risk of not reaching good status by 2015 to be fully implemented by the end of 2012. However, meeting good status poses a major challenge for the Irish Ecoregion. Although measures targeted at preventing P loss from catchments have been implemented, there is inadequate information available on the most appropriate POMs in different environmental settings. Employing a mathematical modelling framework, this thesis examines variations of P in freshwaters as a function of environmental conditions and their impact on the relative success of P remediation attempts by POMs. Three discrete assessments were pursued, comprising:

- (i) Evaluation of the impact of sources of P and environmental conditions on the effectiveness of POMs aimed at reducing loading of P to seven rivers located in an intensively farmed drumlin region of the Irish Ecoregion (the Lough Sheelin catchment). Functional relationships between P discharge and concentration mechanisms for the years before, during and after POM implementation were explored using a novel LAM. The model was calibrated using river TP, MRP and runoff data sampled three times a week during 1995 to 2008. Model outputs were used to infer changes in P loss from point and diffuse sources in subcatchments during P mitigation as a function of environmental condition.
- (ii) Assessment of the influence of internal loading of P on the recovery of a eutrophic shallow lake (Lough Sheelin) that drains the rivers studied in part (i). A TP budget for the lake was reconstructed for 1990 to 2008 to identify the key components of the TP cycle driving the concentration of TP in the lake. A series of widely used TP loading-response models that describe the relationship between TP sources (lake TP loading) and TP response (lake TP concentration) were used to highlight changes in TP sedimentation rates. The relationship between chlorophyll a and TP was examined for changes during the P mitigation programme.
- (iii) Identification and quantification of the relative hierarchy of environmental conditions in catchments that influence concentrations of flow-weighted MRP in 72 rivers across the Irish Ecoregion. A georeferenced database comprising concentrations of MRP from 23 rivers in NI and 49 rivers in the RoI, together with digital spatial data on environmental conditions in the

river catchments was employed in this landscape-scale study. The relative strengths of environmental predictors of MRP in rivers for both winter and summer months were examined using linear regression and multivariate analysis. The residual variation of MRP in rivers unaccounted for by environmental conditions was examined for spatial correlation between river monitoring points using variogram analysis.

Estimations from the LAM showed temporal and spatial heterogeneity of P sources existed within and between subcatchments. These variations were attributed to differences in agricultural intensity, soil type, rainfall and anthropogenically-sourced effluent P loading from both urban and rural areas. Rivers were sensitive to flow regime, which can result in eutrophication of rivers during low flows as a result of point-sourced contributions of P and lake enrichment from frequent flood events that contain large loads of P. The outputs of LAMs demonstrated that lower P export rates followed specific P mitigation measures. For example, the LAM estimated up to 80% decreases in point MRP load after enhanced P removal at WWTPs in urban subcatchments and the implementation of septic tank and agricultural bye-laws in rural subcatchments. However, the effectiveness of some POMs appears to have also been reduced by factors such as high rainfall and accidental pollution events, suggesting that relatively short-duration events outside the control of mitigation management may have attenuated a signal of improving water quality. The TP budget for Lough Sheelin suggested that, for the time studied, overall retention of TP in the sediment exceeded TP release. On average, 73% of TP delivered to the lake was stored in the lake. However, estimated sedimentation rates of TP showed significant decline during the latter stages of the study period, accompanied by a trend of increasing concentrations of TP. These increases occurred despite an overall reduction in the loading of TP from the catchment. Filtration action and homeostatic excretion by an invasive species (zebra mussels) established in the lake by this time were the most likely cause for these findings. The decoupling of the chlorophyll a - TP relationship in the lake during the same period supports this explanation.

Findings at the landscape-scale (Irish Ecoregion) showed that environmental conditions in catchments relating to hydrological transportation and connectivity (mean slope, topographic wetness) exerted the strongest influence on concentrations of MRP in rivers. Furthermore, human population densities accounted for the second strongest predictor of MRP in winter, indicating that nutrient pollution by sewage discharges (WWTP and septic tanks) remains highly significant. Significant spatial correlation between river monitoring points was detected. A geospatial model, incorporating environmental conditions and a spatial structure, to predict concentrations of MRP in unmonitored river catchments was developed and validated.

Acknowledgments

I would like to thank my co-supervisors Dr Yvonne McElarney and Prof David Taylor for providing the opportunity for me to undertake this research. I express my gratitude to Yvonne and David for their guidance, support and patience, as well as the time spent in meetings and reading the various drafts of this thesis. I would also like to extend my thanks to Dr Bob Foy and Prof Phil Jordan who took the time to offer additional advice, support and guidance.

I gratefully acknowledge the provision of financial assistance from the Irish Environmental Protection Agency, under the Science, Technology, Research & Innovation for the Environment (STRIVE) Programme 2007–2013. This research was Work Package 1 of the EFFECT project (project #2007-W-MS-3-S1). The EPA also provided critical commentary from members of the EFFECT project steering group Prof Steve Ormerod and Prof John Quinton, and project management from Dr Alice Wemaere.

I owe many thanks to numerous people who have given their time, advice and assistance to this research. Thanks in particular to Dr Alex Higgins and the staff at Agri-Food and Biosciences Institute (Belfast) for statistical advice and access to data. Thanks are also due to several individuals and institutions, notably the Irish Environmental Protection Agency, Cavan County Council, Inland Fisheries Ireland, the Northern Ireland Environmental Agency, the Irish Central Statistics Office, the Northern Ireland Statistics and Research Agency, the Office of Public Works, Geological Survey Ireland, Geological Survey Northern Ireland and the Forestry Service, for providing and permitting use of their data.

Many thanks to my friends and colleagues in the Department of Geography and School of Natural Science, Trinity College, University of Dublin. I would especially like to express my appreciation to Jennifer Brady for her constant encouragement throughout this research.

I would like to thank my parents for providing me with the opportunity and support to progress to this stage in my education. Many thanks also to my friends and sisters, especially Alice and Claire for their help close to the submission date. Finally, I would like to thank Matthew for his proofreading abilities and continuous encouragement over the full duration of this research.

Publications

The studies presented in this thesis have been published in the following:

Greene, S., Taylor, D., McElarney, Y.R., Foy, R.H. & Jordan, P. (2011) An evaluation of catchment-scale phosphorus mitigation using load apportionment modelling. *Science of the Total Environment*, **409**, 2211-2221.

Taylor, D., McElarney, Y., Greene, S., Barry, C., Foy, B., Allen, M., Jordan, P., Macintosh, K., Arnscheidt, J. & Murnaghan, S. (2012) *An effective framework for assessing aquatic ecosystem responses to implementation of the Phosphorous Regulations (EFFECT)*. Final report to the EPA, Wexford, Ireland.

Taylor, D., McElarney, Y., Greene, S., Barry, C., Foy, B., Jordan, P. (2012) *An Assessment of Aquatic Ecosystem Responses to Measures Aimed at Improving Water Quality in the Irish Ecoregion*. STRIVE Synthesis report to the EPA, Wexford, Ireland.

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List of abbreviations, acronyms and symbols

°C	Degrees centigrade
$\mu\text{g l}^{-1}$	Micrograms per litre
μm	Micrometer
%	Percentage
α	Variogram range (kilometre)
AFBI	Agri-Food and Biosciences Institute
AIM	Animal Identification and Movement
Al-P	Aluminium-bound Phosphorus
AMSL	Above mean sea level
ANOVA	Analysis Of Variance
ANSWERS	Areal Non point Source Watershed Environment Response Simulation
ATP	Adenosine Tri-Phosphate
BMP	Best management practices
BP	Before present
CaCo_3	Calcium Carbonate
Ca-P	Calcium-bound Phosphorus
CEA	Cost-effectiveness analysis
CH_4	Methane
Chl a - TP	Chlorophyll a - Total Phosphorus relationship
CLC	Corine Land Cover
CMMS	Cattle Movement Monitoring System
Co.	County
C_0	Variogram nugget variance
C_0+C	Variogram sill variance
CSA	Critical source areas
CSO	Central Statistics Office
CSTR	Continuous stirred-tank reactor
CV-RMSE	Coefficient of variation of the Root Mean Square Error
DAFF	Department of Agriculture, Fisheries and Food
DANI	Department of Agriculture Northern Ireland
DARD	Department of Agriculture and Rural Development
DED	Digital electoral division
DEM	Digital elevation model

dmf	Daily mean flow
DNA	Deoxyribonucleic acid
DoEHLG	Department of Environment Heritage and Local Government
EA	Environment Agency
EC	European Commission
EEA	European Environment Agency
e.g	For example
EHS	Environment and Heritage Service (Northern Ireland)
E_i	Phosphorus export coefficient
EPA	Environmental Protection Agency
ES	Estimation subset for load apportionment model
EVO	Environmental Virtual Observatory
EU	European Union
Fe	Iron
Fe-P	Iron-bound Phosphorus
fwMRP	Flow-weighted concentration of MRP ($\mu\text{g l}^{-1}$)
GIS	Geographical Information Systems
GLM	General Linear Model
GSI	Geological Survey of Ireland
GSNI	Geological Survey of Northern Ireland
h	Variogram lag distance (kilometre)
ha	Hectare
H_0	Null hypothesis
HSPF	Hydrological Simulation Program – FORTRAN
IFI	Inland Fisheries Ireland
IHP	International Hydrological Programme
INCA-P	Integrated Catchments model of Phosphorus dynamics
IPPC	Integrated pollution prevention control
$\text{kg km}^{-2} \text{yr}^{-1}$	Kilograms per kilometre squared per year
km^2	Kilometre squared
l	Litre
LAM	Load apportionment model
Log_{10}	Base-10 logarithm
LU	Livestock unit
m	Metre

$\text{m}^3 \text{hr}^{-1}$	Cubic metres per hour
$\text{m}^3 \text{s}^{-1}$	Cubic metres per second
mg l^{-1}	Milligrams per litre
mm	Millimetres
MRP	Molybdate Reactive Phosphorus
n	Number of samples
N_2	Nitrogen gas
NAP	Nitrates Action Programme
NI	Northern Ireland
NIEA	Northern Ireland Environmental Agency
NISRA	Northern Ireland Statistics and Research Agency
NO_3^-	Nitrate
NVZ	Nitrate Vulnerable Zones
O_2	Oxygen
OECD	Organisation for Economic Co-operation and Development
OPW	Office of Public Works
OSI	Ordnance Survey of Ireland
OSNI	Ordnance Survey of Northern Ireland
P	Phosphorus
p	Probability
P Regs	Phosphorus Regulation
PCA	Principle Component Analysis
PIT	Phosphorus Indicators Tool
PLUS	Phosphorus Land-Use Slope
POM	Programme of measure
PP	Particulate Phosphorus
PSYCHIC	Phosphorus and Sediment Yield Characterisation in Catchments
Q95: Q5	
ratio	The ratio of the 95% exceedance flow to the 5% exceedance flow
Q-rating	Biological quality rating
r	Pearson correlation coefficient
R	TP sediment retention coefficient
R^2	Regression coefficient of determination
RA	Rivers Agency
RBD	River Basin District

RBMP	River Basin Management Plan
R_e	Runoff point at which point and diffuse sources are equal
REDOX	Reduction-oxidation
RK	Regression-kriging
RMSE	Root Mean Square Error
RNA	Ribonucleic acid
RoI	Republic of Ireland
SIRBD	Shannon International River Basin District
SOP	Soluble Organic Phosphorus
SRP	Soluble Reactive Phosphorus
SUP	Soluble Unreactive Phosphorus
SWAT	Soil and Water Assessment Tool
$t\ yr^{-1}$	Tonnes per year
TDP	Total Dissolved Phosphorus
TP	Total Phosphorus
TRP	Total Reactive Phosphorus
TSP	Total Soluble Phosphorus
TWI	Topographical Wetness Index
UNESCO	United Nations Educational, Scientific and Cultural Organization
USEPA	United States Environmental Protection Agency
VIF	Variance inflation factor
VS	Validation subset for load apportionment model
VSA	Variable source area
WFD	Water Framework Directive
WWTP	Waste water treatment plant
yr	A year
yr^{-1}	Per year

Chapter 1

Introduction

1.1 Research rationale

Freshwater eutrophication, caused by over-enrichment by P as a result of anthropogenic activity, is a pervasive environmental challenge worldwide (Johnson *et al.*, 2010; Dodds *et al.*, 2009; Neal and Heathwaite, 2005). The number of rivers and lakes displaying extensive P pollution events has risen substantially over the last decade (Bennett *et al.*, 2001; Hilton *et al.*, 2006; Smith and Schindler, 2009; Seitzinger *et al.*, 2010), and this trend has potential to show significant growth in the next few decades (Moss, 2011). Future scenarios that are most likely to intensify the amount of P transferred to freshwaters include the short-term certainty of global P resources, rising human population levels, together with the pressures of projected alterations in the environment, such as climate and land use changes (Jennings *et al.*, 2009; Van Vuuren *et al.*, 2010; Dawson and Hilton, 2011; Tong *et al.*, 2012). Therefore, the current importance of understanding, preventing and reversing the effects of P enrichment of rivers and lakes has never been greater.

Widespread recognition that high concentrations of P in freshwaters are a major threat to ecosystem health has led to the development and implementation of legislation at national and international levels (Maguire *et al.*, 2009). For example, in the EU, national legislation of member states has been subsumed within the WFD (2000/60/EC), which seeks to ensure the effective and sustainable management of water resources, and to achieve and maintain good water quality for all water bodies by 2015 (EC, 2000). The WFD management unit, RBD, encourages an integrated catchment-scale approach to water quality management (Rekolainen *et al.*, 2003; Bennion and Battarbee, 2007). Management plans drawn-up by RBDs have to include the design and implementation of POMs that are needed to ensure that the water quality objectives of the WFD are met within the stipulated timeframe. Measures devised to mitigate pollution impacts, including impacts of P, are largely based on existing EU regulations and policies (Crabtree *et al.*, 2009). However, measures may also comprise supplementary intervention attempts deemed necessary to achieve WFD targets (Kavanagh and Bree, 2009).

Inputs from point sources of P, such as from WWTPs or industrial discharge, have been reduced substantially in the last few decades, owing to the relative ease by which they can be identified and managed (Bennion *et al.*, 2005; Kronvang *et al.*, 2007; Grizzetti *et al.*, 2012). The problem of

eutrophication is far from being resolved, however, agricultural (predominantly diffuse) sources of P remain important contributors of P to freshwaters (Jennings *et al.*, 2003; Schindler, 2006; Sharpley *et al.*, 2009). Releases of P from diffuse sources are difficult to manage, owing to their intermittent nature and the challenge of pinning down the actual locations for mobilisation. Phosphorus is introduced to agricultural land in fertilisers, animal feed and manure which, in association with rainfall events and seasonal agricultural practices, is transported to the water network by overland flow, groundwater and infiltration through the soil (Withers and Jarvie, 2008). However, leaking manure and silage stores, farmyard runoff, artificial land drains and livestock defecating onto exposed compacted soils and into waterbodies (Sharpley and Syers, 1979; Edwards *et al.*, 2008; Withers and Jarvie, 2008; Jarvie *et al.*, 2010) comprise important agriculture point sources. Such agricultural point sources have to date escaped the level of attention directed at point sources associated with urban areas and industry.

Agriculture accounts for 68% of total land use in the Irish Ecoregion (comprising the RoI and NI), a high proportion compared with the EU15 average of 40% (CSO, 2010, DARD, 2010; DARD, 2011). Predominant agricultural enterprises include grassland-based dairy and mixed livestock farming, followed by the pig and poultry sectors (CSO, 2010, DARD, 2010). Incidental transfers of P as a result of the timing of manure and inorganic fertiliser spreading, together with losses from soils highly saturated with P, constitute the most important agricultural pressures on water quality across the Irish Ecoregion (Smith *et al.*, 2005; Doody *et al.*, 2012). These diffuse sources of nutrients have been attributed to 47% and 22% of substantiated incidents of water pollution in the RoI and NI, respectively, and continue to prove a significant challenge to water quality improvement efforts in the Irish Ecoregion (NIEA, 2009; McGarrigle *et al.*, 2010; Schulte *et al.*, 2010; Donnelly, 2011).

The first RBMPs describing a POM strategy to protect and improve the quality of waterbodies in the Irish Ecoregion up to 2015 were submitted to the EC in 2010. Measures directed at mitigating P from point sources (typically WWTP discharges) are mainly prescribed by full enforcement of the Urban Waste Water Treatment Directive (91/271/EEC). Diffuse sources of P from agricultural catchments are regulated by the provisions of the Nitrates Directive (91/676/EEC). Measures stipulated by both these directives must be fully operational by the end of 2012, allowing a minimum of three years for the catchment to respond after which they must be evaluated for efficiency and updated to reflect any changes or any additional measures identified as necessary to achieve the WFD objectives (Kavanagh and Bree, 2009).

Although POMs to prevent and reverse the effects of P-induced eutrophication in rivers and lakes have been implemented in catchments across the Irish Ecoregion (EPA, 2006; EHS, 2006), there is insufficient information on the most appropriate POMs for a specific environmental setting. In particular, information pertaining to the underlying environmental factors in a catchment that influence the relative sensitivity of freshwaters to increased P pressure is limited. However, the shortage of resources, poor conceptual understanding of the steps between P production and the aquatic presence and impacts of P and paucity of time series data that span implementation of a particular POM are the main challenges restraining the assessment of mitigation strategies (Wall *et al.*, 2011; Cherry *et al.*, 2008; Kyllmar *et al.*, 2006; Ulén and Jakobsson, 2005). As a consequence, the efficiency of POMs has only rarely been tested, resulting in a lack of unequivocal evidence to guide the implementation of future measures. The need to address this information gap, which is further highlighted by the uncertainty surrounding the suitability, effectiveness and evaluation of some POMs (Mayes and Codling, 2009; Schulte *et al.*, 2010; Balana *et al.*, 2011; EC, 2011; Wall *et al.*, 2011), provided the motivation for the current research.

Modelling P transfers from land to receiving freshwaters is an important part of assessing the risk of pollution and the effectiveness of mitigation strategies to meet the demands of legislation such as the WFD. In the current research, the development, employment and outputs of new and existing mathematical models provide contributions to addressing information gaps relating to the effectiveness of P mitigation. The overall contributions of this study are threefold. First, the outputs of a model (LAM) developed to apportion the P load delivered to rivers before, during and after the application of POMs into point and diffuse components give greater insight into the cause-effect relationships between environmental conditions, sources of P and the effectiveness of mitigation attempts. Second, reconstruction of a long-term TP budget and application of existing TP loading-response models for lakes in a new context provides sufficient evidence to identify the role of sediment dynamics in impairing the recovery of a eutrophic shallow lake. Third, the relative hierarchy of catchment-specific conditions that exert influence on the concentrations of P in multiple rivers across the Irish Ecoregion is quantified.

1.2. Research questions

The aim of this thesis is to better understand the impact of environmental conditions on the sources of P and the effectiveness of POMs in reducing the concentration of P in rivers and lakes. Two main research questions, addressed through the testing of hypotheses, have guided the current research:

- **Research question 1:** Is there a relationship between environmental conditions, sources of P and the effectiveness of POMs aimed at reducing P inputs to rivers and lakes at the level of the subcatchment/catchment (i.e. large scale, small area)?
- **Research question 2:** Is there a relationship between environmental conditions and P values for river water quality at the landscape-scale (i.e. small scale, large area)?

Answering both research questions required the collation and analyses of secondary data describing environmental conditions, sources of P and concentrations of P in rivers and lakes. The data were used for statistical analysis, followed by the development and calibration of mathematical models, the outputs of which provided a basis for testing the hypotheses that underpin the research questions.

1.3. Thesis structure

This chapter began by contextualising the current research, gaps in the existing knowledge were highlighted and the guiding research questions defined. The chapters that follow in the thesis comprise:

- Chapter 2 provides a review of the existing knowledge that is central to the backdrop of this thesis. An overview of the importance of P in the environment and the analytical determination of P is given. A review of the current knowledge on the mechanisms that control the transfer of P from terrestrial to aquatic environments, cycle of P in a lake and eutrophication by P enrichment is presented. The scale of the current eutrophication challenge and previous policy relating to P in freshwaters in the RoI and current policy for the WFD in the Irish Ecoregion are described. Finally, an overview of the most commonly used mathematical estimation and modelling techniques to simulate the movement of P is given.

- Chapter 3 gives an overview of the Irish Ecoregion and defines the criteria that water quality monitoring points and their corresponding catchments must meet to be considered suitable for both scales of study in the current research. Descriptive information on the water quality sampling regime at each monitoring point and the environmental characteristics of their respective catchments are then outlined.
- Chapters 4, 5 and 6, describe the analyses carried out in order to test the hypotheses that underpin the research questions. Within these chapters, a brief introduction to the research problem is first provided, followed by a description of the methods and materials employed, the result obtained and a discussion of the results in view of the research hypothesis and published literature. More precisely, Chapter 4 concerns the development of a LAM to test the efficiency of POMs aimed at reducing P at the level of the subcatchment and to examine environmental constraints on recovery. Chapter 5 details the reconstruction of the TP budget for a lake and the testing of five established TP loading-response models. The response of TP in the lake to POMs and constraints posed by environmental conditions within the lake is highlighted by the estimated outputs. Chapter 6 describes regression and geostatistical analyses to identify and model the deterministic relationships, at the level of the landscape, between environmental conditions in a catchment and the P concentration in a river.
- Chapter 7 contains an overall discussion of the key research findings from Chapter 4 to 6, in relation to the broader aim the thesis and the published literature. The practical applicability of the models developed in the current research for use as decision-support tools in the Irish Ecoregion is considered. Limitations of the research methods and materials employed are acknowledged and recommendations for the direction of future research are provided. Finally, an overall conclusion to the research is presented.

Chapter 2

Research background

2.1. Introduction

Specifically, and focusing in the Irish Ecoregion, the current research sought to better understand the influence exerted by environmental conditions on the sources of P and the effectiveness of POMs in reducing the concentrations of P in rivers and lakes. This chapter presents the background to the current research, and provides a review of the relevant literature in the field of P transfer and P-induced eutrophication. Understanding the relative steps and impacts of P transfer to freshwaters is an important aspect in understanding the main factors that may exert constraints on the effectiveness of P mitigation.

This chapter consists of five sections. The first section summarises the importance of P in the environment, together with a description of the analytical methods typically used to detect the concentration of P in freshwaters. The second section outlines the current knowledge pertaining to P transfer. The third section considers the challenges that P-induced eutrophication present with respect to management resources, time and financial investment. The fourth section describes implementation of P-related POMs for freshwater quality in the Irish Ecoregion. Focus is placed on the last measures introduced in the RoI (P Regs) followed by a review of the POM requirements of the WFD and the current progress in their implementation across the Irish Ecoregion. The final section provides a review of the estimation and modelling methods typically used to simulate P dynamics and quantify loading of P from catchments to freshwaters with attention focused on the types of empirical models adopted in the current research.

2.2 The importance of P in the environment

Phosphorus, a mineral element and macronutrient, is essential for primary and secondary biological production (Wetzel, 2001). In comparison with other macronutrients required for biological growth, P is the least abundant in aquatic systems, and so is generally the limiting element regulating ecosystem health (Vollenweider, 1968; Mainstone and Parr, 2002).

Phosphorus is required to synthesise essential cellular components by both flora and fauna; P is a critical component of phospholipid cell membranes, DNA/RNA, and ATP, which are used for transport of substances into/out of the cell, cell division and energy transformations (Likens,

2009). Hydroxyapatite, a calcium phosphate mineral, is a key component of bones and tooth enamel in fauna and insufficient amounts of P cause brittle bones along with poor growth rates and can lead to tooth decay (MacKenzie *et al.*, 2006). In plants, deficiencies of P lead to low growth and a blue/green colouration of leaves (Mengel *et al.*, 2001).

Phosphorus exists in the environment in particulate and dissolved phases. Unlike other biologically important elements that have well defined redox mechanisms (e.g. denitrification for the conversion of NO_3^- to N_2), a gaseous phase of P is rare (Ashley *et al.*, 2011). Nevertheless, the cycling of P in both terrestrial and aquatic systems can be complex, owing to the large number of biotic and chemical pathways controlling its movement and form (Likens, 2009). Highly available dissolved P may be converted into less-available particulate and organic forms following uptake in sediments or by organisms. In the particulate phase P is bound in mineral complexes (Ca-P, Fe-P, Al-P), clays, humic material, and the structural cells of organisms. Under oxic conditions, chemical binding is sufficient to strongly inhibit P release from insoluble complexes. However, if anoxia occurs, the associated development of reducing conditions may result in the release of highly available P for biotic assimilation.

2.3 Detecting concentrations of P in freshwaters

An analytical chemical approach is commonly used to monitor the concentration of P in rivers and lakes (Closs *et al.*, 2004). The P content of freshwater can be divided into particulate-bound and dissolved fractions for chemical analyses by filtering water samples through 0.45 μm membrane filters (Jarvie *et al.*, 2002). Concentrations of P are determined analytically by the method modified by Murphy and Riley (1962). Water samples are digested in acid, which releases P from organic matter and converts any organic P compounds into water soluble, inorganic phosphates, allowing them to be quantified spectrophotometrically.

The P content of filtered and unfiltered water samples is termed TDP and TP, respectively. Total dissolved P includes suspended colloidal soil particles and organic matter that have high P sorption capacity (Quinton *et al.*, 2001), and is further separated into SRP, which is equivalent to dissolved inorganic P (i.e. bioavailable P), and SUP, which is a non-bioavailable organic P compound. Soluble reactive P is determined analytically, while SUP is established by subtracting SRP from TDP (Jarvie *et al.*, 2002). The PP fraction, determined by subtracting the TDP from the TP, is the P sorbed to soil particles and organic matter with a diameter greater than 0.45 μm . The dissolved P fraction referred to as MRP is equivalent to: (a) SRP, for filtered samples; and (b) SRP plus a fraction of particulate P (which is reactive to phosphomolybdenum blue method reagents)

for unfiltered samples (Jarvie *et al.*, 2002). Determinations of MRP on unfiltered samples are referred to as *orthophosphate as P* by the EPA in the RoI and the EA in the UK (Jarvie *et al.*, 2002; Jennings *et al.*, 2003).

2.4 P transfer to freshwaters

The transfer of P from land to freshwaters is an important process, impacting on chemical and biological water quality. The P transfer continuum conceptualises the process by which P is transferred from its source in the terrestrial environment to the aquatic environment (Haygarth *et al.*, 2005a). The four-tiered framework (Figure 2.1), describes how sources of P as inputs from land are exposed to a mobilisation mechanism and, by way of hydrological pathways, are delivered to a river channel. Depending on concentrations of P and sensitivity of the receiving waterbody, P mobilized and transferred in this way may have ecological effects. Although there is now a comprehensive knowledge base to support the first two tiers of the P transfer continuum (sources and mobilisation), understanding of the third and fourth tiers (delivery and impacts) is limited.

The spatial scale of P measurement (e.g. subcatchment or catchment level) may affect understanding of P transfer in catchments; the P transfer processes that are able to be measured may vary with the scale of observation or certain P transfer processes may only operate at particular scales. These complexities and the potential for the transfer of P to be influenced by land management increases as scale increases, as the larger scale incorporates all the processes which occur at the small scale (e.g. infiltration, surface runoff, macropore flow). In the following review, a description of the process by which P is transferred from land to water is divided into the four steps of the P transfer continuum model: source-mobilisation-delivery-impact (Haygarth *et al.*, 2005a).

2.4.1 Source

Sources are entities in a catchment that have the potential to supply P to a drainage network and are both natural and anthropogenic (Withers and Jarvie, 2008). Natural sources of P include atmospheric deposition, natural weathering of soil and detritus from riparian vegetation; anthropogenic sources are often categorized into point or diffuse (Pieterse *et al.*, 2003; Jarvie *et al.*, 2006; Liu and Chen, 2008). Phosphorus from point sources is generally regarded as being discharged continuously from discrete points such as WWTPs, septic tanks with direct connection to rivers, farmyards and industrial activities, and is most commonly in soluble form (Withers and

Jarvie, 2008). Conversely, P from diffuse sources is incorporated in surface or sub-surface runoff, originating from large expanses of area dispersed throughout a catchment. Diffuse sources of P tend to be active only when a hydrological pathway is available. Diffuse sourced P has a larger fraction of particulate P and is invariably linked with runoff from urban areas, septic tank soak-aways, forestry, and agriculture (Withers and Jarvie, 2008). Some sources of P, such as road and track runoff, septic tank discharges and farmyard runoff, share characteristics with both point and diffuse categories (Arnscheidt *et al.*, 2007; Edwards and Withers, 2008; Jarvie *et al.*, 2010).

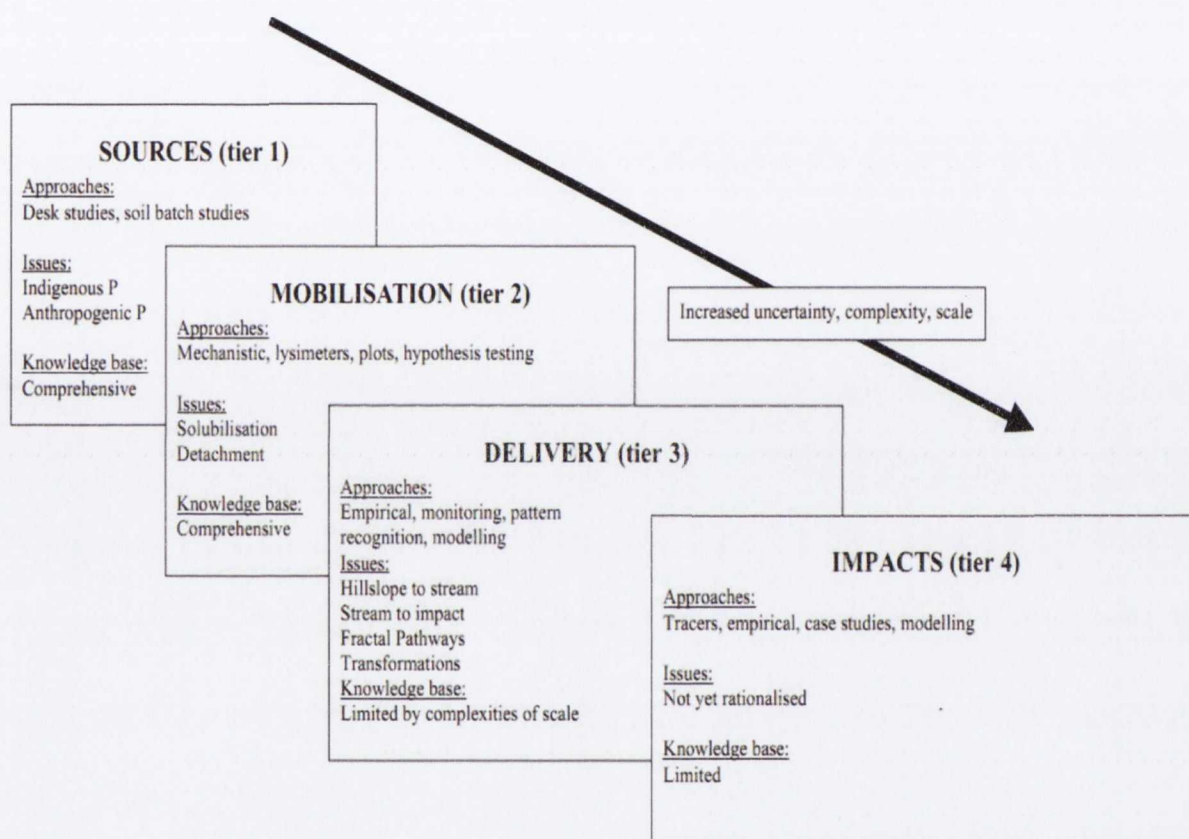


Figure 2.1. The P transfer continuum is a conceptual four-tiered model that describes the transfer of P from sources in the terrestrial environment (tier 1) to the aquatic environment in which they can exert an impact (tier 4). The research approaches and gaps in the understanding of this process (mainly tier 3 and tier 4) are noted as being limited. Diagram from Haygarth *et al.* (2005a).

2.4.2 Mobilisation

Mobilisation, the process by which P molecules are activated from soil, initiates the transfer of P to water (Haygarth *et al.*, 2005a). The mobilisation process, a combination of chemical and physical processes operating in the soil profile that are P-compound specific, operates either by solubilisation or detachment mechanisms (Quinton *et al.*, 2001; Jordan and Rippey, 2003; Dougherty *et al.*, 2004; Hodgkinson and Withers, 2007). Solubilisation releases P molecules from surface soil to soil water for potential transfer by surface runoff. Sorption/desorption kinetics and biochemical reactions are key to this process (Guppy *et al.*, 2005). The detachment and entrainment of soil particles containing P compounds ($> 0.45 \mu\text{m}$) is a physical means of mobilising P from soil to surface water. Detachment of P is predominantly associated with soil erosion, which is the main method of PP transfer to receiving waterbodies (Haygarth and Jarvis, 1999; Quinton *et al.*, 2010). Mechanical detachment of P is a complex amalgamation of erosion rates and processes (Jarvis *et al.*, 1999; Dougherty *et al.*, 2004). Similar mechanisms (solubilisation and detachment) for the sub-surface mobilisation of P to soil matrix water, and movement via macropores and artificial drains, have been identified (Jarvis *et al.*, 1999; Heathwaite and Dills, 2000; Hesketh and Brookes, 2000).

Agricultural activities are a landscape-scale pressure with high potential for P transfer to watercourses (Schindler, 2006). Agricultural P (typically inorganic fertilisers and livestock manure) comprise the major component of diffuse-sourced P discharges that are initially applied to the soil surface. Rainwater, passing over or through the soil at variable rates, mobilises inorganic and organic P for potential transfer along surface and sub-surface hydrological pathways. Phosphorus mobilised thus can vary greatly, both spatially and temporally (Withers and Jarvie, 2008). If fertiliser or livestock waste applications coincide with extreme rainfall, especially on compacted or exposed soil, large amounts of P can be mobilised before entering the soil profile (Preedy *et al.*, 2001). Furthermore, high concentrations of P can potentially be mobilised from slurry stores and farmyards and from livestock with direct hydrological connection to a waterbody (Edwards *et al.*, 2008). Extreme rainfall events can provide a mechanism for this connection.

2.4.3 Delivery

Pathways along which P may be transported to a waterbody include: (i) direct point discharge; (ii) surface overland runoff; (iii) subsurface flow as base-flow; and (iv) storm flow (Arnscheidt *et al.*, 2007; Jordan *et al.*, 2007). The amount of P transferred through these paths is primarily determined by a combination of factors that include source type, intensity and duration of rainfall events, soil structure, P composition, catchment shape and topography, and anthropogenic

infrastructure (e.g. artificial drainage/irrigation) (Dils and Heathwaite 1999; Haygarth *et al.*, 1999; Jordan *et al.*, 2005b; Armstrong *et al.*, 2011; Kim *et al.*, 2011; Vidon and Cuadra, 2011).

Point and diffuse sources of P delivered to freshwaters differ in terms of their predominant transfer pathway (Jordan *et al.*, 2007). Phosphorus from both of these sources has contrasting statistical relationships with measured river flow (Bowes *et al.*, 2008). Phosphorus from point sources delivered to rivers as direct discharge are relatively constant, and are therefore independent of flow, typically containing a high fraction of soluble P (Jordan *et al.*, 2007). By comparison, levels of P from diffuse sources are highly dependent on runoff, and have a positive linear relationship with discharge (Edwards and Withers, 2008). During extreme rainfall/storm events, diffuse sources of P, containing large quantities of PP, dominate instantaneous river loads (Tunney *et al.*, 2000; Jordan *et al.*, 2005a). In the intervals between high flow events with runoff pathways disconnected, P loads to rivers are low, especially when point sources are absent or a sufficient dilution factor exists. When fertiliser application overlaps with an extreme rainfall episode, critical transport pathways (incidental transfers) open, resulting in immediate overland surface transfers of P load to waterbodies (Withers *et al.*, 2003; Wood *et al.*, 2005). Any P remaining on the soil surface after hydrological pathways are closed is incorporated into the soil profile in soluble form by biota.

2.4.4 Impact

Once present in a waterbody, P may undergo transformation for assimilation by periphyton, phytoplankton, microorganisms and macrophytes (Withers and Jarvie, 2008). However, high levels of P cause eutrophication, which leads to the alteration of ecosystem structure and function by promoting enhanced biological growth, decreasing biodiversity and increasing fish mortality (Smith *et al.*, 1999; Mainstone *et al.*, 2002). Furthermore, these ecosystem effects quickly evolve into human-related challenges, such as toxic cyanobacterial blooms, O₂ depletion, and reduced water quality, leading to increased treatment costs for the water industry and recreational activities (Carpenter *et al.*, 1998; Smith *et al.*, 1999; Hilton *et al.*, 2006; Qin *et al.*, 2010). Eutrophic conditions may ultimately result in restrictions on access and use.

While links between concentrations of P and phytoplankton growth are well established for lakes (Vollenweider, 1968), understanding of the ecological impact of P on rivers is more limited (Neal *et al.*, 2008; Withers and Jarvie, 2008; Wall *et al.*, 2011). Research has shown, however, that high P concentrations in summer, little diluted by low flows, associated with point sourced P, can be more influential in maintaining a eutrophic status than the P load would otherwise indicate

(Bowes *et al.*, 2010; Jarvie *et al.*, 2010; Withers *et al.*, 2011). Conversely, high diffuse loads of P that are quickly washed into a receiving lake have little local impact on the ecology of the rivers they initially enter; however, these types of loads can have a negative impact on aquatic biota further downstream and in lakes (Withers and Jarvie, 2008).

Physico-chemical retention of P in sediments and the subsequent remobilisation of P also control the impact of P in freshwaters (Søndergaard *et al.*, 2003; Withers and Jarvie, 2008). Retention processes in lakes temporarily remove and/or transform P from the water column for storage in the surface sediment. The sediment-bound P may be released (remobilised) at a later stage allowing the opportunity for biotic assimilation. Such as, P can be bound in the lakebed sediment to redox-sensitive Fe compounds or fixed in labile forms (Selig *et al.*, 2002). Sediment-bound P is released by mechanisms initiated by increases in organic matter in the sediment, which in turn, reduces O₂ composition, encouraging low redox conditions. Under low redox conditions, Fe is chemically reduced, allowing for the release and mobilisation of P for diffusion into the water column, making it available for biological uptake (Moore *et al.*, 1998). This internal loading of P may have impacts on the restoration of an ecosystem by continuing to support nuisance algal growth after external sources of P have been reduced (Welch and Jacoby, 2001).

2.5 Scale of the eutrophication challenge

An excessive amount of P is considered to be the main cause of eutrophication in freshwaters (Smol, 2008). Although rivers and lakes naturally receive P from their catchments over time (e.g. P from the weathering of bedrock to soil, decay of organic material and atmospheric deposition), this type of natural eutrophication rarely causes environmental concern (Rafferty, 2011). Cultural eutrophication, the acceleration of natural eutrophication by anthropogenic activity, however, is a major challenge to ecosystem health.

Cultural eutrophication first received much attention during the 1960s and 1970s, especially in the USA and Europe (Schindler, 2006; Schindler and Vallentyne, 2008). Urbanisation and increases in the use of P-based detergents, combined with large rise in the use of fertilisers in agriculture, led to the impairment of freshwater quality through P-induced eutrophication (Smith *et al.*, 1999; Mainstone and Parr, 2002). Eutrophication has since become one of the most common causes of pollution of freshwaters, accounting for up to 60% of impaired freshwater bodies in the USA (USEPA, 2009). Similarly, eutrophication is currently a pan-European environmental problem; eutrophic or hypertrophic conditions exist in 33% of the freshwater bodies monitored across Europe (EC, 2010; EEA, 2010). In Switzerland, for example, eutrophic

conditions in shallow parts of Lake Geneva have led to an increase of bacterial abundance and activities in freshwater sediments (Thevenon *et al.*, 2011), while in Greece, increased P concentrations in Lake Koronia have led to a shift from ecological autotrophy to hypertrophy characterised by massive cyanobacteria blooms (Mitraki *et al.*, 2004). A recent assessment of the quality of European waters indicates that mass populations of toxic cyanobacteria are relatively widespread and occur in water resources used for drinking water supply, aquaculture, recreation and tourism (UNESCO/IHP, 2005).

Eutrophication events in Europe is usually attributed to agricultural releases of P to freshwater which may exceed $10 \text{ kg km}^{-2} \text{ yr}^{-1}$ but can reach more than $100 \text{ kg km}^{-2} \text{ yr}^{-1}$ (EEA, 2010). Greater application rates of P-based fertilisers typically occur in Western Europe, including the Irish Ecoregion and the UK, with applications usually greater than the assimilation capacity of crops and grassland (EEA, 2010; Schröder *et al.*, 2011). Surplus P thus build up in the soil (potentially up to $2000 \text{ kg P km}^{-2} \text{ yr}^{-1}$) and, when the soil is saturated with P during high rainfall events, high loads of P are transported to the nearest waterbody (Schröder *et al.*, 2011). In NI, a surplus of P in soil has occurred since at least 1925 (Foy *et al.*, 2002). Heaney *et al.* (2001) reported that increases of P from diffuse sources entering Lough Neagh correlated better with this increasing soil P rather than with the growth in the intensity of agricultural production. However, agricultural activities often take an unfair proportion of responsibility for P transfer to freshwaters, especially in the Irish Ecoregion. For example, recent reports from an assessment of WWTPs in the RoI reveal that almost 50% do not meet national or EU standards (Monaghan *et al.*, 2012) and continue to discharge high loads of P directly into freshwaters.

Considerable effort and finance is associated with the ecological restoration of eutrophic freshwater systems in Europe. In the UK, for example, a 20-year programme to restore a shallow lake, Barton Broad, cost €7 million (Johnes, 2009). However, restoration attempts were only partially successful; further damage to ecosystem structure was halted and recolonisation by macrophytes had commenced, but full restoration was constrained by the impacts of uncontrolled P losses from agriculture. Similarly, despite investment since the late 1990s to reduce P loading to the Thames river, P concentrations are still too high ($\text{SRP} > 100 \mu\text{g l}^{-1}$ in spring and summer) and the effects of eutrophication remain apparent (Bowes *et al.*, 2011).

The WFD advocates using a framework based on economic analysis (CEA and CBA) to help guide decision making (Balana *et al.*, 2011). These models aim to achieve an exogenously determined environmental quality standard at a minimum economic cost (CEA) or one that is consistent with establishing benefits greater than or equal to the costs incurred (CBA). Using CEA, Vinten *et al.*,

(2011) estimated the costs of restoring 77% of lakes in Scotland to good ecological status by 2015 using proportionate source mitigation (marginal costs of pollution abatement equates to marginal benefit of improvement) would cost £25.6 million per year. Costs associated with the mitigation of P have also been estimated for the RoI; in 2007 the resolution of diffuse pollution from septic tanks was estimated to range from €975 million to approximately €3 billion, while in catchments in which WWTPs are the major contributors to eutrophication, required investment between €57 and €99 million to achieve a good ecological status in the freshwaters into which they discharge by 2015 (McCarthy *et al.*, 2007).

2.6 Mitigating P losses to freshwaters

The previous sections have identified a need, both environmentally and economically, to control the flux of P between terrestrial and aquatic environments using the most effective means possible. Mitigation methods must be introduced in catchments drained by freshwaters that have been identified as at risk of eutrophication or not meeting a prescribed baseline standard for water quality.

Numerous mitigation measures to reduce high concentrations of P in rivers and lakes are available. For example, physical, chemical or biological treatments of P may be employed before discharge of point sources of P, eliminating a proportion of P from sources such as WWTP, septic tanks and industrial effluents (Gray, 2010). Agricultural losses of P can be avoided by using best management practices (BMPs) such as reducing livestock density, improving feed management and entry to watercourses, suitable quantities, application, and timing of manure spreading and fertilisation, appropriate manure storage, treatment and transport infrastructure, winter cover crops, and reducing surface runoff and soil erosion by introducing conservation tillage, contour ploughing, riparian shading and buffer strips (Sharpley *et al.*, 2004; Cherry *et al.*, 2008; Deasy *et al.*, 2010; Malmaeus and Karlsson, 2010). Measures aimed at reducing eutrophication events in lakes have most frequently involved a variety of these attempts to control the external loading P from a contributing catchment (e.g. Foy *et al.*, 1995; Jeppesen *et al.*, 1999; Özkundakci *et al.*, 2010). However, biomanipulation (Kairesalo *et al.*, 1999), chemical treatment (Dittrich *et al.*, 2011) or the dredging of lake sediments (Zhang *et al.*, 2010) are also potential means by which a lake may be restored from eutrophic conditions.

In practice, remedial strategies to reduce the concentration of P in freshwaters have shown variable rates of achievement. For example, Räike *et al.* (2003) found that although improvements in wastewater purification effectively improved the P water quality of freshwaters

in Finland over a 25 year time span, no significant impacts of decreasing diffuse loading were evident. Similarly Foy *et al.* (1995) reported that, between 1974 and 1991, a slow but steady increase in SRP loadings to Lough Neagh occurred from estimated diffuse sources in the catchment, which most likely negated the benefits of reduced discharges of P from point sources. According to Moss *et al.* (2005), many successful cases of lake restoration involve large, deep lakes polluted by identifiable point sources of P in non-intensive agricultural catchments. Restoration of shallow lowland lakes, where diffuse, agricultural sourced P is more influential, has been less successful showing variable levels of effectiveness (Søndergaard *et al.*, 2005; Kagalou *et al.*, 2008; Özkundakci *et al.*, 2010). This causes particular concern; shallow polymictic lakes are more abundant worldwide than deep lakes and are typically of great importance because they tend to provide vital resources to the human population (Padisák and Reynolds, 2003).

2.6.1. Examples of P mitigation in areas of the Irish Ecoregion

Measures to address the impact of P enrichment in the RoI and NI are implemented by means of national legislation. However, since the early 1990s, environmental legislation from the EU has increasingly influenced the adoption of national environmental policies and measures. The most recent of these is the WFD. The following section provides an overview of the main national mitigation programme for P in the RoI from 1998 to 2008 (P Regs). Following this, an overview of the measures currently adopted in the Irish Ecoregion to reach WFD targets by 2015 is given.

2.6.1.1. Previous P mitigation in the RoI (1998-2008)

Observation of a trend of increasing eutrophic events in freshwaters across the RoI in the early 1990s was followed by the publication of a strategy document that set out the Government's approach to reducing freshwater pollution by P (DoEHLG, 1997). As part of this strategy, interim water quality standards for P in rivers and lakes were identified. In order to enforce compliance, the government launched the Water Quality Standards for Phosphorus Regulations, 1998, S.I. No. 258/1998, more commonly known as the P Regs. The P Regs were developed to maintain existing cases of good water quality and to facilitate improvements in water quality where there had been impairment (Clenaghan *et al.*, 2005).

The P Regs required that water quality be maintained or improved according to biological and chemical quality indices and with reference to prescribed baseline conditions. Where water quality was deemed satisfactory, the P Regs required that the existing water quality be maintained (i.e. that there is no deterioration). Where quality was found to be unsatisfactory, the

P Regs required that improvements to water quality be made within ten years of the original baseline survey (Clenaghan *et al.*, 2005). The P Regs required set water quality standards to be met by 2007. In rivers, standards were achieved by meeting either the target biological quality rating (Q-value) or the target MRP concentration, whereas average TP concentration was used as an indication of current and target trophic status in lakes. The target river standards specified in the P Regs are based on a well-established relationship between ecological quality in rivers in the RoI and concentrations of P (McGarrigle *et al.*, 1992; Lucey *et al.*, 1999), which suggests that, once annual median MRP values exceed $30 \mu\text{g P l}^{-1}$, there is a strong statistical likelihood of the occurrence of a significant eutrophication problem.

The EPA and relevant local authorities in RoI were required to act to secure compliance with the quality standards specified in the P Regs, with the responsibility for compliance lying principally with the local authorities (Clenaghan *et al.*, 2005). In order to meet their responsibilities, local authorities were required to submit information on POMs aimed at reducing P inputs to be implemented, as part of a Measures Report, to the EPA by 31 July 1999. Submission of an Implementation Report to the EPA followed 12 months later, with updates submitted every two years until 2008. The EPA was similarly obliged to produce National Reports on the Implementation of the Regulations every two years until 2008. By 2008 the EPA in the RoI had made available three such reports (Clenaghan *et al.*, 2001, 2005; Clenaghan, 2003), with no reports yet available for the period 2005-2008.

The POMs cited first in the Measures reports and subsequently, with updates, in the Implementation reports of local authorities are described in the National Implementation reports. The measures can be grouped into five categories. Planning, control and enforcement measures include the implementation of catchment and waste management plans; upgrade of existing or construction of new WWTPs; appraisal of septic tank systems and related legislation; carrying out of farm surveys, including surveys of the state of farm infrastructure; introduction of new agricultural bye-laws; and enforcement of water pollution acts. Monitoring measures include increased river, lake and groundwater monitoring, including investigations of catchment pollution hotspots, and the development of GIS for catchment management. Other measures comprise liaison between the various actors involved in catchment management.

The most recently available National Implementation Report (Clenaghan *et al.*, 2005) collates and summarises information contained within the implementation reports submitted to the EPA in the RoI by local authorities for the two year period to 31 July 2004. According to this report, no significant improvement in national water quality is evident when compared with baseline

conditions (generally 1995-1997), although some local improvements are apparent (Clenaghan *et al.*, 2005). In the case of rivers, slightly more monitoring stations nationally report water quality values compliant with the P Regs than was the case during the baseline period and when compared with 1998-2000 (Clenaghan *et al.*, 2005). Notable variation exists between the local authorities in levels of compliance, however. Marked increases in compliance between the baseline and 2001-2003 periods are apparent in some local authorities, whereas a significant decline in compliance is apparent in others, the latter in part because of the loss of high quality stations. As stations recording high quality water are primarily found in headwaters, documented declines in water quality at these will adversely impact attempts to improve the quality of polluted waters downstream.

2.6.1.2. Current attempts of P mitigation in the Irish Ecoregion

Strong political pressure from the EU for an integrated approach to manage water quality resulted in the adoption of the WFD (2000/60/EC) by all member states in 2000. The WFD was subsequently transposed into national legislation in the RoI and NI by 2003. The WFD requires all surface waters to be of good ecological status by 2015. A host of pollutants and their impacts are covered by the WFD, but specific consideration is given to P-induced eutrophication. Under the WFD, the overall status of waterbodies is defined as *high* and *good* quality according to a combination of ecological and chemical quality elements. The ecological status for water bodies are classified according to a five category scheme: *high*, *good*, *moderate*, *poor* and *bad*, and these categories are colour-coded on maps as: blue, green, yellow, orange and red, respectively (EPA, 2006). The biological, hydromorphological and physico-chemical quality elements that may be used when calculating ecological status for rivers and lakes are available in the SI No 272 of 2009 - European Communities Environmental Objectives (Surface Water) Regulations 2009. Chemical status is classified according to a simple binary condition – either *good* or *failing to achieve good*, mapped as blue and red, respectively.

Major changes occurred in the management of freshwater in the Irish Ecoregion when the WFD was adopted into national legislation; aquatic ecology was placed at the core of management decisions (EPA, 2008). The WFD management unit, RBD, centres management strategies on the basis of hydrological catchments rather than administrative or political borders (Bennion and Battarbee, 2007). Eight RBDs have been identified on the island of Ireland; three RBDs are shared between the RoI and NI and are referred to as International RBDs (Shannon, Neagh Bann, and North Western); four are entirely within the RoI (Eastern, South Eastern, South Western and Western); and one is completely within NI (North Eastern). Management plans drawn-up by RBDs

are required to include the design and implementation of POMs that are needed to mitigate the impacts of P (Crabtree *et al.*, 2009; Kavanagh and Bree, 2009).

The major POMs for the RoI and NI are mainly implemented through the enforcement of two pre-existing EU directives, both previously adopted in 1991:

- The Urban Waste Water Treatment Directive (91/271/EEC) targets point sources of P from domestic sewage and industrial waste water. This Directive outlines the standards required before urban waste water can be discharged, and where areas are designated as sensitive to eutrophication, higher standards of treatment must be achieved.
- The Nitrates Directive (91/676/EEC) is the main instrument for the implementation of POMs to regulate the management of N and P in the agricultural sector under the WFD. To meet the requirements of the Nitrates Directive, various measures must be adopted. Vulnerable zones must be designated on the basis of monitoring results, which indicate that the surface waters in these zones may be affected by nutrient pollution from agriculture (specifically when the concentration of nitrates in surface water reaches 50 mg l⁻¹ or when the surface water is eutrophic or is at risk of being so). Alternatively, the whole territory may be designated as vulnerable, as in the case of the Irish Ecoregion, omitting the need for designating specific zones. A voluntary code of good agricultural practice to be followed by all farmers must be put into practice. Fundamentally, a programme (NAP) for mitigating N and P loss from agriculture must be established and reviewed for effectiveness at least every four years, with amendments if necessary (Fealy *et al.*, 2010). Mitigation measures include standards for livestock manure storage and restrictions on land fertilisation (inorganic and organic) based on season, geographic location, topographical slope, proximity to drainage networks and crop requirements.

Three types of monitoring programmes are specified and described in the WFD:

- Surveillance monitoring, to assess long-term changes in water quality resulting from natural and anthropogenic activities
- Operational monitoring, in order to establish the status of those water bodies identified as being at risk of failing to meet their environmental objectives; and assess any changes in the status of such water bodies resulting from the POMs

- Investigative monitoring, carried out where the reason of any exceedance for ecological and chemical status is unknown; where surveillance monitoring indicates that the objectives for a water body are not likely to be achieved (and determine the causes); or to ascertain the magnitude and impacts of accidental pollution.

The most recent general report on water quality in the RoI covers the period 2007-2009 (McGarrigle *et al.*, 2010). According to this report the most conspicuous changes in chemical water quality, when compared with the previous reporting period (2004-2006), are a slight increase in the length of river classed as slightly polluted and a concomitant decline in those characterised as unpolluted (McGarrigle *et al.*, 2010). A small increase in the percentage area of lakes classed as moderately eutrophic along with a commensurate decrease in percentage area of hypertrophic conditions is also noted. However in terms of the WFD classification method, taking into account the various biological and supporting physico-chemical quality elements, just 52% of rivers in the RoI achieve a good status. Using similar WFD criteria, a report for water quality in NI for 2008-2009 showed similar small improvements; however the proportion of rivers attaining a good status was just 25%. This was, however, an increase of 4% on 2008 values (NIEA, 2011).

2.7 Modelling of P transfer

Mathematical modelling tools have an increasingly essential function in guiding nutrient mitigation planning in freshwater catchments (Kronvang *et al.*, 2009). There are three main reasons why models that simulate the dynamics of P are useful to a consideration of the causes and effects of eutrophication and measures aimed at their mitigation: (i) models formalise and test current understanding of P transfer, identifying knowledge gaps; (ii) models allow the quantification and apportionment of P load; and (iii) models can predict P concentrations where monitoring is not possible or to simulate the potential outputs of scenarios if environmental and management situations are changed in a catchment. The WFD stipulates the use of mathematical models in assessing the risk of pollution, and in developing and assessing the impact of POMs. Mathematical modelling provides catchment managers with robust scientific evidence on the outcome of management strategies, allowing the most appropriate use of resources to reverse the impact of eutrophication.

A wide range of mathematical models has been used to describe sources, transfer dynamics and risk assessment of P in freshwater systems (Schoumans *et al.*, 2009). There is, however, no universally accepted model of transfers of P to a waterbody for a particular catchment typology or scale. Furthermore, P transfer is a complex assemblage of processes, many of which show

considerable variability in respect of their interconnections and behavior at different scales (Haygarth *et al.*, 2005b), and this complexity and variability leads to uncertainty in the models available.

Most *in-situ* research of P dynamics has been based on the controlled plot experimental approach, which involves a high resolution monitoring programme over a small area (e.g. Deasy *et al.*, 2008). The knowledge derived from such research, however, is specific to a very particular type of landscape and is easily undermined by landscape or flow path variability (Haygarth *et al.*, 2005). The application of P transfer models that have been developed from field sites to a large area that comprises a range of catchment types is challenging and under-researched. Furthermore, verification of the modelled outcomes requires high resolution datasets that rarely exist (McGechan *et al.*, 2005; Page *et al.*, 2011). Coarse-scale data (10-12 samples annually) more commonly exist for most rivers and lakes at the landscape-scale (large area, small scale), and the most efficient use of these data is parameterization of simple models which describe the main governing controls of P transfer (Johnes, 1996). Successful model validation at the landscape-scale promotes field experiments at the next larger scale (smaller area), with the potential for the generation of increased model complexity for various landscape types (Steinhardt and Volk, 2003).

The complexity of mathematical models used to simulate the transfer of P to a waterbody tends to be constrained by the nature of available data (Heathwaite *et al.*, 2005b). Low complexity models provide a generalisation of the main controls on the transport of P and calculates annual or seasonal load, such as the empirical-based export coefficient approach that relies on an assigned value for P input and export from land cover, fertilisation, atmospheric deposition and human and animal stocking data (e.g. Johnes, 1996). Models of medium complexity, for example regression-based statistical models, use the statistical relationship between measured P concentrations in a waterbody and the environmental attributes of the catchment. Highly complex conceptual or process-based models simulate the processes that transport P in greater detail. Such models include the following: ANSWERS (Beasley *et al.*, 1980); SWAT (Arnold *et al.*, 1993); INCA-P (Wade *et al.*, 2002); PIT (Heathwaite *et al.*, 2003); PSYCHIC (Davison *et al.*, 2008); and HSPF (Bicknell *et al.*, 1997). These types of models are expensive to develop and difficult to calibrate in large catchments because of their dependency on high resolution data. As a result they are usually applied to data-rich catchments with small areas. In this respect, the modelling approach followed in this thesis does not include complex models because the research aims and available data restrict analysis to using empirical and statistical downward-scale types of models.

The P models of relevance to this thesis can be divided into four generic categories: (i) empirical P load estimation for rivers; (ii) annual or seasonal export models; (iii) empirical TP loading - response models for lakes; and (iv) chlorophyll a - TP models for lakes.

2.7.1 Empirical load estimation models

River flow is typically measured on a more-or-less continuous basis. However, corresponding concentrations of P can be relatively expensive to sample and analyse, thus measurements of P are generally obtained at a lower frequency than discharge. Seasonal or annual P load delivered to a river can be estimated by the statistical analysis of periodic measurements. Broadly, three generic types of methods to calculate P load from empirically measured data exist: those based on (i) averages; (ii) ratios; and (iii) interpolation/extrapolation (Quilbé *et al.*, 2006).

Average estimates quantify the P load delivered to a river as the product of P and flow, using either instantaneous or daily mean measurements of both parameters, over a stated number of days (e.g., 365 for annual P load) (Dolan *et al.*, 1981). The different types of average estimators use various pairings of data (instantaneous, daily or annual) and some employ weights on P concentrations (i.e. flow-weighted, time-weighted). For a sampling regime based on daily or sub-weekly basis, estimates of P load based on paired instantaneous flow and P concentration data are the most precise and least biased (Johnes, 2007; Salles *et al.*, 2008).

Ratio estimation, after Beale (1962), is based on a multiplication of flow-weighted P loads by a specified ratio that accounts for the covariance between load and flow (Quilbé *et al.*, 2006). Ratio estimators are especially applicable when high resolution flow data are accompanied by lower frequency P data (Dolan *et al.*, 1981; O'Connor *et al.*, 2011).

Estimation of P loads based on interpolation/extrapolation involves defining the empirical P-flow relationships by regression analysis, either by linear log P-log flow rating curves (Quilbé *et al.*, 2006) or non-linear LAMs (Bowes *et al.*, 2008). Fitted to the data by least square regression, log P-log flow rating curves generate P concentrations for unsampled periods. Once a full record has been estimated, annual P load is calculated as the product of daily P concentration and flow. Additive LAMs conceptualise the empirical relationships (point and diffuse behaviour) between P and flow (Bowes *et al.*, 2008) and are based on intrinsic relationships that have been noted in previous studies (Mohaupt, 1986; Chapman, 1996; Lennox *et al.*, 1997; Edwards and Withers, 2007). The LAMs, by apportioning of P loads delivered to a river as point or diffuse sources, supply additional information about the source composition of the total loading of P.

The estimation of accurate loads of P estimation remains a challenge, especially in terms of obtaining representative data from monitoring programmes (Bechmann and Stålnacke, 2005). Regardless of sampling frequency, uncertainties in annual P load estimation increases as population density increases, baseflow index decreases and river flow regime becomes more extreme (Johnes, 2007). Phosphorus hysteresis, the variation of P concentrations according to whether discharge is rising or falling, may not be detected by coarse-scale sampling, causing perturbations in the P-flow relationship and inaccurate P load estimations (Langlois and Mehuys, 2003). Recently, to address these issues, P concentrations have been monitored at higher temporal resolutions (sub-hourly), thus enabling a range of flow to be recorded, which in turn provides the basis for increased accuracy of P load estimates (Jordan *et al.*, 2005a, 2007; Cassidy and Jordan, 2011; O'Connor *et al.*, 2011). O'Connor *et al.* (2011) addressed the hysteresis effect by stratifying P and flow data (30 minute resolution) according to both season and hydrograph. A Bayesian framework has been incorporated into some of the empirical load estimation techniques (Zobrist and Reichert, 2006; Cha *et al.*, 2010). Bayesian models yield probability distributions, rather than discrete loads, permitting the uncertainty of predictions to be estimated (Hanrahan, 2010).

2.7.2 Annual or seasonal export models

Models in this category quantify loss of P (annual or seasonal) from catchments based on the environmental attributes of the catchment. Two techniques can be adopted: export coefficient models that build on the conceptual understanding of P transfer and statistical or geostatistical models that are inferred from the data by multivariate analysis.

2.7.2.1 Export coefficient models

The export coefficient modelling approach was developed in the USA (Omernik, 1976), and versions have been developed for the UK (Ferrier *et al.*, 1996 ; Johnes, 1996; McGuckin *et al.*, 1999) and other countries (Salvia-Castellví *et al.*, 2005; Shrestha *et al.*, 2008; Ding *et al.*, 2010). The export coefficient model for England and Wales developed by Johnes (1996) estimates annual TP load as a linear function of P losses from fertiliser application, atmospheric deposition, livestock densities and human population levels. Model parameters are the export coefficients, i.e. the rates of P loss from the different sources.

Numerous studies have adopted the export coefficient model method: some studies relied upon an original published model (Smith *et al.*, 2005), others an adapted model (Hanrahan *et al.*, 2001;

May *et al.*, 2001; Cooper *et al.*, 2002; Ding *et al.*, 2010). For example, the Johnes (1996) model has been adapted through the development of a series of sub-models within the original export coefficient framework, thereby providing separate groups of coefficients of P transfer for each one of six major geoclimatic regions in England and Wales. The sub-models represent major landscape units with broadly similar climate, geology, soil types, topography and natural vegetation cover that have, therefore, broadly similar ranges of nutrient export potential (and nutrient retention capacity) as a function of flow, timing and routing from land to water network. Similarly, the PLUS model for Scotland separates TP export coefficients into sub-coefficients based on the slope of land in a catchment. Moreover, McGuckin *et al.* (1999) developed an export coefficient model for fractions of P (SRP, SOP and PP) according to the CLC classes that occur in NI. Export coefficient models have also been merged with process based models, such as SWAT (White *et al.*, 2010) to produce hybrid models with increased accuracy of prediction. These modifications, however, have resulted in increased data needs to meet the requirements of model calibration.

The export coefficient approach is attractive owing to minimum data requirements; however, as with all models, export coefficients are uncertain, and values for major catchment attributes reported in the literature can disagree considerably. Furthermore, the approach is limited by an inability to account for hydrologic variability and random pollution events that have the potential to be captured by alternative load estimators that use in-stream measurements of P.

2.7.2.2 Statistical models

The most commonly used statistical models of P loads are based on additive regression equations. These models link river P concentrations to P sources and/or the percentage surface area of a catchment covered by particular environmental attributes (Daly *et al.*, 2002; Donohue *et al.*, 2006; Rothwell *et al.*, 2010). Once regression models are calibrated and validated, they can then be used to predict P concentrations in unmonitored waterbodies. Globally, the catchment attributes that have been studied include land use (cover and fertiliser application), soil characteristics, P transport pathways, regional geology, topography, climate, human population density and livestock density (Ekholm *et al.*, 2000; Hart *et al.*, 2004; Scanlon *et al.*, 2004; Donohue *et al.*, 2006; Styles *et al.*, 2006; Liu *et al.*, 2000; Jarvie *et al.*, 2010). The advent of GIS has accelerated development of statistical models of P loads in recent years. GIS has facilitated the development of regression models, typically through the spatial expression of relationships between catchment attributes and P loads (Daly *et al.*, 2002; Rothwell *et al.*, 2010).

2.7.2.3 Geostatistical models

Conventional statistical methods for modelling P export from catchment attributes to water, such as regression, are based on the assumption that spatial correlation between points is random. Geostatistical methods, however, take into account the random and structured nature of spatial variables that exists in many environmental datasets (Webster and Oliver, 2007). Geostatistical techniques are based on the assumption that points situated close to one another in space share more similarities than those further apart. This means that the squared difference in values between two sites depends only on the distance between them and not on their absolute positions. This is known as the intrinsic hypothesis of Matheron (1971) or the Theory of Regionalized Variables.

Geostatistical methods such as kriging were first used with success to estimate the spatial variability of a range of environmental parameters, such as soil constituents, and continue to do so (McGrath *et al.*, 2004; Li, 2010; Di Piazza *et al.*, 2011; Sun *et al.*, 2011). The application of geostatistical methods to water quality is a relatively new field and comparatively few models for river networks have been developed (but see examples of Gardner *et al.*, 2003; Yuan, 2004; Ganio *et al.*, 2005; Peterson and Urquhart, 2006; Yang and Jin, 2010). Geostatistics comprehend a number of techniques designed to detect spatial patterns and predict values at unsampled locations, and can be used as a tool to optimise a sampling regime (Webster and Oliver, 2007). This is an important advantage, as the spatial density of sampling measurements will have a strong impact on the cost of the sampling programme, the quality of the results, and the feasibility of a long-term study.

The geostatistical methodology involves two main stages: experimental variogram modelling followed by prediction based on interpolation by kriging. Variograms (also called semivariograms) are the central tool of geostatistics. The variogram quantifies the spatial scale of variation by measuring the degree of spatial correlation between sampling sites (Webster and Oliver, 2007). Variograms express mathematically the way in which the variance of a property changes as the distance and direction separating any two points varies. An experimental variogram first shows the degradation of spatial correlation between two points in space when the separation distance is increased. A theoretical curve-fitting model (spherical, exponential, gaussian, circular) is then fitted to the variogram plot, yielding information about spatial structure and providing a basis for interpolation through kriging (Cressie, 1985; Webster and Oliver, 2007). A typical variogram model has three components (Figure 2.2):

- The parameter C_0 , the intercept of the variogram, occurs when a spatial process is discontinuous as the distance, h , approaches zero. This nugget effect may occur owing to measurement error or purely random variation.
- The parameter a is the maximum distance of spatial dependence over which two sites are related. Sites separated by a distance greater than the correlation range are assumed to have spatial independence.
- The sill variance (C_0+C) is the semivariance value at which the variogram levels off. Spatial correlation can be examined in two formats: anisotropic and isotropic (Webster and Oliver, 2007). Anisotropic spatial correlation is based on the distance between paired points and the specific direction of the correlation, whereas isotropic correlation reflects the distance between points regardless of directional relationship.

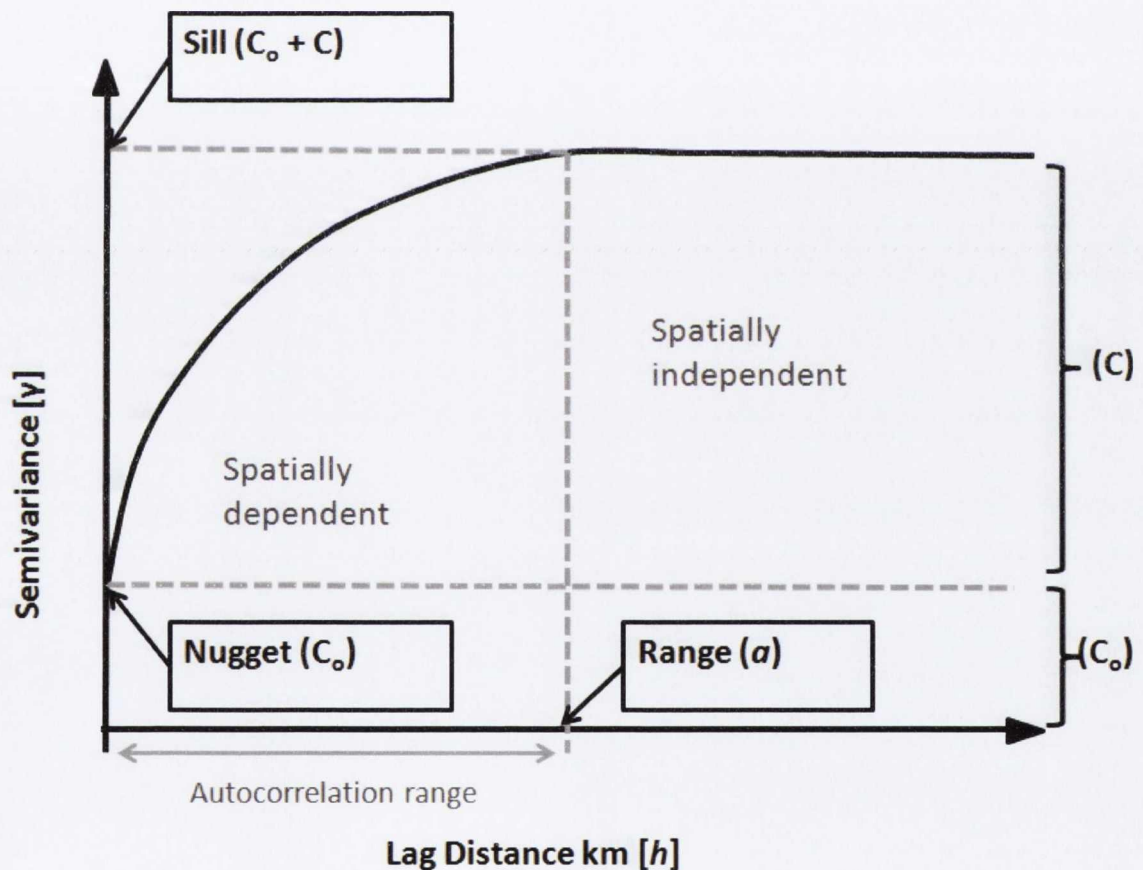


Figure 2.2. Schematic of the characteristics of a variogram model. In a variogram, the semivariance (γ) typically increases with increased lag distance (h), until it eventually reaches a maximum (the sill variance, (C_0+C)) at which the graph flattens out. Such a variogram is called bounded. The distance at which the variogram reached its sill is called the autocorrelation range (a), which is the limit of spatial dependence over which two points are correlated. Points separated by greater distances than the range are spatially independent. The nugget (C_0), the intercept of the variogram, occurs when a spatial process is

discontinuous as the distance h approaches zero lag. If the semivariance increases with distance but does not reach a maximum value at the largest distance measured, the variogram is termed unbounded. In the event of no spatial dependence in the data (e.g. measurement errors and variation that occurs over distances less than the shortest sampling interval), the variogram is called pure nugget

Kriging involves the application of least-square linear regression algorithms to predict (by interpolation) the value of a variable at unobserved locations based on the spatial structure (variogram) of the available dataset (Webster and Oliver, 2007). Predictions are linear sums of weighted observations within a given neighborhood. Kriging can be used to provide reliable estimates of unobserved variables where environmental conditions are relatively homogeneous. However, where conditions vary over relatively short distances, predictions to reasonable levels of confidence can be difficult. Variations of local topography, land use, nutrient sources and transport mechanisms may not display an identifiable spatial structure. In such cases, the strength of the kriged estimates decreases, since catchment specific measurements are impacted by strong local variation. Adaptations of the kriging technique have been developed to surmount this weakness, with the adapted technique referred to as RK (Hengl *et al.*, 2007). In RK, the data undergo a regression analysis followed by variogram modelling of the residuals, which retain the unexplained spatial variability of the target variable. A combination of the regression model and the variogram model of residuals is kriged and interpolated to predict the target variable at unobserved locations.

2.7.3. Lake loading-response models for TP

A mass balance budget approach has been used as a basis for modelling the TP balance of lakes (Schindler *et al.*, 1987). Mass balance models provide a framework for identifying and quantifying sources, and for determining losses and storages of TP in a catchment. A lake TP budget can be expressed by a simple mass balance equation:

$$\text{TP inputs} = \text{TP outputs} \pm \text{TP storage} \quad [2.1]$$

Thus, all TP inputs to a catchment are balanced by equal outputs, unless changes in storage take place. If outputs are less than inputs, a proportion of TP is likely to have been taken up by biomass or sequestered in sediment, representing storage in the lake (Figure 2.3). Theoretically,

outputs may exceed inputs if previously stored TP is mobilized and released to the water column for export.

Vollenweider (1969, 1975, 1976) developed the first TP loading-response model to relate the amount of TP entering to a lake with the concentration of TP in the lake. The components of such models comprise parameters representing the morphometric and hydraulic characteristics of a lake. Steady state variations of the models are based on the CSTR concept adopted from chemical engineering kinetics (Reckhow and Chapra, 1983). Models employing the CSTR concept are required to meet the assumption of the steady state of TP (i.e. mass is conserved): (i) a well mixed basin with continuous interaction between water and sediment; (ii) temporally constant TP and flow influx and efflux rates; and (iii) exclusive loss of TP by advection in outflow or TP retention by the sediment in the lake. The typical model predicts annual steady state lake TP concentrations that are generalised throughout the lake (Dillon and Molot, 1996).

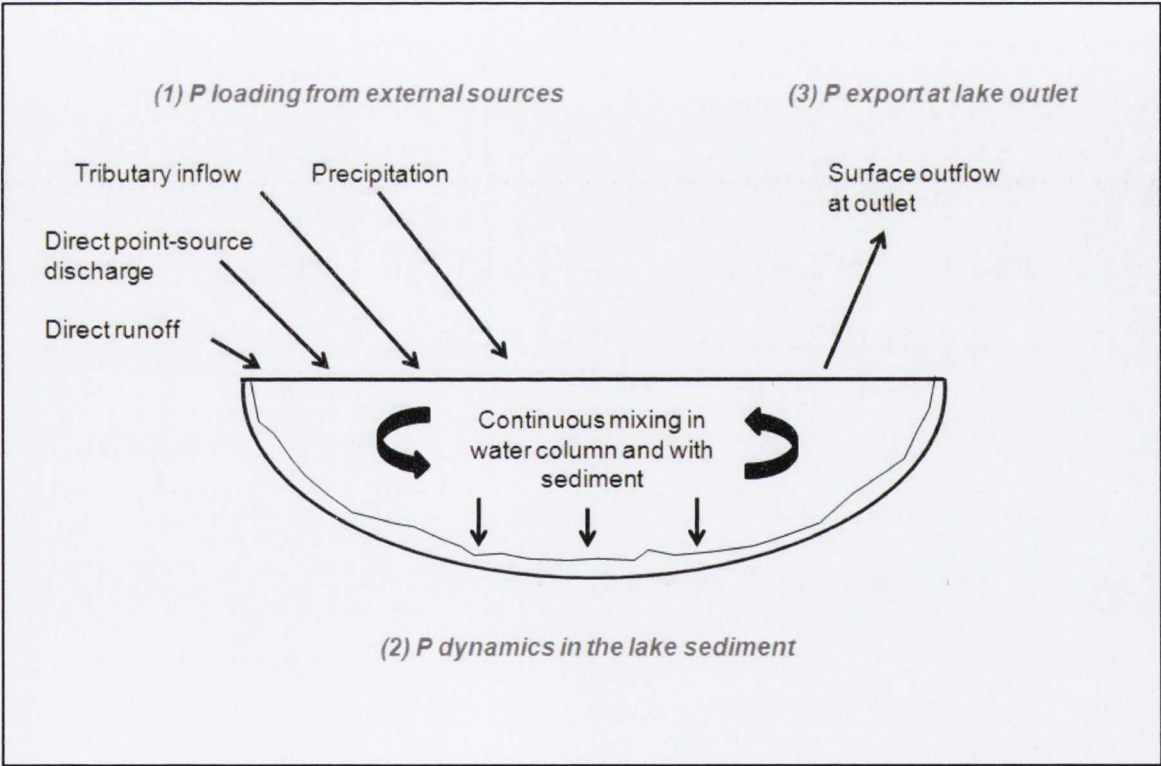


Figure 2.3. Schematic of the steady state mass balance system of P dynamics in a lake, consisting of inputs from several sources of P, continuous mixing of P between the water column and the lake sediment, net sedimentation of P, and export of P from the lake via an outlet.

Since Vollenweider's initial study (Vollenweider, 1969), numerous models have been developed to predict concentrations of TP in lakes based on attributes such as areal TP loading rate, mean lake depth, fractional TP sediment retention and areal hydraulic loading (Brett and Benjamin, 2008). The rate of retention of TP by loss to sediment is the most difficult model component to measure directly. Loading models have therefore attempted to provide estimates of TP retention based on proxies. Models usually provide estimates as a constant proportion of either (i) the mass of TP in a lake using a TP sedimentation coefficient, σ , (Vollenweider 1975), (ii) the TP loaded into a lake using a TP retention coefficient, R (Dillon and Rigler, 1974) or (iii) a combination of both measures (Prairie, 1989). The Vollenweider (1975) model is expressed mathematically as:

$$TP_{\text{lake}} = \frac{L}{z(\rho + \sigma)} \quad [2.2]$$

(see Table 2.1 for a definition of model parameters)

In theory, equation [2.2] uses the TP sedimentation coefficient, σ , or the number of times a mass of TP equal to the lake mass of TP is lost to the lake sediments in a year. While most model parameters in equation [2.2] can be determined directly, in practice σ is very difficult to measure *in situ*. Therefore, a proxy estimate of σ involves using a water residence time scaling factor as a surrogate for TP sedimentation. Vollenweider (1976) found that σ could be approximated by an empirical relationship with water residence time, τ_w yr. Therefore, substitution of the proxy for σ in equation [2.2] gives the following model (Vollenweider, 1976):

$$TP_{\text{lake}} = \frac{TP_{\text{in}}}{(1 + \sqrt{\tau_w})} \quad [2.3]$$

As can be seen in Table 2.2, the scaling factor, $1/(1 + \sqrt{\tau_w})$, is also incorporated in the general TP loading-response model and the model for shallow lakes attributed to OECD (1982). Foy (1992), on finding that the OECD models consistently underestimated TP concentrations when applied to data from lakes in NI that had τ_w values of 0.04 to 1.67 yr, developed a modified version, also employing a proxy for σ based on τ_w (Table 2.2). Prairie (1989) introduced a second type of TP loading-response model, explaining the TP lost to sediment as a fraction of both the areal TP loading rate (L) and lake content (τ_w as a proxy for σ).

Table 2.1. Definitions of the symbols used in TP loading-response models for lakes

Symbol	Definition
A_L	Lake surface area (m^2)
L	Areal TP loading rate ($g\ m^2\ yr^{-1}$)
Q	Hydraulic flow rate ($m^3\ yr^{-1}$)
q_s	Areal hydraulic loading rate ($m\ yr^{-1}$) (zp)
R	TP retention in lake sediment - predicted (unitless)
R_{cal}	TP retention in lake sediment - calculated from TP budget
TP_{in}	Flow-weighted TP external annual load to lake ($ug\ l^{-1}$)
TP_{lake}	Lake TP annual average concentration ($ug\ l^{-1}$)
V_L	Lake volume (m^3)
z	Mean lake depth (m)
ρ	Lake flushing rate (yr^{-1})
σ	sedimentation coefficient of TP loss (yr^{-1})
τ_w	Lake water residence time (yr)

Table 2.2. Formulae of TP loading-response models

Model type ⁱ	Reference	Model formula
σ	Foy (1992)	$TP_{lake} = \frac{1.234(TP_{in})^{0.991}}{(1 + \sqrt{\tau_w})^{1.130}}$
σ	OECD (1982) general	$TP_{lake} = 1.55 \left(\frac{TP_{in}}{1 + \sqrt{\tau_w}} \right)^{0.82}$
σ	OECD (1982) shallow	$TP_{lake} = 1.02 \left(\frac{TP_{in}}{1 + \sqrt{\tau_w}} \right)^{0.88}$
σ plus R	Prairie (1989)	$TP_{lake} = \frac{L(1 - 0.30\tau_w^{40} L^{1.1} z^{0.25})}{q_s}$
R	Dillon and Rigler (1974)	$TP_{lake} = \frac{L(1 - R)}{q_s}$

ⁱ Model type refers to how TP sedimentation is described by the model

As an alternative to using σ in models (by means of the τ_w scaling factor), sedimentary TP loss can also be estimated as R , the retention coefficient describing the fraction of influent TP load lost to sediments. Dillon and Rigler (1974) estimated TP concentrations of a lake by incorporating the R coefficient into a TP loading-response model (Table 2.2). However, as with σ , a value for R is also difficult to measure *in situ*. Therefore R coefficients that fit to the model can be estimated according to several different types of ancillary models (retention models), all based on areal hydraulic loading, q_s , or water residence time, τ_w (Table 2.3):

- The most common retention models describe the settling velocity of TP containing particles (m yr^{-1}) as constant values (a and b) and are of the following form:

$$R = \frac{a}{b + q_s} \quad [2.4]$$

When $a = b$, this form reduces to $R = v/(v + q_s)$, where v is TP settling velocity. Three values for v have been suggested: $v = 10$ (Vollenweider, 1975), $v = 13.2$ (Dillon and Kirchner, 1975b) and $v = 16$ (Chapra, 1975). Models in which a and b differ were developed by Ostrofsky (1978a) and Nürnberg (1984).

- A model to estimate R as a function of TP settling velocity ($a = 1$, $b = 1$) and lake flushing rate was proposed by Larsen and Mercier (1976).
- The R coefficient can also be estimated using a double exponential function of q_s (Kirchner and Dillon, 1975; Ostrofsky, 1978b).

Often, process-based dynamic models for lakes are preferable to empirical loading-response models because they better describe mechanistic principles and processes. Dynamic models, however, tend to have complex conceptual frameworks and require detailed data on P driving variables. Examples of the detailed data required are weather variables, water temperature, sedimentation rates, sediment type and constituents, P fraction composition and O_2 levels (Malmaeus and Håkanson, 2004; Lewis *et al.*, 2007; Meals *et al.*, 2008; Janse *et al.*, 2010). Such process based models are generally very costly to develop and validate. According to Heathwaite (2003), dynamic models may not be suitable for the simple decision support frameworks required by policy makers, owing to the complexity involved.

Table 2.3. Model formulae for the TP retention coefficient (R) used in the Dillon and Rigler (1974) model described in Table 2.2

Reference	Model formula
Vollenweider (1975)	$R = \frac{10}{10 + q_s}$
Dillon and Kirchner (1975b)	$R = \frac{13.2}{13.2 + q_s}$
Chapra (1975)	$R = \frac{16}{16 + q_s}$
Ostrofsky (1978a)	$R = \frac{24}{30 + q_s}$
Nürnberg (1984)	$R = \frac{15}{18 + q_s}$
Larsen and Mercier (1976)	$R = \frac{1}{1 + \rho^{0.5}}$
Kirchner and Dillon (1975)	$R = 0.43 \exp(-0.27q_s) + 0.57 \exp(-0.0095q_s)$
Ostrofsky (1978b)	$R = 0.2 \exp(-0.043q_s) + 0.57 \exp(-0.0095q_s)$

2.7.4. Chlorophyll a - TP models for lakes

The statistical relationship between chlorophyll a and TP concentrations (Chl a - TP) is another well studied association in limnology (Wetzel, 2001). Globally, chlorophyll a concentration is used as a metric of lake phytoplankton biomass (Jiménez *et al.*, 1987; Gregor and Maršálek, 2004; Kasprzak *et al.*, 2008; Boyer *et al.*, 2009), which is a response variable of TP concentration (Lagus *et al.*, 2004; Vuorio *et al.*, 2005). Deevey (1940) first described the correlation between chlorophyll a and TP concentrations in a lake, while Sakamoto (1966) showed the response of phytoplankton to TP was linear on a log-log scale. Since then, the Chl a - TP regression relationship has been used as a basis for the control of cultural eutrophication worldwide (Philips *et al.*, 2008). Standards for lake P quality in the Irish Ecoregion are directly related to chlorophyll a concentrations. In the context of the WFD, TP conditions capable of supporting good ecological status are defined according to the Chl a - TP relationship, therefore directly influencing the implementation of remediation measures to resolve eutrophication.

Chapter 3

The Irish Ecoregion: selection of water quality monitoring points and a description of corresponding catchments

3.1. The Irish Ecoregion

The research that underpins this thesis was carried out at both large (individual freshwater catchment) and small (Irish Ecoregion-wide) scales. The Irish Ecoregion (number 17 according to the WFD) refers to the island of Ireland and proximate smaller islands, as illustrated in Figure 3.1. Ecoregions are relatively large extents of land and water that contain distinct homogeneous ecological systems, exhibiting similar land forms, vegetation and climate (Olson *et al.*, 2001). The Irish Ecoregion is situated in the eastern part of the North Atlantic (53° 00' N, 8° 00' W), off the northwestern part of Europe, and comprises a land mass of 84,431 km² (Love and O'Brien, 2003). A temperate climate prevails, determined by the proximity to the North Atlantic and the warming impacts of the Gulf Stream, generating constant humidity with mild wet winters and cool wet summers (Boardman and Poesen, 2006).

The topography of the Irish Ecoregion results from a lowland limestone plateau, covered with glacial deposits, and rimmed by coastal mountain ranges (Holland and Sanders, 2009). River characteristics typically reflect these underlying geologies; fast-flowing, upland spate systems occur on old hard bedrock and slow-moving productive rivers exist in limestone regions (Reynolds, 1998). Compared to other EU member states, the Irish Ecoregion contains a relatively dense river network 14,000 km in length and a large number of lakes that account for approximately 2% of the land surface.

Owing to high levels of rainfall (average 750–1250 mm, but exceeding 2500 mm in the mountainous areas of the west) and low rates of evapotranspiration (20–50% of rainfall), soils in the Irish Ecoregion develop under conditions of abundant moisture (Boardman and Poesen, 2006). Poorly drained peats and gleys, including peaty podzols, generally dominate the northern and western areas, whereas the south and east typically comprise free-draining brown earths, brown or grey-brown podzols (Brogan *et al.*, 2002). Over 64% of land mass is used as improved

land for agriculture, of which approximately 80% is devoted to grasslands (silage, hay and pasture), the remaining being allocated to rough grazing and crop production (CSO, 2000; DARD, 2010). Pasture land has a higher concentration in the midlands and north-midlands represented by a large proportion of small dairy and beef cattle farms with rough grazing. Arable and mixed agricultural practices are limited to the free draining soils in eastern regions. Phosphorus is a fundamental agronomic nutrient but is naturally deficient in soils across the Irish Ecoregion. Soil P fertilisation is therefore recommended on an addition or replacement basis for low and optimum soil P concentrations respectively at rates specific to grassland, arable and crop requirements (Schulte *et al.*, 2010). Urban land covers approximately 2% of the total landmass, with large urban centres concentrated near the eastern and southern coastal areas, leaving lower human population densities in rural areas of the midlands, north-midlands, west and north-west.

3.2. Criteria for the selection of water quality monitoring points and drainage catchments

In order to be considered suitable for the current research, water quality monitoring points and their corresponding catchments were required to satisfy the following criteria:

Small scale

- Selected water quality monitoring points on rivers must be subjected to drainage from catchments that accommodate sources of P and environmental conditions characteristic of those typically found in the Irish Ecoregion (proportions of landuse were used as an indicator for these criteria).

Specifying these conditions served to ensure an adequate representation of the pressures delivering P to rivers across the Irish Ecoregion.

- Selected water quality monitoring points should be located on rivers of different Strahler stream order, with each corresponding catchment exhibiting an area from a wide range. The Strahler (1952) stream order system is a simple approach to classify stream/river segments based on the number of tributaries upstream.

This condition ensured that the effects of processes acting in catchments or rivers on account of differences in both the spatial size of the catchment (Haygarth *et al.*, 2005b) were sufficiently represented in the research.

- Data should be available for P and flow measured at frequent intervals at river monitoring points over the most recent three-year timeframe.

This condition guaranteed the use of the most current and comprehensive dataset for the research.

Large scale

- The selected freshwater catchment should contain waterbodies assigned an *at risk* typology for the WFD owing to conditions in the drainage catchment (e.g. rivers/lakes draining agricultural catchments that contain impermeable soils). As it is these types of waterbodies that require management, they are the focus of this component of the research. The sources of P and environmental conditions in the catchment should represent those commonly attributed to posing a risk to waterbodies of a similar risk status.

Meeting this condition ensured that results obtained were suitable for addressing P-induced problems in other impacted catchments of similar typology.

- Implementation of POMs for the P Regs in the catchment over the full duration (1998-2008) is essential.

This proviso was crucial in providing the structure around which environmental influences on P dynamics were assessed.

- Long-term, high resolution data for P from waterbodies covering the period before, during and after POM implementation in the catchment is required.

This condition ensured the application of the most comprehensive dataset for the research.

3.3. Selected water quality monitoring points and drainage catchments

The EPA (RoI) and the NIEA (NI) regularly monitor P water quality at 1,919 river sampling points across the Irish Ecoregion, as illustrated in Figure 3.1. Based on the stipulated selection criteria for study at the small scale, 77 river monitoring points (23 in NI and 54 in RoI) and their respective catchments were identified as suitable for the current research. Location and descriptive data for these points are provided in Figure 3.2 and Table 3.1. The selected water quality monitoring points are located on rivers with Strahler orders ranging from 2 to 6, the greatest proportion being orders of 4 or 5 (Table 3.1). Study catchments have areas ranging from 16.19 km² (Newtownbutler river in NI, catchment number 51) to 23,333.87 km² (Blackwater river in RoI, catchment number 39). For the purposes of the large scale study, a survey of all freshwater

catchments in the RoI that had undergone POMs for the P Regs, suggested that the Lough Sheelin catchment, containing ten rivers draining into the lake was the most appropriate site for this research. The position of the Lough Sheelin catchment within the Irish Ecoregion is illustrated in Figure 3.3. The locations of seven river monitoring points (for which sufficient data were available for use in this research) are shown in Figure 3.4.

The following sections describe the water quality sampling regime at the selected study sites. The analytical methods performed on the water samples in the laboratory to generate the water quality data used in this research are also detailed. Finally, descriptions of the environmental characteristics of the study catchments are provided, confirming the satisfaction of the proposed selection criteria.

3.3.1. Sampling regime at water quality monitoring points

Small scale (77 river monitoring points in the Irish Ecoregion)

- Discrete water samples at the 23 selected river monitoring points in NI were taken by the NIEA on a monthly basis from 2006 to 2008. The procedure involved lowering a clean plastic bucket from the downstream side of a bridge above the monitoring point. The sampling bucket was rinsed and used to fill a clean 2l plastic bottle which was returned to the NIEA laboratory for analysis within 24 hours. The RA measured water depth in the rivers from 2006 to 2008 at automatic data logger stations on the river close to the water quality monitoring points. Mean daily flow rates ($\text{m}^3 \text{s}^{-1}$) were estimated by applying these water level measurements to rating curves (water level-flow relationships) developed by NIEA.
- The EPA carried out discrete water sampling at the selected 54 river monitoring points in the RoI from 2006 to 2008. Water samples were taken by staff standing at the side of the river on a monthly basis. Sampling procedure involved rinsing a clean plastic bottle (typically 1 or 2l) in the river, after which a sample was collected. Water samples were transported to the appropriate EPA regional laboratory for analysis within 24 hours. Water levels in the rivers for 2006-2008 were estimated from readings taken by automatic data loggers at sites close to the water quality sampling point. Mean daily flow rates ($\text{m}^3 \text{s}^{-1}$) were estimated from rating curves; however the EPA or the OPW were responsible for the collection and estimation of these flow data for particular rivers.

Large scale (Lough Sheelin catchment)

- Discrete water samples and spot gauge readings for water level from the seven river monitoring points in the Lough Sheelin catchment were carried out by the IFI. Monitoring was conducted three times per week from 1982 to 2008. Exceptions to this procedure include the Bellsgrrove, Mountnugent and Ross rivers where automatic data loggers maintained by the EPA recorded data on water levels. Examples of these sites are shown in Figure 3.5. Water samples were taken from the mid-point of Lough Sheelin along with transparency depth readings (m) using a secchi disk once per month from 1982 to 2008. All water samples were taken in a 1l plastic bottle which was rinsed twice before the sample was collected. Water samples were sent to the IFI laboratory in Swords, Co. Dublin and analysed within 24 hours of sampling. Mean daily flow rates ($\text{m}^3 \text{s}^{-1}$) for rivers were estimated by applying the recorded water levels to calibrated rating curves developed by the EPA.

3.3.2. Analytical methods on water samples

The concentration of TP ($\mu\text{g l}^{-1}$) in the unfiltered water samples from both jurisdictions was determined using methods based on Murphy and Riley (1962); digestion followed Eisenreich *et al.* (1975). In NI, reactive P was determined on a filtered sample (45 μm cellulose nitrate filter) (SRP). In contrast, in the RoI, reactive P was determined on an unfiltered sample (MRP). The concentration of chlorophyll a ($\mu\text{g l}^{-1}$) from a mid-lake water sample was determined by hot methanol extraction and measured spectrophotometrically (Talling, 1974).

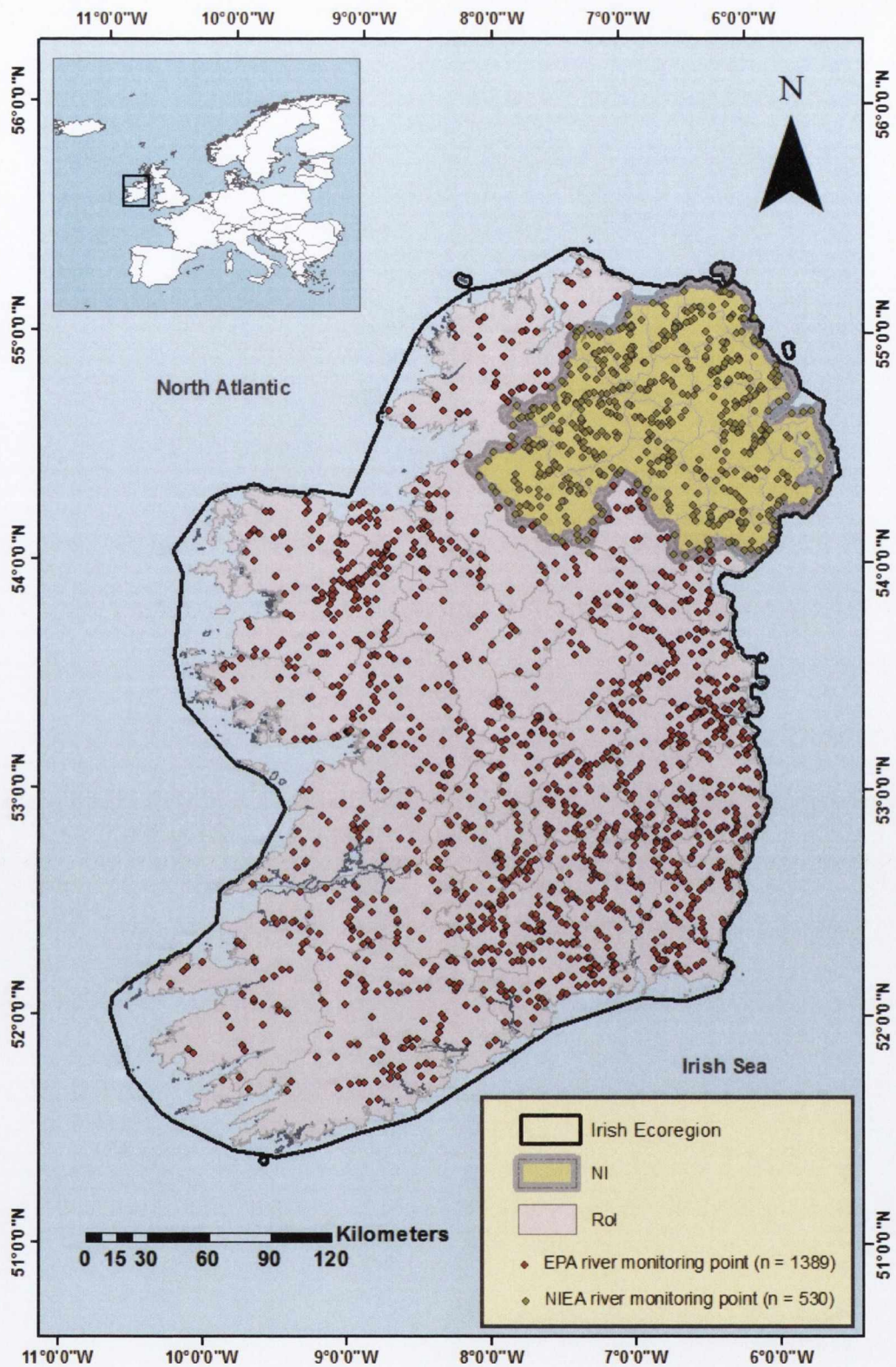


Figure 3.1. Geographical distribution of 1,919 EPA (RoI) and NIEA (NI) river water quality monitoring points across the Irish Ecoregion, out of which 77 river monitoring points for the small scale study were selected based on specific criteria. The outline of the Irish Ecoregion, encompassing the RoI, NI and proximate smaller islands, is also shown. River water quality monitoring points are projected over county border lines using the Irish National Grid and easting and northing coordinates provided by the EPA (RoI) and NIEA (NI). Inset (left) depicts the position of the Irish Ecoregion within Europe

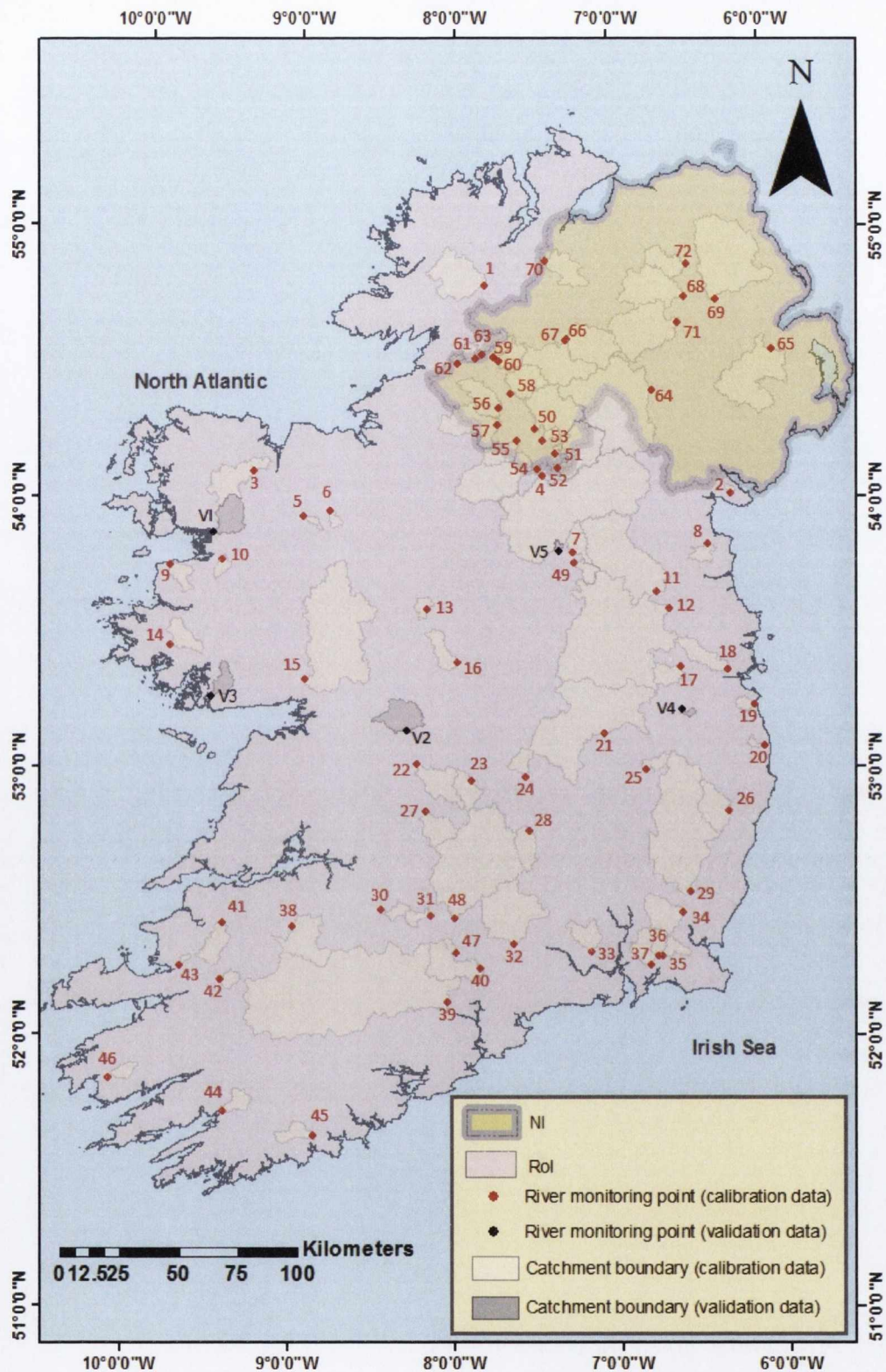


Figure 3.2. Locations of the 77 river water quality monitoring points and corresponding catchment boundaries used in the small scale study. Numbers in red correspond to those listed in Table 3.1 (1-72 indicates points used for analysis and numbers in black (V1-5) signifies points used for validation purposes). Catchment areas range from 10.45 km² (monitoring point number 51 in NI) to 2,333.87 km² (monitoring point number 39 in the RoI). Catchment boundaries were delineated in ArcGIS 9.3 using a DEM (20m RoI, 50m NI) and geographical coordinates (easting and northing) of river monitoring points provided by the EPA (RoI) and NIEA (NI)

Table 3.1a. Location and descriptive information for river monitoring points and their associated catchments in the RoI (EPA) and NI (NIEA) used for the small scale study. Catchment numbers correspond to those given in Figure 3.2.

Catchment number	River name	Name of river monitoring point	Catchment area (km ²)	Strahler stream order	Agency responsible
1	Finn (Donegal)	Bridge 2.5 km u/s Ballybofey	309.74	6	EPA
2	Big (Louth)	Ballygoly Bridge	10.56	3	EPA
3	Deel (Crossmolina)	Knockadangan Bridge	226.77	5	EPA
4	Erne	Kilconny Belturbet (RHS)	1491.19	6	EPA
5	Swinford	Swinford: Bridge on Foxford Road	17.73	3	EPA
6	Charlestown stream	Bridge W N W of Bellahy	25.20	4	EPA
7	Mountnugent	Mountnugent Bridge	91.03	4	EPA
8	White (Louth)	Coneyburrow Bridge	55.23	4	EPA
9	Bunowen (Louisburgh)	Bridge in Louisburgh	70.37	5	EPA
10	Carrowbeg (Westport)	Cooloughra Bridge	36.04	4	EPA
11	Blackwater (Kells)	Liscartan Waterworks	698.54	5	EPA
12	Boyne	Ballinter Bridge	1575.64	6	EPA
13	Hind	Bridge E of Ballymartin	44.11	3	EPA
14	Recess	Canal Bridge	111.82	6	EPA
15	Clare (Galway)	Claregalway Bridge	1072.39	5	EPA
16	Cross (Roscommon)	Bridge S of Doyle's Bridge	103.27	4	EPA
17	Lyreen	Just u/s Rye Water confl	87.62	3	EPA
18	Tolka	Violet Hill Drive Finglas	133.21	4	EPA
19	Shanganagh	At Commons Road	32.52	4	EPA
20	Newtownmountkennedy	Bridge S of Ballyphilip	16.19	2	EPA
21	Barrow	Pass Bridge	1063.12	5	EPA
22	Ballyfinboy	Bridge just u/s L Derg	186.46	4	EPA
23	Little Brosna	Milltown Bridge (near Mt Lucas)	113.84	4	EPA
24	Delour	Derrynaseera Bridge	69.68	4	EPA
25	Greese	Bridge near Greese Bank	49.41	2	EPA
26	Aughrim (Wicklow)	Coat's Bridge	188.18	5	EPA
27	Nenagh	Bridge near Tyrone Abbey	136.29	4	EPA
28	Goul	Fertagh Bridge	118.10	4	EPA
29	Slaney	Scarawalsh Bridge	1030.71	6	EPA
30	Mahore	Bridge at Riverville	44.28	3	EPA
31	Ara	Railway Bridge (Tipperary town)	44.18	3	EPA
32	Anner	Bridge near Anner House	444.70	5	EPA
33	Blackwater (Kilmacow)	Dangan Bridge	109.98	4	EPA
34	Boro	Ballynapierce Bridge	173.90	4	EPA
35	Mulmontry	Goff's Bridge	56.64	4	EPA
36	Corock	Bridge E of Foulkesmills	62.57	4	EPA
37	Owenduff	Taylorstown Bridge	103.09	3	EPA
38	Deel (Newcastlewest)	0.8 km u/s Castlemahon Bridge	261.89	5	EPA
39	Blackwater (Munster)	Ballyduff Bridge	2333.87	6	EPA
40	Tar	Ford u/s Tar Bridge	229.65	5	EPA

Table 3.1b. Location and descriptive information for river monitoring points and their associated catchments in the RoI (EPA) and NI (NIEA) used in the small scale study. Catchment numbers correspond to those given in Figure 3.2. Dashed lines indicates the river monitoring points/catchments were used for validation purposes (V1-5)

Catchment number	River name	Name of river monitoring point	Catchment area (km ²)	Strahler stream order	Agency responsible
41	Smerlagh	Ford u/s Feale R confl (LHS)	127.94	5	EPA
42	Shanowen (Maine)	Ford Bridge u/s Maine R confl	41.11	3	EPA
43	Big (Tralee)	At Dunnes Stores	10.65	4	EPA
44	Owvane (Cork)	Pierson's Br (LHS)	72.13	5	EPA
45	Argideen	Jones Bridge	78.71	4	EPA
46	Cummeragh	Dromkeare Bridge	47.99	4	EPA
47	Thonoge	Bridge u/s Ballylooby	19.15	3	EPA
48	Suir	Bridge near Suirville House (New Bridge)	1090.80	6	EPA
49	Inny	Ballinrink Bridge	58.30	3	EPA
V1	Newport (Mayo)	400 m u/s Newport Bridge	145.48	5	EPA
V2	Kilcrow	West Bridge 2 km d/s Samp St 0300	180.7	5	EPA
V3	Cashla	Cashla Bridge	72.81	4	EPA
V4	Rathmore stream	Bridge S W of Arthurstown	12.4	3	EPA
V5	Bellsgrave	Belsgrave Bridge	11.64	3	EPA
50	Colebrooke	Colebrooke r at Ballindarragh Bridge	314.14	5	NIEA
51	Newtownbutler	Newtownbutler r at Newtownbutler	10.45	3	NIEA
52	Finn (Tyrone)	Finn (Erne) r at Wattle Bridge	274.16	5	NIEA
53	Hollybrooke	Hollybrook r at Aghalurcher	29.30	4	NIEA
54	Woodford	Woodford r at Aghalane	396.65	5	NIEA
55	Swanlinbar	Swanlinbar r at Thompsons Bridge	104.42	5	NIEA
56	Sillees	Sillees r at Thompsons Bridge	151.82	4	NIEA
57	Arney	Arney r at Drumane Bridge	247.91	5	NIEA
58	Ballinamallard	Ballinamallard r at Ballycassidy Bridge	166.73	5	NIEA
59	Bannagh	Bannagh r at Bannagh Bridge	33.88	4	NIEA
60	Kesh	Kesh r at Kesh Bridge	88.53	4	NIEA
61	Waterfoot	Waterfoot r at Letter Bridge	36.47	3	NIEA
62	Garvary	Garvary r at Larkhill	16.23	3	NIEA
63	Termon	Termon r at Tullyhommon	61.98	4	NIEA
64	Blackwater (Benburb)	Blackwater r at Benburb	963.98	6	NIEA
65	Lagan	Lagan r at Shaws Bridge	492.64	5	NIEA
66	Camowen	Camowen r at Donnelly's Bridge	276.17	5	NIEA
67	Drumragh	Drumragh r at Campsie Bridge	318.38	5	NIEA
68	Moyola	Moyola r at Moyola new Bridge	305.84	5	NIEA
69	Main (Dunmore)	Main r at Dunmore Bridge	706.97	5	NIEA
70	Burndennet	Burndennet river at Burndennet Bridge	146.32	4	NIEA
71	Ballinderry	Ballinderry r at Ballinderry Bridge	433.24	5	NIEA
72	Clady	Clady r at Glenone Bridge	125.23	4	NIEA

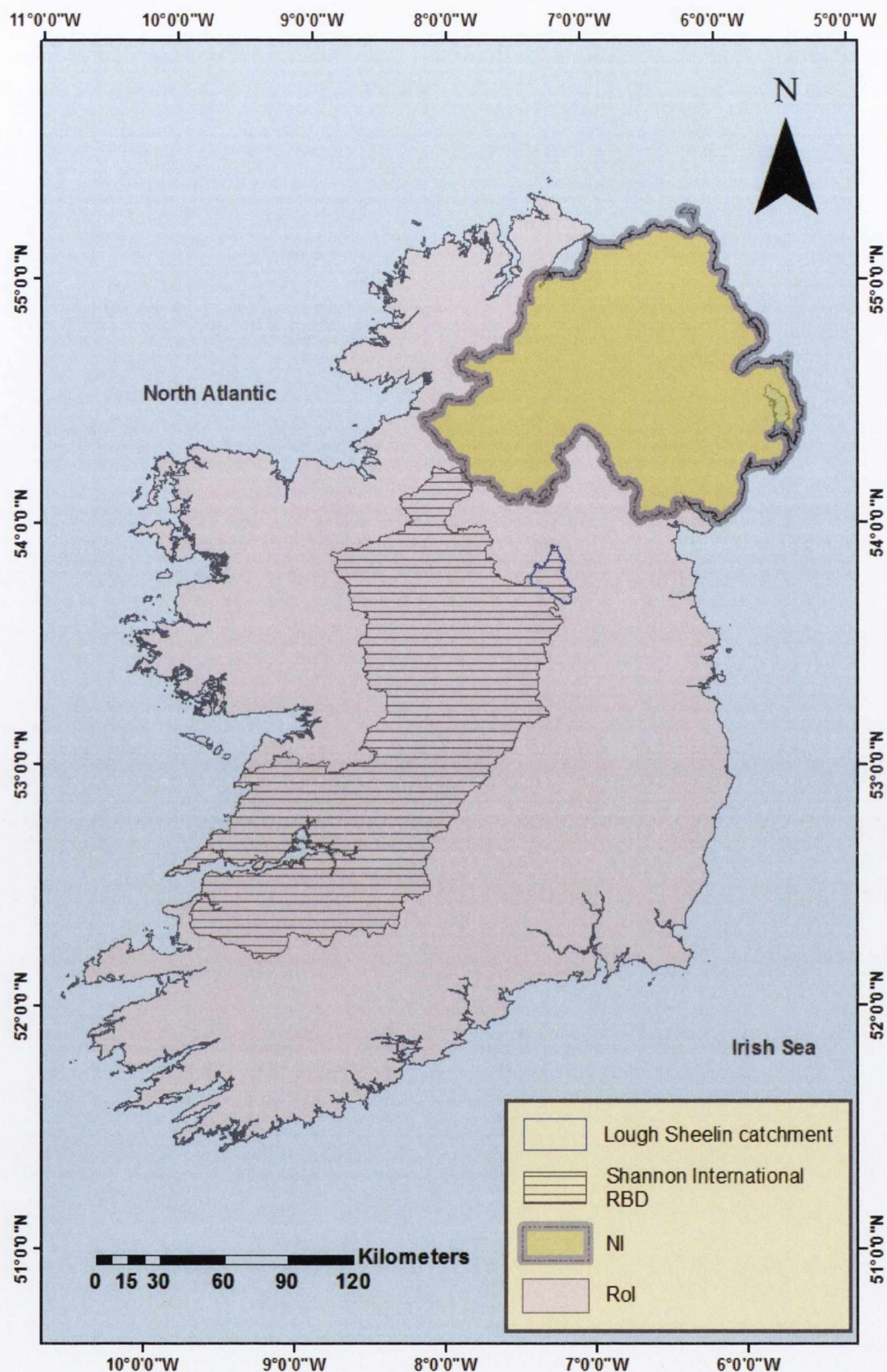


Figure 3.3. Illustration of the location of the Lough Sheelin catchment in the SIRBD and the Irish Ecoregion. Lough Sheelin and its catchment are the focus for the large scale study. The catchment boundary was delineated in ArcGIS 9.3 using geographical coordinates (easting and northing) of river monitoring points supplied by the IFI and a 20m DEM provided by the EPA. The SIRBD boundary was provided by the EPA

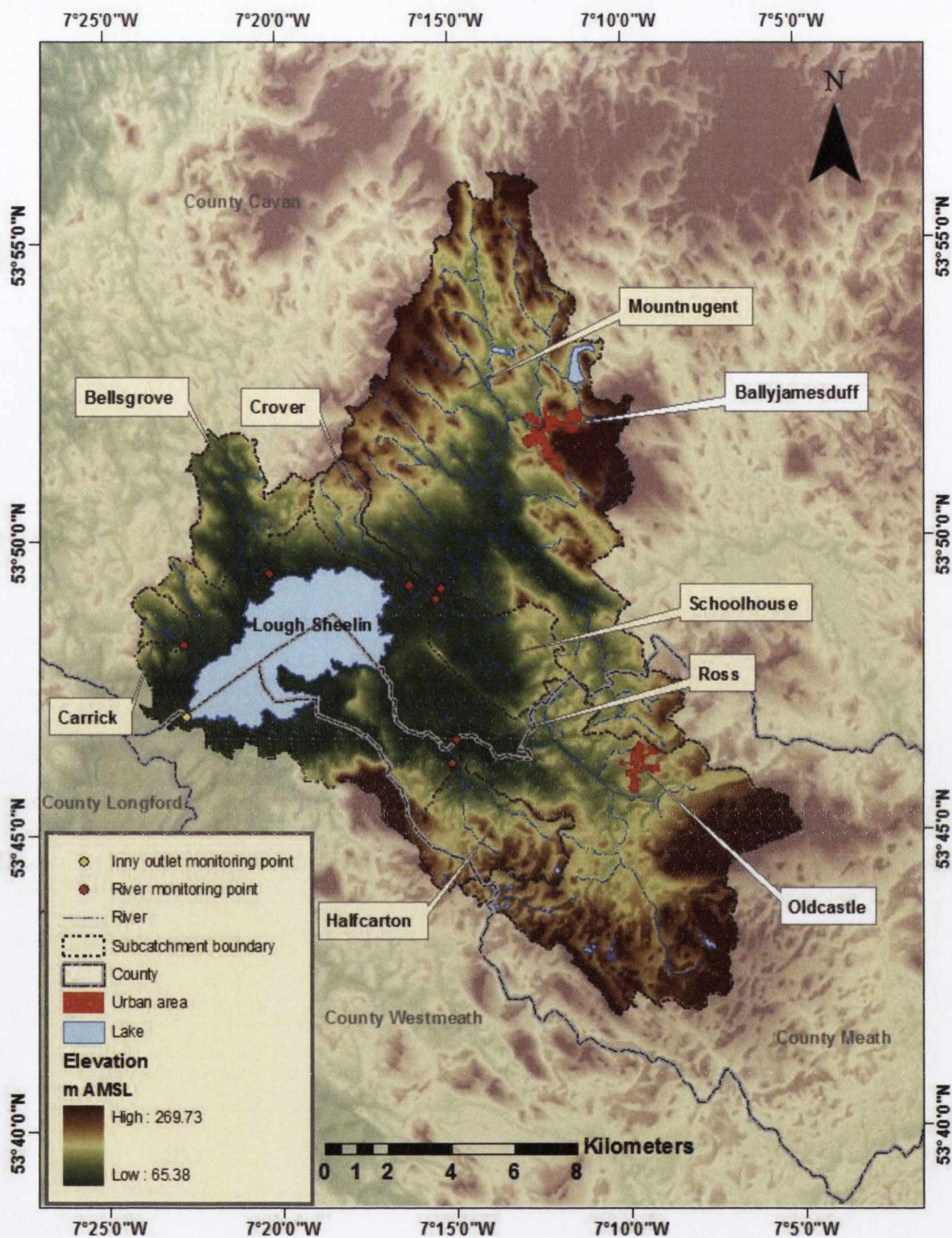


Figure 3.4. Topographic map of the Lough Sheelin catchment (large scale study), showing the location of river water quality monitoring points, subcatchment boundaries, urban areas and administration districts (counties). Catchment and subcatchment boundaries were delineated in ArcGIS 9.3 using geographical coordinates of river monitoring points (easting and northing) and projected using the Irish National Grid. Location data for the monitoring points were supplied by the IFI and 20m DEM data were provided by the EPA. County divisions and river and lake network delineations in GIS vector shapefile format (1:50,000) were sourced from the EPA



Figure 3.5a. View of the automatic data logger station for water level (Ballinarink Bridge, EPA station code 26058) and water quality sampling point located on the Ross river in the catchment draining to Lough Sheelin. Water quality samples were taken by IFI staff and automatic water level readings were monitored remotely by the EPA

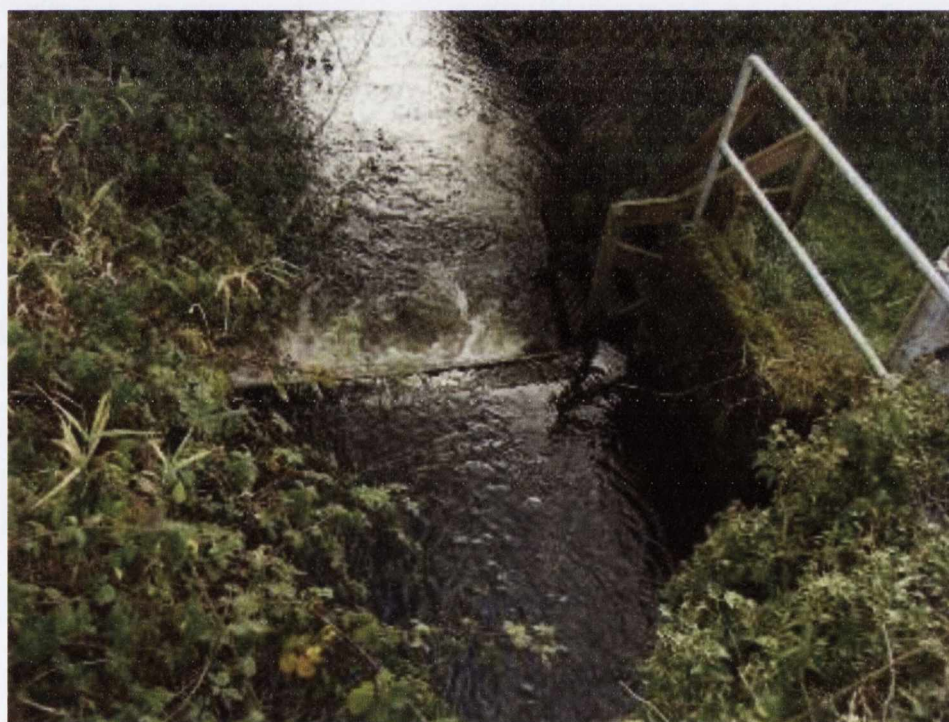


Figure 3.5b. View of the weir and access steps from road bridge for water quality sampling on the Bellsgrrove river. The automatic data logger station for water level (The Cottage, EPA station code 26054) is located just to the right of the photograph. Water quality samples were taken by IFI staff and automatic water level readings were monitored remotely by the EPA



Figure 3.5c. View of the automatic data logger station for water level (Finnea Bridge, EPA code 26059) and the water quality sampling point at the river Inny outlet of Lough Sheelin. Water quality samples were taken by IFI staff and automatic water level readings were monitored remotely by the EPA



Figure 3.5d. View of the water level gauge at the water quality sampling point on the Halfcarton river in the Lough Sheelin catchment. Spot readings of water level and quality were taken by the IFI three times a week

3.3.3. Environment conditions in river catchments for small scale study

Although the Irish Ecoregion is formed from ancient solid geology, the final elements of the topographical diversity of landforms are influenced by recent glaciations from the Quaternary period (Holland and Sanders, 2009). The peak of the most recent ice sheet, the Midlandian period (ca. 22,000 years BP) enclosed most of the island, leaving areas of ice-free tundra in the extreme west and south-west regions. Glacial ice retreated in an east-west direction, ca. 10,000 years BP, stripping upland areas of regolith and shaping lowlands with glacial and glaci-fluvial deposits of clay and sand, producing a land surface that is comparable with the form and outline of present times: characterised by many lakes, bogs, drumlins and eskers. Where the drifts are absent, as in part of the lowlands near Galway Bay, the landscape is karstic.

The study river catchments located in the central lowlands are predominately underlain by Carboniferous limestone (Figure 3.6). The altitude of these catchments range from 60m AMSL to 120m AMSL, characteristic of the topography of the region (Figure 3.7). The remaining study catchments encompass parts of the highlands that rim the central plateau, with altitude reaching up to 920m AMSL in catchment 27 in the RoI. Catchments based in the southern regions constitute parts of mountain ridges composed of Devonian (Old Red) sandstone separated by limestone river valleys that tend to run in an east-west direction. Granite predominates in the catchments containing mountainous regions of counties Galway, Down and Wicklow, while a basalt plateau underlies the catchments in the north-east (Missteart and Fitzsimons, 2007).

Brown earths are the predominant type of soil found in the Irish Ecoregion, covering 64% of the land mass. The study catchments located in the drier lowlands of the south, midlands, and east (Figure 3.8), predominately comprise these fertile mineral soils that possess a medium texture, good structure and high drainage capacities. Such soils are typically used for both pasture and tillage production (Brogan *et al.*, 2002). Gley soils, having developed under the influence of permanent or intermittent waterlogging, constitute much the river catchments located in the drumlin belt from Strangford Lough in County Down to Clew Bay in Mayo (Figure 3.8). Gley soils exhibit low drainage capacities, producing ground water gleys when a high water table occurs, or surface water gleys in the event of a perched water table owing to a low infiltration rate. Poor physical conditions and restricted growth seasons typical of gley soils give low quality pastures, however these soils are usually improved by artificial drainage. The third type of soils predominant in the study catchments are poorly-drained peat soils. Characterised by a high level of organic matter, blanket peats are found in regions of high rainfall and humidity, predominately in the study catchments in western regions and upper part of mountain ranges. Basin peats occur in the study catchments that contain waterlogged areas of the central lowlands. The restricted

drainage and adverse physical and fertility conditions of blanket peat soils are unsuitable for agriculture; however the agricultural use of basin peats can be increased following drainage and reclamation (Brogan *et al.*, 2002).

Over 68% of the land mass across the Irish Ecoregion is used as improved land for agriculture; most of the remaining land comprises forestry plantations (9.30%), wetlands (including peat land), semi-natural areas and water (20.57%) and artificial surfaces such as cities, towns, houses and roads (1.94%). The catchments used in this study are representative of these proportions (Figure 3.9, Table 3.2). Study catchments in the north-west, west and south-west regions comprise larger areas of wetlands while pasture land, although predominate in most study catchments, has a higher concentration in the midlands and north-midlands owing to the greater occurrences of small dairy and cattle farms with rough grazing. Accordingly, the largest percentage of pasture lands (98%) and cattle densities (202 cattle km⁻²) occur in the study catchments located in these regions. Arable and mixed agricultural practices dominate much of the land cover in the catchments located nearer the eastern coast. Higher human population densities are concentrated in the catchments in the east and south, which also comprise a large proportion of WWTPs. Lower human population occurs in the midlands, north-midlands, west and north-west; those that do not live in small towns with a sewer structure rely on private domestic septic tank systems.

Table 3.2. Percentage composition of major land cover classes (CLC, Level 1) in the 77 river catchments used for the small scale study and the corresponding coverage across the Irish Ecoregion

Land use	% composition	
	77 study catchments	Irish Ecoregion
Arable	16.05	14.70
Forestry	7.17	9.30
Pasture	60.40	53.49
Wetlands	11.19	14.59
Urban	2.54	1.94

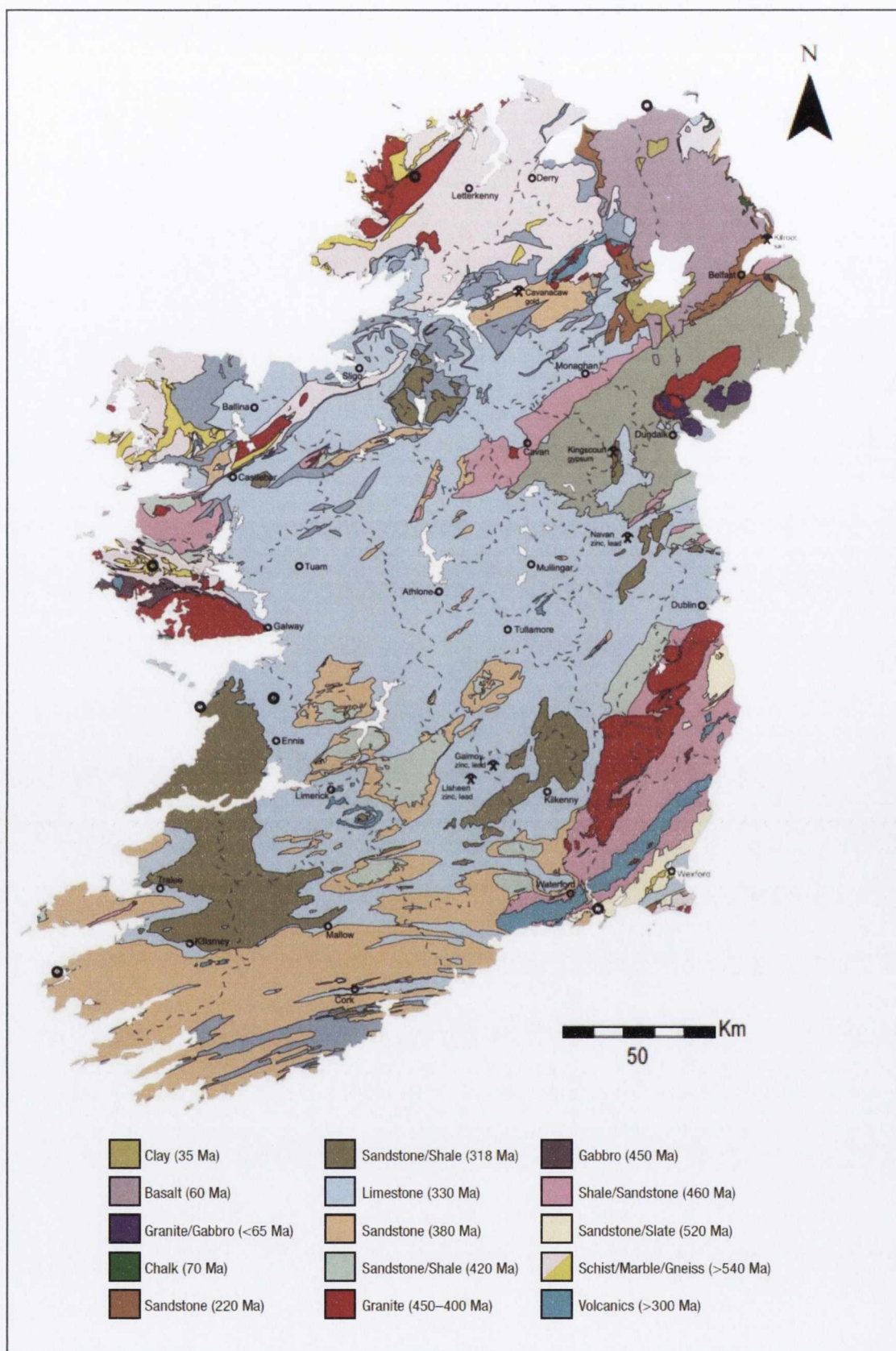


Figure 3.6. Bedrock geology map denoting the major geological typologies of the Irish Ecoregion. The location of major towns and cities and outlines of county borders are also included. The map is adopted from GSI (2004) which simplified the GSI 1:100,000 scale Bedrock Map Series (1993 - 2003) and the GSI 1:250,000 scale Geological Map of Northern Ireland (1997)

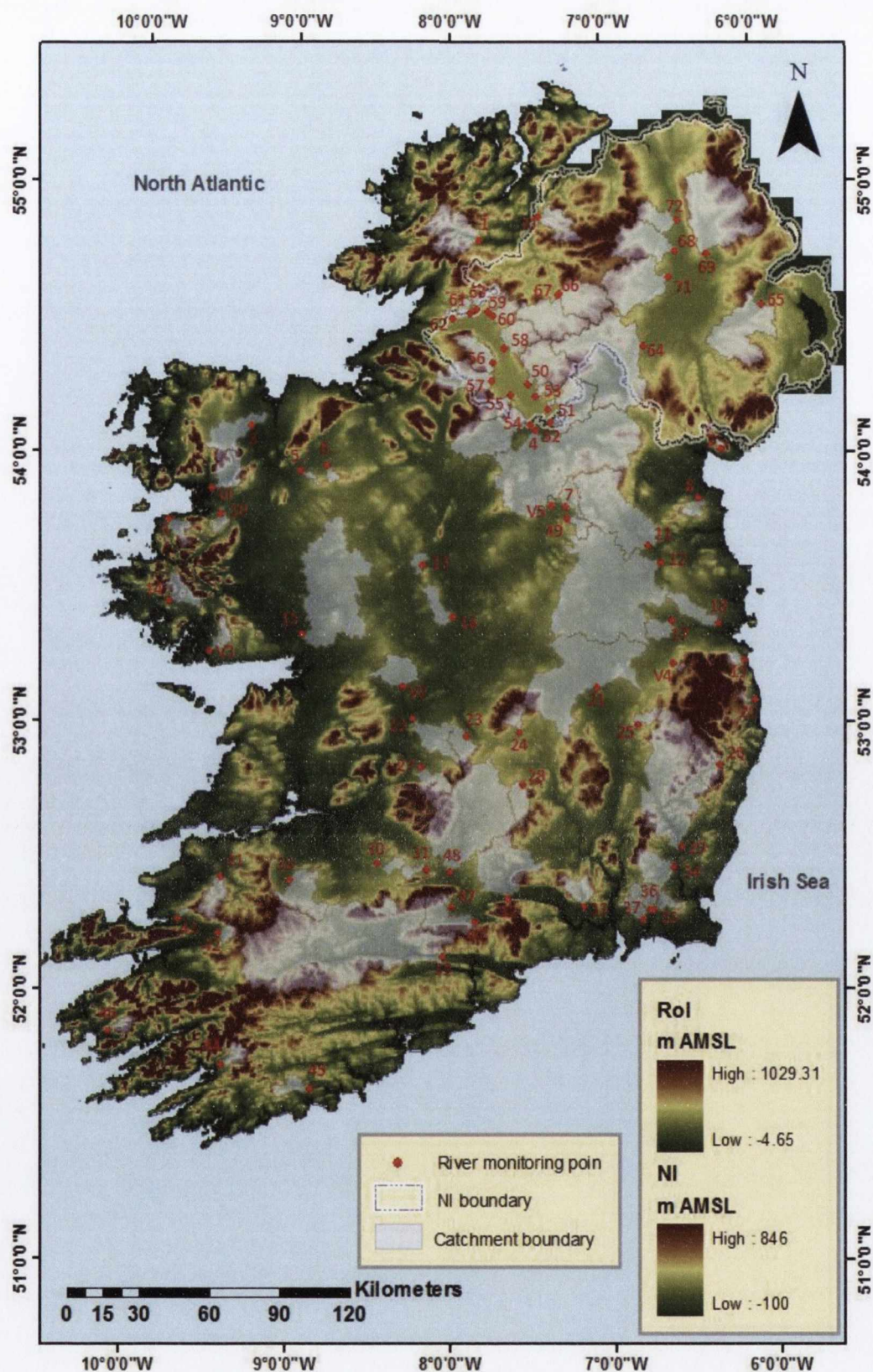


Figure 3.7. Topographical map of the Irish Ecoregion, showing the selected river monitoring points and corresponding catchment boundaries used in the small scale study. Location and descriptive information regarding the water quality monitoring points, denoted by numbers (1-72, V1-V5), is found in Table 3.1. Elevation data in the form of a DEM (20m (Rol) and 50m (NI)), were provided by the EPA and AFBI, respectively, and projected onto the Irish National Grid using ArcGIS 9.3

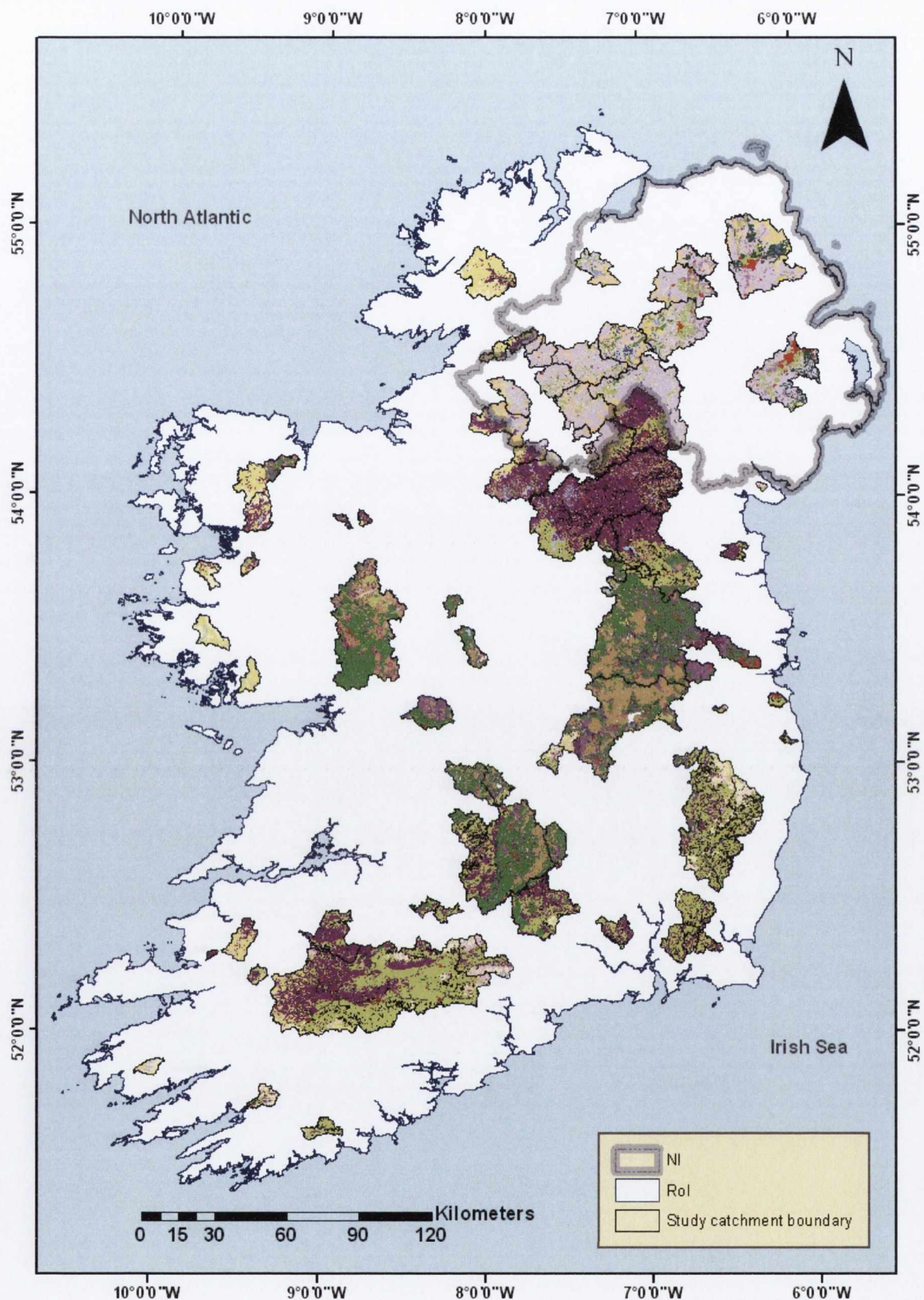


Figure 3.8a. Illustration of soil composition in the river catchments used in the small scale study. An accompanying legend for soil type is provided in Figure 3.8b. Data for soils of the Rol were sourced from the EPA. These data were generated by Teagasc with co-operation of the Forest Service, EPA and GSI (project completed in May 2006). Data on soils for NI were acquired from AFBI (Jordan and Higgins, 2009)

Soil type (RoI)

Soil Group

- Basin and blanket peats - cutaway/cutover peat
- Basin peats - fen peat
- Blanket peat
- Deep, poorly drained mineral, surface water gleys and ground water gleys (Mainly calcareous)
- Deep, poorly drained mineral, surface water gleys and ground water gleys (Mainly non-calcareous)
- Deep, well drained mineral, acid brown earths and Brown Podzolics (Mainly non-calcareous)
- Deep, well drained mineral, grey brown podzolics and brown earths (Mainly calcareous)
- Lacustrine-type soils (Alluvium)
- Lake
- Made or built land
- Marl type soil (Alluvium)
- Mineral alluvium
- Poorly drained mineral with peaty topsoil, peaty gleys (Mainly calcareous)
- Poorly drained mineral with peaty topsoil, peaty gleys (Mainly non-calcareous)
- Poorly drained mineral with peaty topsoil, peaty gleys (shallow) (Mainly calcareous)
- Poorly drained mineral with peaty topsoil, peaty gleys (shallow) (Mainly non-calcareous)
- Reed swamp or marsh
- Scree
- Shallow, poorly drained mineral, surface water gleys, ground water gleys (Mainly calcareous)
- Shallow, poorly drained mineral, surface water gleys, ground water gleys (Mainly non-calcareous)
- Shallow, well drained mineral, lithosols and regosols (Mainly non-calcareous)
- Shallow, well drained mineral, renzinas and lithosols (Mainly calcareous)
- Shallow,lithosolic-podzolic with peaty topsoil (Mainly calcareous)
- Shallow,lithosolic-podzolic with peaty topsoil (Mainly non-calcareous)

Soil type (NI)

Soil Group

- | | | |
|--------------------|------------------------|---------------------------------|
| Alluvium | Groundwater Gley | Raw Skeletal Millstone grit |
| Brown Earth | Humic Ranker | Raw Skeletal Old Red Sandstone |
| Brown Podzolic | Peat | Raw Skeletal Yoredale Sandstone |
| Brown Ranker | Peaty Podzolic | Shallow Brown Earth |
| Disturbed | Podzolic Ranker | Shallow Brown Podzolic |
| Gleyed Brown Earth | Podzols | Shallow Peaty Podzolic |
| Gleyed Ranker | Ranker | Stagnopodzol Basalt |
| | Raw Skeletal Basalt | Surfacewater Gley |
| | Raw Skeletal Dolerite | Urban |
| | Raw Skeletal Limestone | Water |

Figure 3.8b. Legend for the map characterising the soil type in the 77 river catchments (Figure 3.8a) used in the small scale study

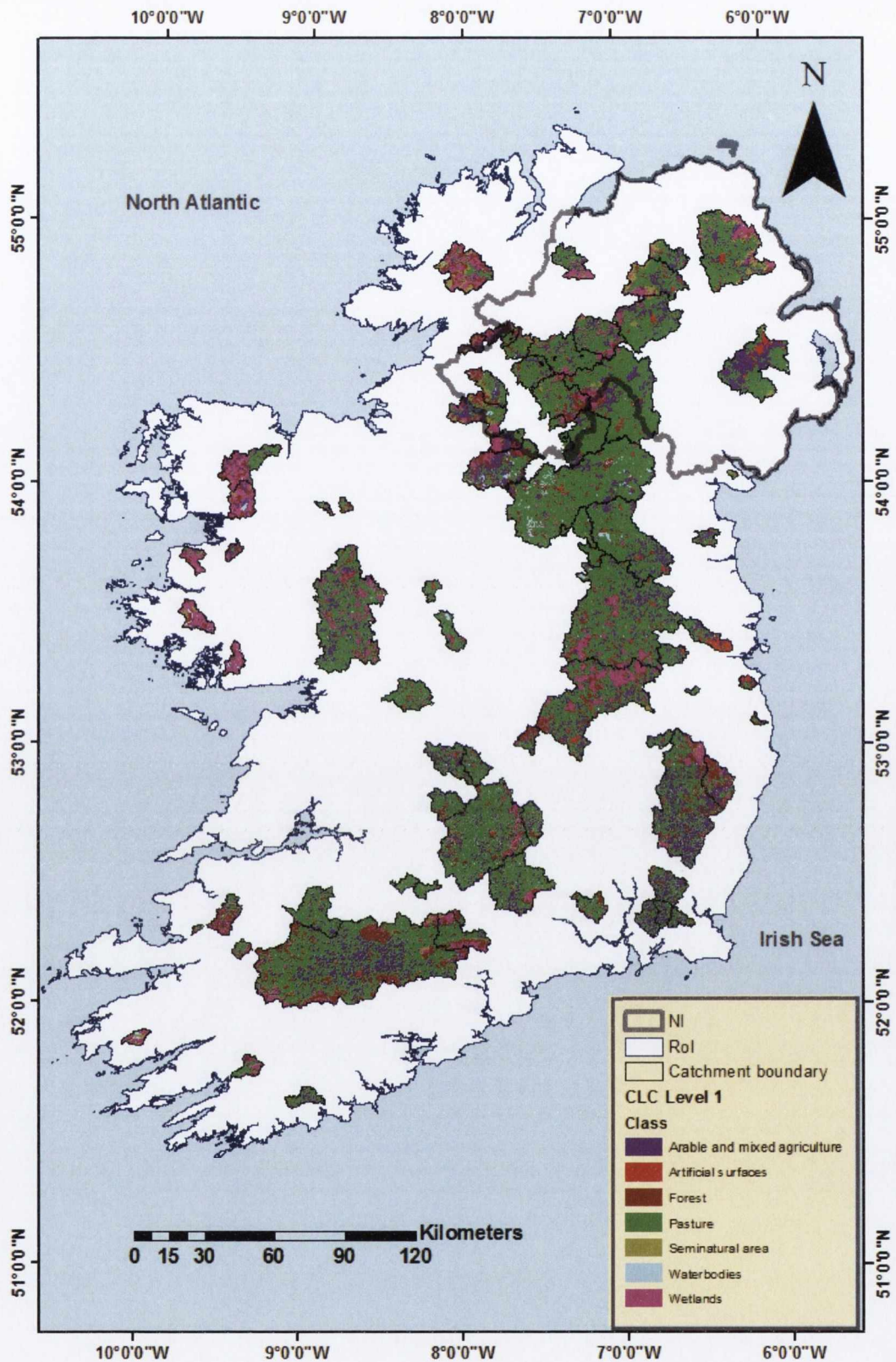


Figure 3.9. Illustration of the composition of land cover classes (CLC Level 1) within the 77 selected river catchments used in the small scale study. Collectively, the catchments contain 60.40% pasture land, 16.05% arable land, 11.19% wetlands, 7.17% forestry and 2.54% urban land. These proportions coincide with the overall percentage composition of land cover classes in the Irish Ecoregion (Table 3.2). Data for the Rol is from the year 2006 and data for NI is from 2000. Data were provided by the EPA (Rol) and AFBI (NI)

3.3.4. Environmental conditions in the catchment for Lough Sheelin

Lough Sheelin (53°08' N, 7°33' W, 65.4 m AMSL) (Figure 3.10 and 3.11) is a shallow lake (mean depth 4.5 m) with a surface area of 18.1 km². The lake has a volume of 81.5 x 10⁶ m³, exhibits a hydraulic residence time of six months and drains a catchment comprising an area of 256 km². The catchment is located in the drumlin belt of the central-northern part of the Irish Ecoregion, situated on the upper reaches of the Inny river, a tributary of the River Shannon (Figure 3.3). The region experiences rainfall of approximately 1,000 mm per year. The largest proportion of the catchment lies within Co. Cavan with the remainder divided between Co. Meath and Co. Westmeath (Figure 3.4). Ten tributaries drain into Lough Sheelin, which has a single outflow via the Inny river, located in the southwest end of the lake. The research that underpins the large scale proportion of this research focuses on the seven tributaries (Bellsgrave, Carrick, Crover, Halfcarton, Mountnugent, Ross and Schoolhouse) described in Table 3.3. Subcatchment rivers have Strahler orders ranging from 2 to 4 and areas ranging from 2.4 km² to 91.6 km².

In the Lough Sheelin catchment, the Halfcarton, Mountnugent and Ross subcatchments are characterised by high relief and steep slopes (maximum 270m AMSL), whereas the topography in the remainder of the catchment has lower altitude (minimum 65m AMSL) (Figure 3.4). A major geologic strike divides the catchment into a northern, upland part that is predominately underlain by Ordovician and Silurian strata, and a southern part characterised by Carboniferous limestone (Figure 3.12). Glacial drift deposits cover the bedrock with sediments predominately of boulder clays, which gives the catchment its distinctive drumlin landscape. The till deposits provide aquifers with protection from surface contamination.

The hydrological behavior of the rivers varies across subcatchments (Table 3.3). The Mountnugent river displays a high Q95:Q5 flow ratio, owing to impermeable gley soils and the poor aquifer abilities of a Ordovician and Silurian substrate, indicating limited seasonal groundwater transfer and a rapid response to high rainfall events. The Ross and Halfcarton subcatchments, however, contain predominately brown earths with a Carboniferous limestone geologic structure, this allows greater soil permeability and improved aquifer functionality resulting in lower Q95:Q5 ratios.

As is typical of the Irish drumlin region, gley soils in the northern and western parts of the Sheelin catchment result in low soil permeability, vulnerability to waterlogging and nutrient loss via surface and near-surface hydrological pathways (Figure 3.13, Table 3.3). By contrast, deep, well-drained brown podzolics, grey-brown podzolics and brown earths are predominant in the eastern

subcatchments while the soils closer to the lake shore and around the Inny outlet are composed of blanket and basin peats.

The type and extent of land use in the Lough Sheelin catchment is directly influenced by local climate, relief, hydrology and soils. Managed grasslands are predominant, occupying 84.72% of the catchment area, followed by forestry (4.38%), arable and mixed agriculture (5.81%), wetlands (2.49%), artificial (1.59%) and seminatural areas (1.01%) (Figure 3.14). The percentage of land farmed and fertilised in subcatchments varies from 84% - 50% and 53% - 30%, respectively (Table 3.3). The general high percentage of managed grasslands reflects the catchment's role as part of the organised and structured agri-business sector that is characteristic of the central region of Ireland. Agricultural activity is extensive but generally restricted to the grazing of beef cattle (e.g. Figure 3.15), piggeries, mushroom production, dairy cattle and poultry farming, indicating the limiting factors imposed by poor soil conditions, with almost 57% of farms located on wet drumlin soils. Farms are small with an average area of 2.5 km² and tend to be fragmentary (CSO, 2000) (e.g. Figures 3.15 and 3.16). The cattle stocking density is 150 cattle km⁻², typically average for the region and catchment type (CSO, 2000). Poor grass growth and severe poaching caused by waterlogging influence the common practice for cattle to be housed up to seven months in the winter with grass silage used as primary winter forage.

Two small towns, Ballyjamesduff (human population 1,700 as of 2006) and Oldcastle (human population 1,300 as of 2006) (CSO, 2006), are located in the Mountnugent and Ross subcatchments respectively (Figure 3.4). Each town has a WWTP that discharges into its respective river. Human settlement in the remainder of the catchment is characterised by scattered dwellings, each linked to domestic septic systems for waste water treatment (Keys and Gibbons, 2008). Meat plants and abattoirs comprise the major commercial activity in the Lough Sheelin catchment. The largest business enterprise is Liffey Meats located close to Ballyjamesduff town which discharges effluent into the Mountnugent river.

Lough Sheelin is a high alkalinity lake (> 100 mg l⁻¹ CaCO₃) with a low average depth, supporting a diverse and highly specialist ecology. It is one of only 12 lakes in Western Europe capable of supporting substantial stocks of large wild brown trout (O'Grady, 2000). The lake has been under threat since the 1970s owing to a constant contribution of excessive loads of nutrients entering the lake from anthropogenic sources in the catchment (Champ, 1993; EPA, 1994; Keys and Gibbons, 2006). Owing to the combination of sources of P and environmental conditions, the Lough Sheelin catchment was identified as *high risk* by the EPA in the 2005 WFD Characterisation Report (EPA, 2005). Prior to the WFD, however, several phases of P mitigation as part of the P

Regs were implemented in the catchment from 1998 to 2008. An upgrade and expansion of the Ballyjamesduff WWTP from primary to tertiary chemical treatment of discharge and the issue of an IPPC license to limit the loading of P from a meat processing plant both occurred in 1999. An interim P removal regime was introduced at the overloaded Oldcastle WWTP in 2003. Catchment-wide, septic tank bye-laws were officially introduced in 2004, following small progress initiated in 2000. Agricultural bye-laws to regulate the storage and management of livestock wastes were in place by 2003. Licensing of trade discharges to water, septic tank compliance, pollutant investigations and farm surveys were also introduced in 2003. Notably, landuse changed little during the duration of the P Regs, however between 1996 and 2006 the populations of Ballyjamesduff and Oldcastle increased by 60% and 40%, respectively, while rural population densities also increased, ranging from 10% in Carrick to 53% in Mountnugent (Table 3.3, CSO, 2006).



Figure 3.10. View of Lough Sheelin from Crover, looking southwards



Figure 3.11. Aerial view of Lough Sheelin looking towards the southern end of the lake. Photograph provided by IFI (Kerins *et al.*, 2007)

Table 3.3. Descriptive information of the environmental conditions in the seven study subcatchments in the Lough Sheelin catchment (large scale study)

River name	Subcatchment area (km ²)	Strahler stream order	Q95:Q5 ratio	Soil type		Land use	Human population (1998 & 2008)
				P desorption Index ^a	soil type	Land use ^b	
Bellsgrave	11.6	3	63.2	2.8	Acid brown earths, podzolics, gleys	Permanent pasture 50% farmed 51% improved	186 - 249
Carrick	2.4	2	101.8	3.1	Acid brown earths, podzolics, gleys	Permanent pasture 60% farmed 35% improved	39 - 42
Crover	6.1	2	39.6	3.0	Gleys, brown earths, podzolics	Permanent pasture 62% farmed 53% improved	105 - 125
Halfcarton	14.3	2	28.8	1.8	Brown earths, grey brown podzolics, rezinas, lithosols	Permanent pasture 58% farmed 35% improved	204 - 246
Mounthugent	91.6	4	30.2	2.7	Gleys, peatland	Permanent pasture 78% farmed 36% improved	2884 - 5143
Ross	63.1	3	17.2	1.8	Brown earths, grey brown podzolics	Permanent pasture 71% farmed 30% improved	1782 - 2232
Schoolhouse	10.9	2	98.0	1.9	Brown earths, peatland, podzolics	Permanent pasture 84% farmed 51% improved	247 - 329

^a potential of P desorption from soil (Daly and Mills, 2006). A high value indicates an increased risk of P loss by desorption.

^b CORINE (2000)

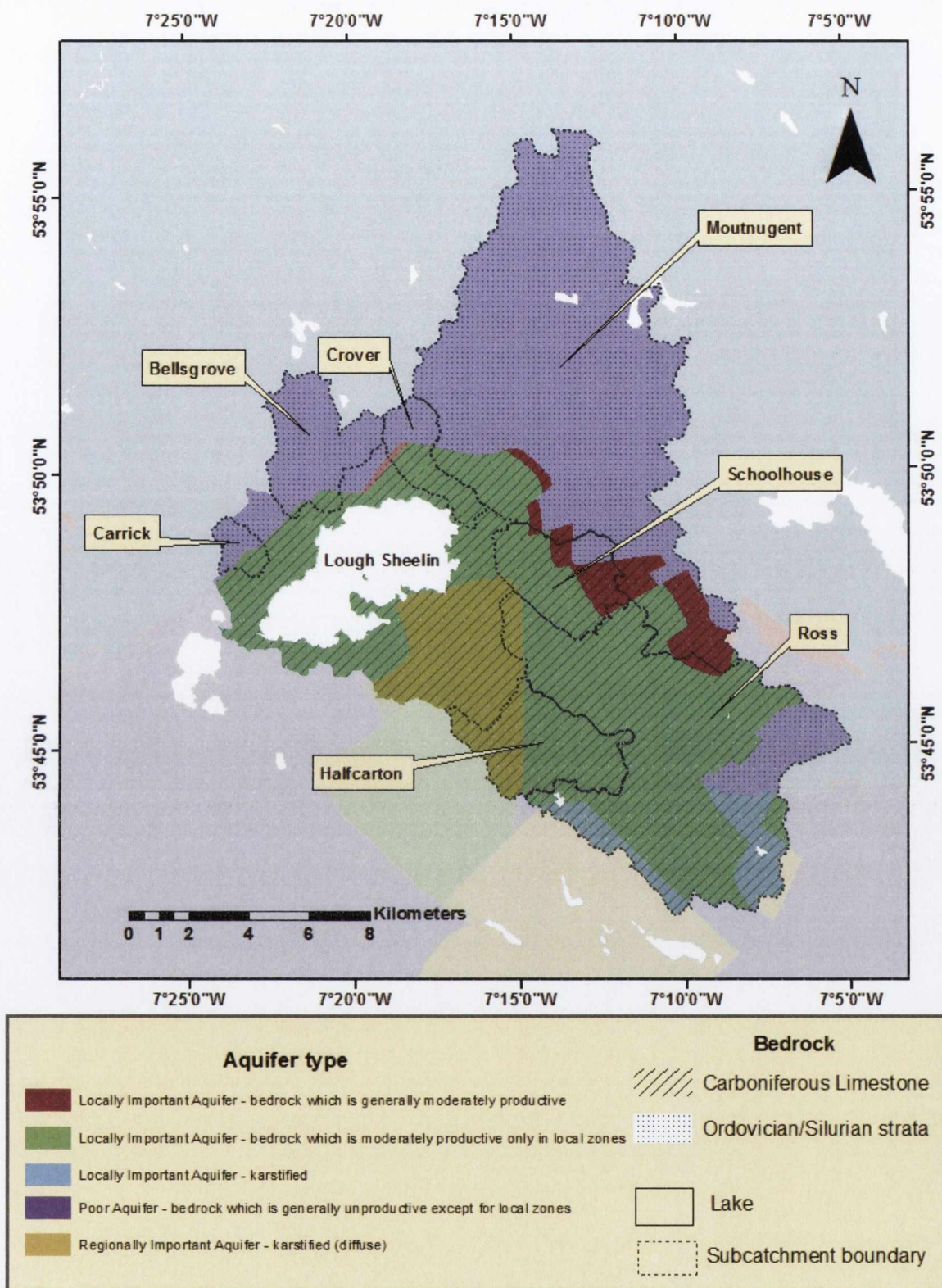


Figure 3.12. Illustration of the bedrock geology and aquifer characteristics of the Lough Sheelin catchment, showing the seven study subcatchments. A major geologic strike divides the catchment into a northern, upland part that is predominately underlain by Ordovician and Silurian strata, and a southern part characterised by Carboniferous limestone. Bedrock and aquifer data were acquired from GSI (National Draft Generalised Bedrock Map (Groundwater Rockunits) and Groundwater Aquifers, both at a 1:500,000 scale)

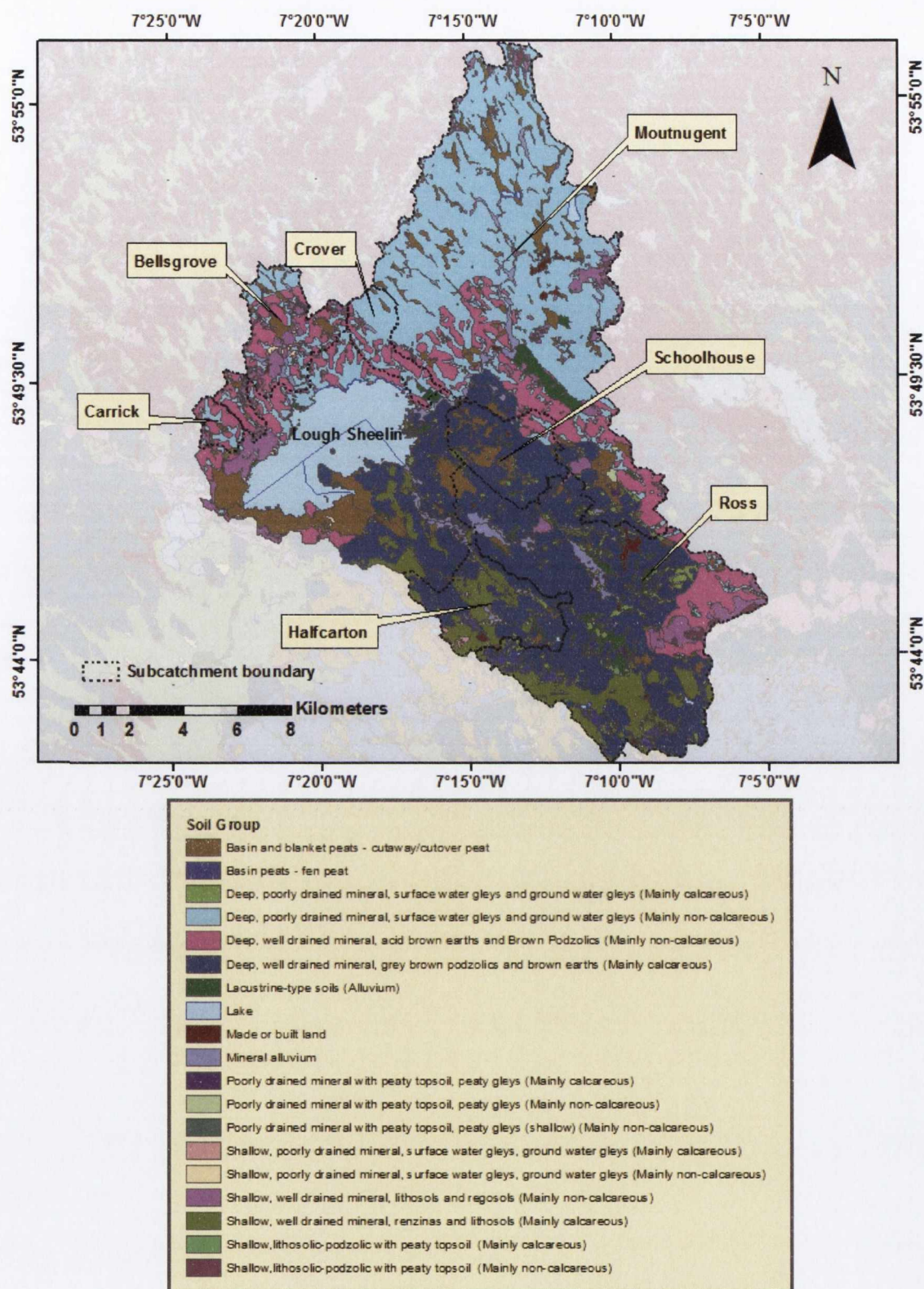


Figure 3.13. Illustration of the soil composition of the Lough Sheelin catchment, showing the boundaries of the seven study subcatchments. Gley soils are predominant in the northern and western subcatchments. Deep, well-drained brown podzolics, grey-brown podzolics and brown earths are mainly found in the eastern subcatchments while the soils closer to the lake shore in the south are composed of blanket and basin peats. Soils data for were sourced from the EPA, and were generated by Teagasc with co-operation of the Forest Service, EPA and GSI (project completed in May 2006)

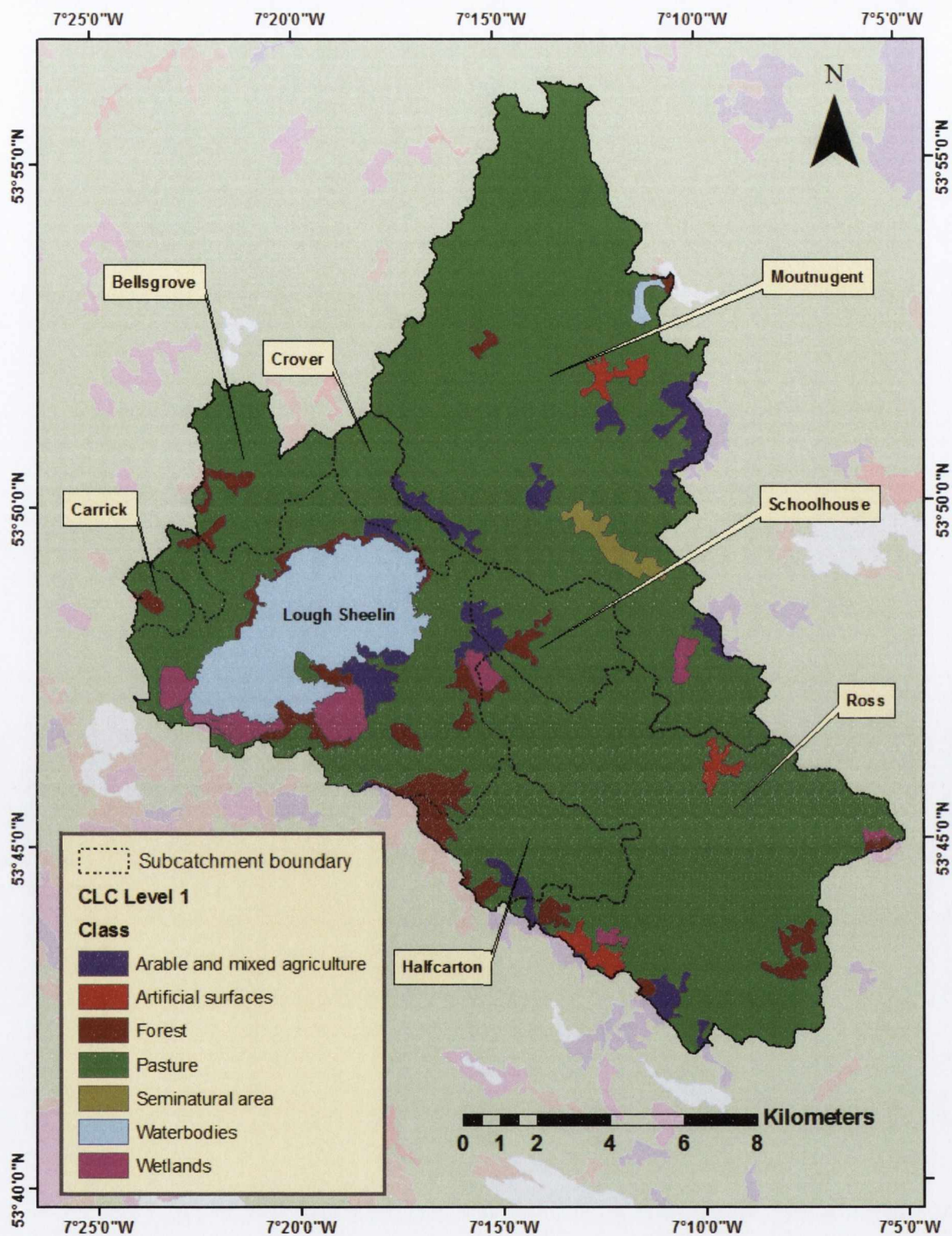


Figure 3.14. Illustration of land cover categories (CLC 2006, Level 1) within the Lough Sheelin catchment, showing the seven study subcatchments. The catchment contains 84.72% pasture land, 4.38% forestry, 5.81% arable and mixed agricultural land, 2.49% wetlands (including peat land), 1.59% artificial surfaces (mainly urban areas) and 1.01% semi natural areas. Data were provided by the EPA



Figure 3.15. View of an example of permanent pasture land and grazing beef cattle in fields of the catchment that drains into Lough Sheelin



Figure 3.16. Example of a typical small farmyard for beef cattle farming and rural houses that are scattered across the catchment that drains into Lough Sheelin

Chapter 4

Evaluating of the effectiveness of subcatchment-scale P mitigation using load apportionment modelling of river P and flow data

4.1. Introduction

Observations of apparent failures of POMs have produced uncertainty pertaining to whether sources of P were adequately targeted, if conditions within the environmental setting of freshwaters confounded outcomes or if stricter guidelines are needed (Sharpley *et al.*, 2009; Sharpley, 2011). As P-related water quality problems require a catchment-based approach, there is a need to understand catchment-specific delivery pathways, mechanisms and impacts of catchment management policies on the sources of P entering rivers and lakes (Jordan *et al.*, 2005a; Neal and Heathwaite, 2005; Neal and Jarvie, 2005; Arnscheidt *et al.*, 2007). In this context, the research described in this chapter seeks to determine how environmental conditions in seven independent subcatchments may have affected loads of P delivered to rivers during the implementation time of a long-term P mitigation programme. This large scale study focused on the catchment for Lough Sheelin in the RoI, of which seven subcatchments, ranging in area from 2.4 km² to 91.6 km², were studied (Figure 3.4, Table 3.3). The research presented in this chapter tests the H₀ that there is no relationship between environmental conditions at the level of subcatchment, sources of P delivered to rivers and the effectiveness of measures aimed at reducing P inputs. The following steps were carried out in testing this objective:

- Examination of the relationships between concentrations of P and values for flow measured in seven rivers in the Lough Sheelin catchment to guide the construction a LAM. A LAM can apportion the total load of P delivered to rivers into point and diffuse source components.
- Application of the LAM to a long-term dataset covering the time before, during and after the implementation of P mitigation measures for the P Regs in subcatchments containing the seven study rivers.

- Using the outputs of the LAM to aid the assessment of catchment response to the implementation of POMs, and to determine if environmental conditions in the subcatchments constrained the effectiveness of the POMs at reducing concentrations of P in the rivers.

4.2 Materials and methods

Testing the H₀ for this research used TP ($\mu\text{g l}^{-1}$), MRP ($\mu\text{g l}^{-1}$) and flow ($\text{m}^3 \text{sec}^{-1}$) data together with digital representations of environmental conditions in the study subcatchments (hydrogeology, agricultural intensity, soils, urbanisation, rural human settlement and industrialisation). This section outlines the sources of the data, together with manipulations of the data in preparation for statistical analysis. Construction and validation of the LAM are also described here.

4.2.1. Assembly of research database

River TP, MRP and flow data for the study were sourced from IFI and EPA. The methods for the sampling and analytical determination of these data are described in Chapter 3. Data from major point sources (industrial discharges and WWTPs) in the catchment were acquired from IPCC license information held by the EPA. Digital spatial data representing rivers, lakes, geology, land cover and soils were sourced from the GSI and the EPA. These datasets were acquired in the format of ESRI raster layers and vector shapefiles, and were projected according to the Irish National Grid. Data on human population and cattle stocking density in the catchment were sourced from the CSO and were acquired in Microsoft Excel format on the basis of DEDs.

Censored P concentrations (values recorded as below detection limit) were replaced with one half of the detection limit (e.g., $< 6 \mu\text{g l}^{-1}$ was replaced with $3 \mu\text{g l}^{-1}$) (Qian *et al.*, 2007; Reimann *et al.*, 2008). A full annual discharge record was created by estimating values for missing or omitted flows on the basis of strong correlations ($R^2 > 0.8$) with yearly flow values for neighbouring rivers with a continuous flow record (Mwakalila, 2003). Flow values for each river were normalised per unit area by calculating the surface runoff depth (mm day^{-1}) (e.g. Lennox *et al.*, 1997). The calculation of runoff depth enabled direct comparison of water drainage between the subcatchments. The P loads estimated from modelling the relationships between P and runoff by LAM application were also normalised according to subcatchment area. Data on P export per unit area were thus provided and disproportionate fluxes of P from subcatchments highlighted. Surface flow is the main delivery pathway to the rivers in the catchment (Kerins *et al.*, 2007).

Runoff between and within subcatchments was assumed to be spatially uniform and influenced by the same catchment characteristics and processes.

Flow and P data were paired according to date and organised in a database by hydrological year (1st October to 30th September). The database was divided into seven periods, each comprising two hydrological years (e.g. 1995-1996 ranges from 1st October 1994 to 30th September 1996). Runoff and P concentration data were log-transformed to achieve a normal distribution and to minimise the affect of outliers. GIS software and extensions (Maidment, 2002; Ormsby, 2008) were used to manipulate spatial data. Subcatchment boundaries were delineated from a DEM and river vector data by using each monitoring site as a pour-point. Data on flow, geology, land cover, soils, human population and cattle stocking density statistics were extracted using the subcatchment boundary outlines. An estimation of human population numbers between census years for each subcatchment was calculated from linear interpolation of census data (CSO, 2006).

4.2.2. LAM construction

Three concentration-discharge relationships are commonly recognised for P in rivers (Figure 4.1): point sources (a – inverse curve), diffuse sources (b, c – linear or exponential curve) and a third (d – u-shaped curve) describing a situation where contributions from both point and diffuse sources occur (Mohaupt, 1986; Chapman, 1996; Jordan *et al.*, 2005a,b; Arnscheidt *et al.*, 2007; Edwards and Withers, 2007). In the latter scenario, when both point and diffuse P sources contribute to river loading, P dilution is the critical factor at a low discharge range, but at higher flows dilution is suppressed and diffuse sourced P has the largest influence on loading. The R_e parameter provides an estimation of the runoff depth at which point sources (runoff < R_e) or diffuse sources (runoff > R_e) are the predominant influence on the river expressed as a temporal proportion of flows in any hydrological year.

Plotting median monthly values for MRP provided a visual interpretation of any seasonality component in the data. The statistical significance of any apparent seasonal component was tested using GLM analysis on all available data. To present a normal distribution and to minimize the effect of outliers within the data, MRP and runoff values were log-transformed. GLM was applied to test for statistically significant differences between the MRP and runoff relationships with respect to month, season (summer and winter) and hydrological year. For the two interaction terms (MRP*runoff and MRP*1/runoff) and all seven rivers, the MRP concentrations contained in the S1 (November-May) combination was statistically compared with S2 (June-

October) values. Statistical analysis was carried out using SPSS v.16 software (Ho, 2006; Field, 2009).

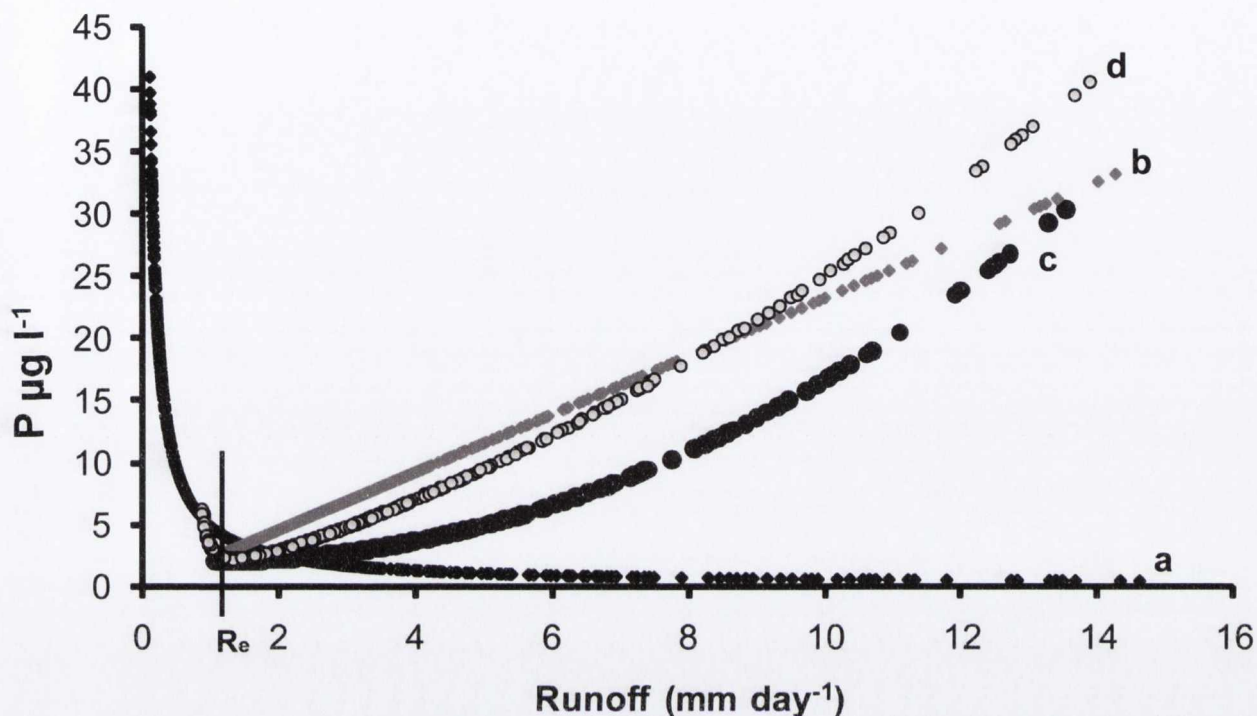


Figure 4.1. Relationships between P concentration ($\mu\text{g l}^{-1}$) and discharge (mm day^{-1}) indicating sources of P, (a) point source - inverse relationship (b) diffuse source - linear relationship (c) diffuse source - exponential relationship (d) combined point and diffuse relationships - U shaped relationship and the load apportionment model (d) showing R_e . The R_e value represents the runoff depth at which the magnitude of point and diffuse sources are equally contributing to the magnitude of the full P load

GLM indicated a seasonality trend in the data ($p < 0.001$). As a result, the database was split into S1 and S2 time periods. Several additive models combining the relationships between P concentrations as a function of runoff were tested by calibration to the study database using non-linear least square regression in PRISM 5 Graphpad software (Motulsky, 2007). The model that most accurately described the behaviour of the data and provided realistic outputs was selected and is described in equation 4.1;

$$C_p = a * \left(\frac{1}{Q} \right) + b * (Q) + c * (Q^2) \quad [4.1]$$

where:

C_p is measured P ($\mu\text{g l}^{-1}$)

Q is measured runoff depth (mm day^{-1})

a , b and c are estimated model coefficients ($\text{g P km}^{-2} \text{day}^{-1}$)

The model components describe the relationship of P with runoff along a hydrograph. The assumptions underlying the model consist of the dilution of point sources of P , flow dependence for diffuse sources contributions of P and a calibration database with a temporal resolution that captures representative samples. The 'a' coefficient, modelled with the inverse of Q (Figure 4.1), estimates P from continuous sources. Diffuse sources represented by the 'b' coefficient multiplied by Q are dependent on moderate runoff. The 'c' coefficient on the square of Q represents exponential increases in concentration, owing to sheet erosion during storm events. The model coefficients were not constrained to a numerical range prior to model calibration in order to permit consideration of concentration-discharge hysteresis. Uncertainties in estimations were quantified by confidence intervals ($p < 0.05$). Individual models were derived for each season type (S1 and S2), hydrological year combination (e.g. 1995-1996 etc.) and river monitoring site.

The 'a' coefficients ($\text{g P km}^{-2} \text{day}^{-1}$) of the inverse of Q estimated from equation 4.1 were converted to annual (S1 plus S2) point P loading (kg y^{-1}) using equation 4.2;

$$P_{\text{point}} = \frac{a * 365.25 * CA}{1000} \quad [4.2]$$

where:

P_{point} is the annual point P loading (P kg y^{-1})

a is the LAM coefficient of $1/Q$ ($\text{P g km}^{-2} \text{day}^{-1}$)

CA is the subcatchment area (km^2).

Measured daily runoff data were applied to each estimated seasonal model to derive the annual total P (point and diffuse) load (L_f , kg yr^{-1}) delivered to each river. L_f was then used to quantify the percentage of P derived from point and diffuse sources and was calculated through a two stage

process. First, individual models for each season and time period were fitted using measured daily runoff data (Q) and the estimated model coefficients a , b and c (P load from each delivery source estimated from equation 4.1) to predict a daily P concentration when no samples were taken (C_{p_d}) using equation 4.3;

$$C_{p_d} = a * \left(\frac{1}{Q} \right) + b * (Q) + c * (Q^2) \quad [4.3]$$

Second, estimated (C_{p_d}) values from equation 4.3 were incorporated with the measured daily P values (C_p) to construct a complete database of daily P concentrations (C_{p_d}). Values of C_{p_d} were multiplied by daily runoff (Q) to give daily P loading, which was summed to calculate annual total P loading (365.25 days per annum) in equation 4.4;

$$L_f = \sum_{j=1}^{n=365.25} C_{p_d} * Q \quad [4.4]$$

where:

Q is measured daily runoff (mm day^{-1})

C_{p_d} is daily P concentration ($\mu\text{g l}^{-1}$)

L_f represents total P load per unit area ($\text{kg km}^{-2} \text{yr}^{-1}$) for a hydrological year ($n = 365.25$)

The minimum point of the LAM equations, R_e (mm day^{-1}), the position at which point and diffuse sources of P loads were equal, were calculated by finding the real root, with respect to runoff, of each calibrated LAM when the first derivative turned to zero. Calculations were performed using Mathematica 8.0 software (Wolfram Research, 2011) and R_e points were validated using visualisation of model plots. The number of runoff observations with a value less than the R_e was used to determine the percentage of time point sources were the dominant contributor of P to each river.

4.2.3. LAM validation

Model accuracy was tested through a 10-fold cross validation method using 28 calibrated MRP models (two summer and two winter models for each of the seven rivers). A randomised subset of the data (10%) was partitioned into a validation subset (VS). The remaining 90% of the data, (EV), were used to estimate model coefficients from equation 4.1. The predicted MRP values were compared with the measured VS data. The success of model prediction was established by the percentage of MRP values estimated accurately in the VS (95% confidence interval) and expressed as the RMSE between measured and predicted values divided by the number of data points in VS. The RMSE was divided by an average MRP value in each VS to compare results of each subcatchment (CV-RMSE).

4.2.3.1. Alternative methods of P load estimation

Although septic tank systems are usually considered potentially important diffuse sources of nutrients (Hanrahan *et al.*, 2001; Drolc and Zagorc Koncan, 2002), they are also known to operate as an accumulation of small and constant point sources (Arnscheidt *et al.*, 2007). Consequently, E_i values for MRP transfer from septic tank systems were used in the current research as an alternative method for approximating MRP load from point sources. The loadings of MRP from septic tanks in rural areas for each of the subcatchments were calculated as the product of their resident populations and an E_i of 0.26 kg MRP cap⁻¹y⁻¹ (LLCMMS, 2000; Carvalho *et al.*, 2005). A 30% overall improvement of septic tank efficiency was anticipated when the regulatory controls on septic tanks were officially implemented in 2004 (Keys, 2008). This reduction factor was incorporated into the estimated export coefficient point source MRP loads.

MRP concentrations in discharges from large point sources in the Mountnugent and Ross subcatchments for 1999 onwards were calculated from averaged values from effluent discharge records (flow m³ day⁻¹ and MRP mg l⁻¹). MRP loadings for WWTPs prior to 1999 were estimated as the product of the town population and an export coefficient of 0.66 kg P cap⁻¹ yr⁻¹ (Azzellino *et al.*, 2003), which included the soluble P removal rates at WWTPs of 7.5% at Ballyjamesduff WWTP and 30% at Oldcastle WWTP (Carvalho *et al.*, 2005). Long-term monitoring records were not available prior to the IPPC licensing of the Ballyjamesduff meat processing plant, and an average effluent volume of 10.12 m³ hr⁻¹ and an MRP concentration of 1.85 mg l⁻¹, as described by Cooney (2006), were therefore used. Annual flow-weighted loads for TP and MRP, using the product of all measured concentration-discharge pairs, divided by total discharge, were calculated for comparison with total loads (diffuse plus point) calculated from the LAM in equation 4.4 (Salles *et al.*, 2008).

4.3. Results

4.3.1. Exploratory data analysis

Data for 1995-2008 indicate a trend of declining MRP in all seven subcatchments (Figure 4.2). Seasonal Kendall trend tests (Helsel and Hirsch, 1991) on the hydrograph data did not reveal any significant long-term shifts in runoff values that could have influenced P trends. The largest reduction in measured MRP was in Mountnugent; the smallest was in Halfcarton. A distinct seasonal cycle of P concentration and runoff values was evident in the dataset: higher P concentrations in the summer to autumn months, corresponding with lowest runoff, highlighted the influence of point sources. Estimations of TP and MRP model coefficients for S1 (November to May) were significantly different ($p < 0.01$) from S2 (June to October) coefficients, according to GLM analysis, and both S1 and S2 components were therefore included in the LAM.

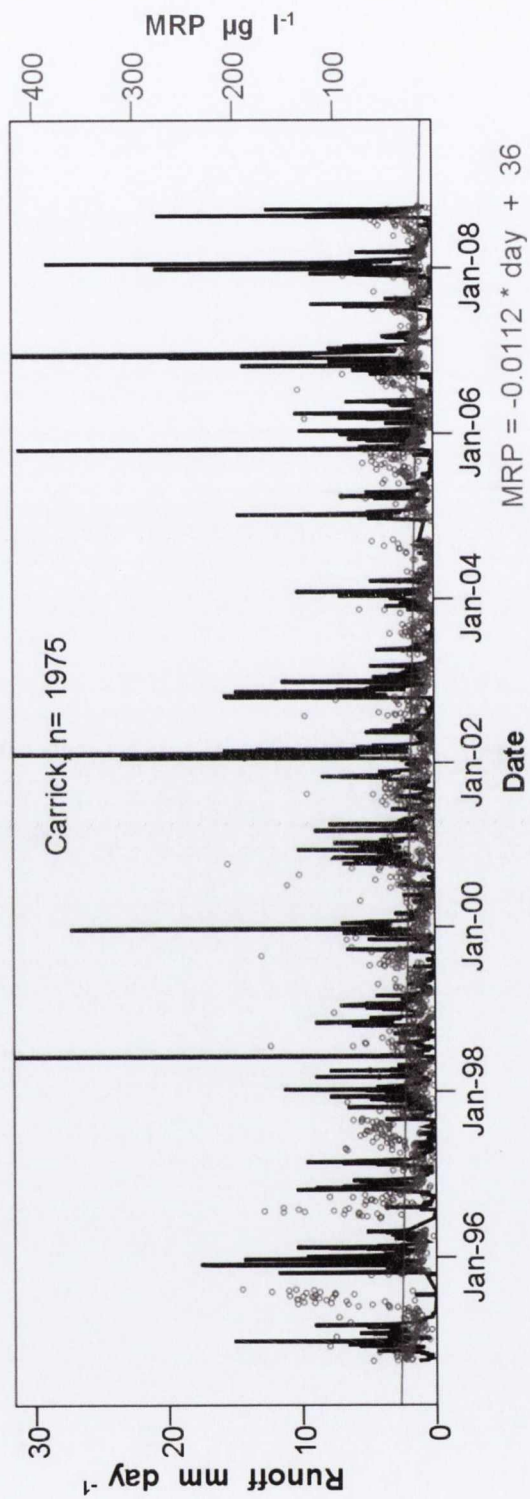
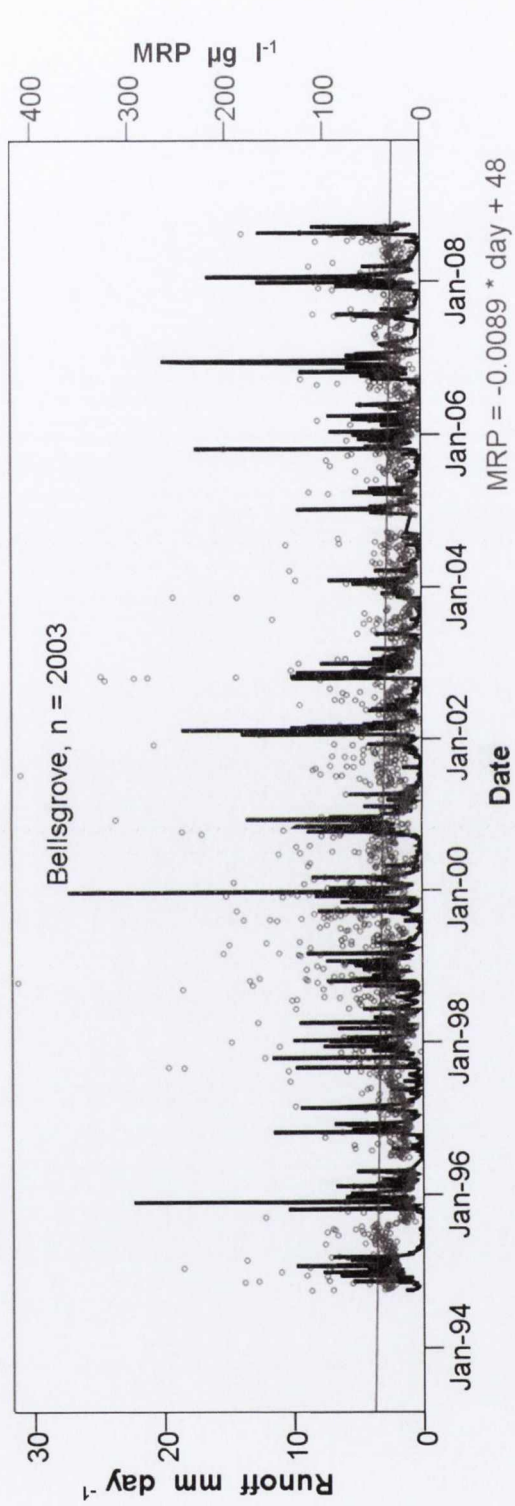
4.3.2. LAM outputs

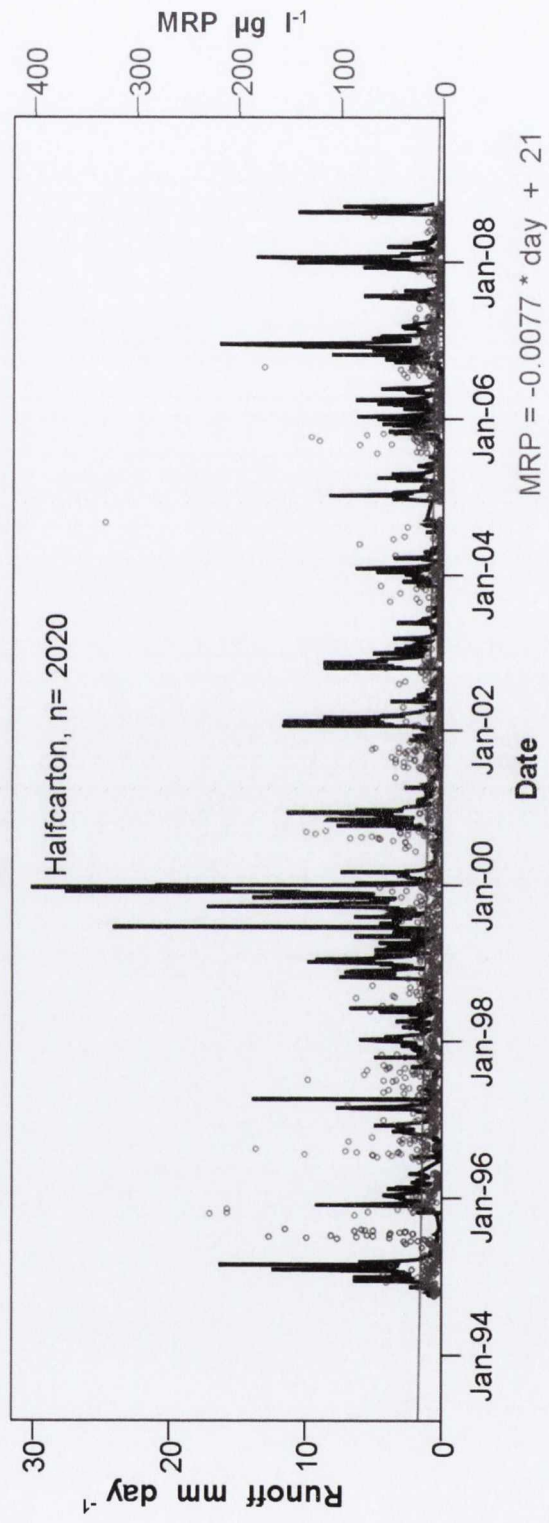
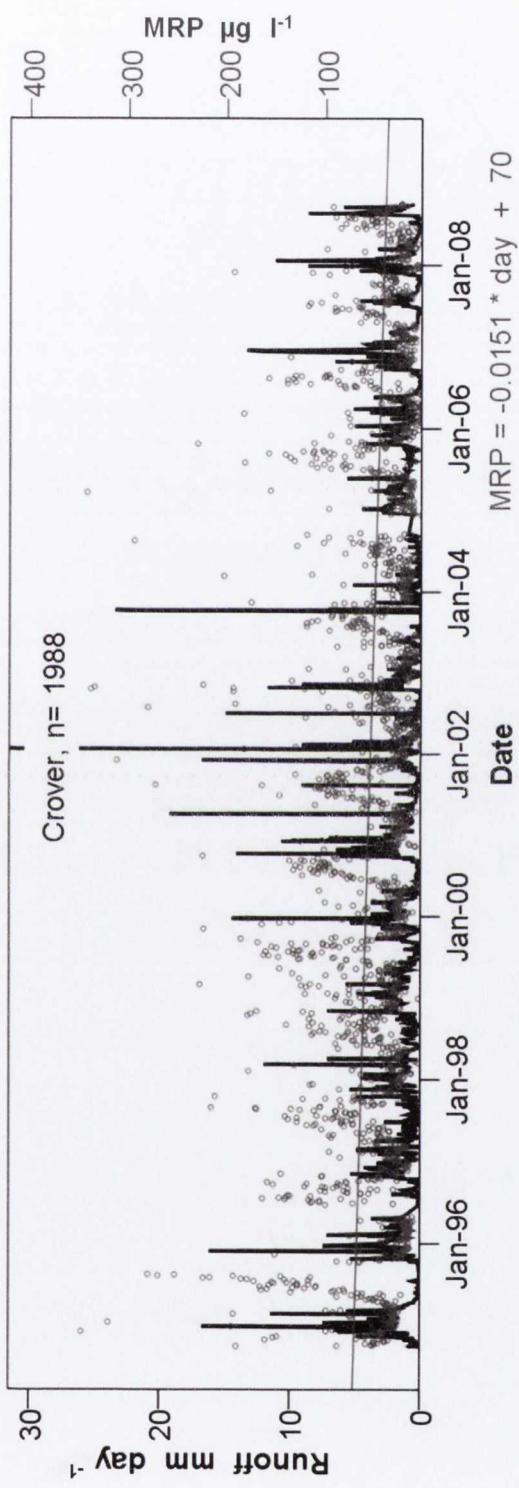
Using the LAM methodology on the full, seasonally adjusted dataset generated 195 individual model and 585 model coefficient estimates of MRP and TP loads. The models showed a typical, intermediate concentration-runoff relationship (u-shaped, Figure 4.3) indicating input from both point and diffuse sources. Seasonal models were fitted for all cases except Crover MRP (2005-2006) in which full biennial values were used because the estimated point source winter coefficient was negative. All point source coefficients were significantly different from zero except for Bells Grove MRP (2005-2006, S1), Schoolhouse MRP (2003-2004, S1 and S2) and Schoolhouse TP (2003-2004, S1). A negative 'c' coefficient, evident in several models (e.g. Figure 4.3d), was likely a result of hydrochemical hysteresis. The percentage of times that the river load was dominated by point source ($\text{runoff} < R_e$) was also calculated for each seasonal model. Model estimates of annual TP and MRP loads (point and diffuse sources) were standardised for catchment area (km^2) and the dominance in time (%) was expressed for each source, fraction and subcatchment (Table 4.1).

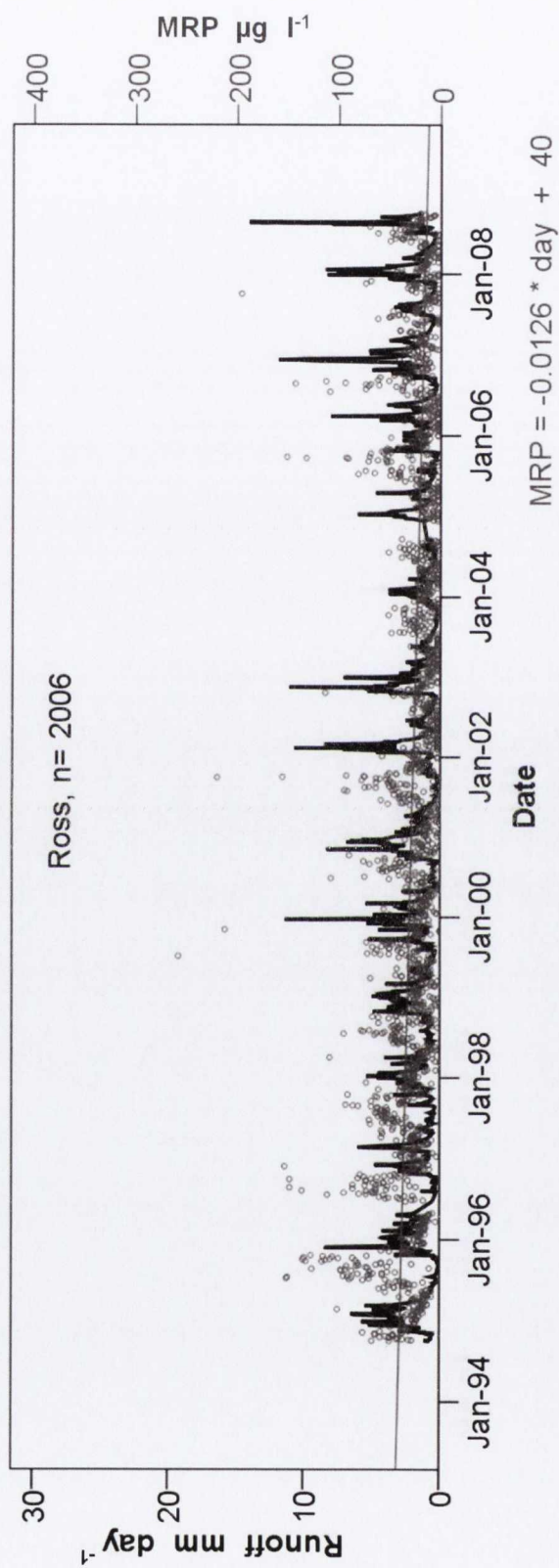
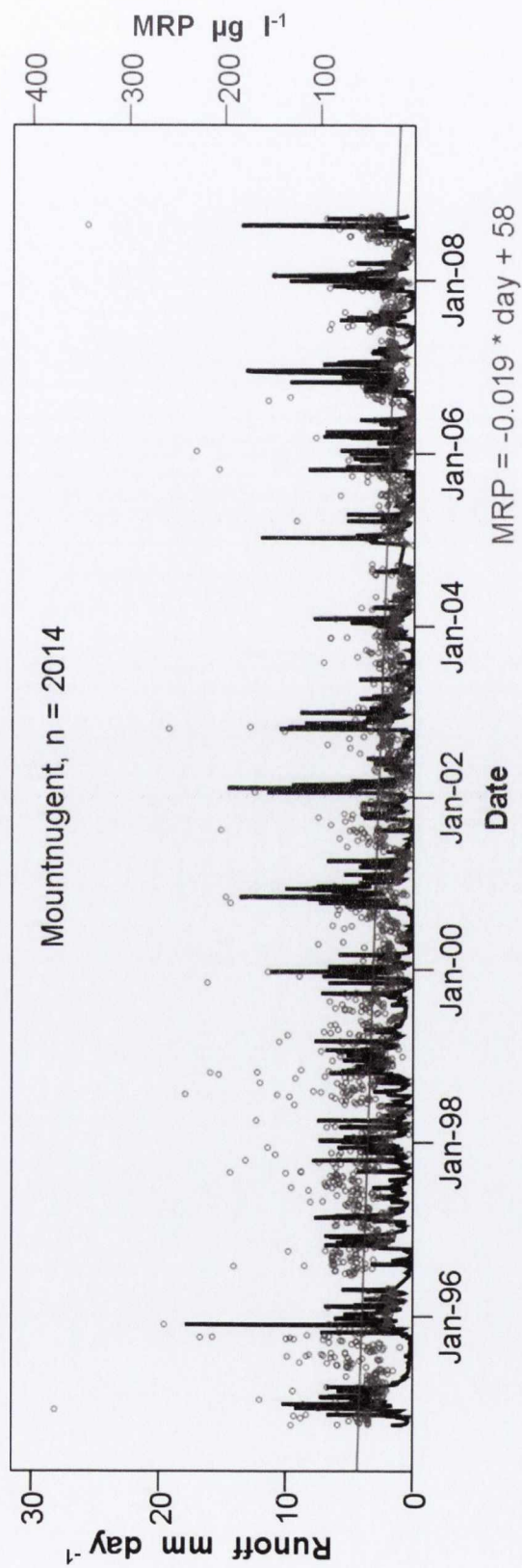
4.3.3. Outcome of LAM validation

On the basis of the 10% subset, winter models had a higher percentage of validation and lower CV-RMSE values (Table 4.2). The highest validation (78%) and the lowest CV-RMSE (41%) were in Ross winter models. However, these values decreased in summer months to 39% and 52%, respectively. The highest validation in the summer models was Halfcarton (57%). LAM loads were compared with two alternative methods of load estimation: export coefficient and flow-

weighted. The relationship between point source MRP loads from LAMs and export coefficients are shown in Figure 4.4. The correlation has an overall R^2 of 0.51 ($p < 0.01$). However individual subcatchment correlation coefficients range from R^2 of 0.07 to 0.66 ($p < 0.01$). The relationships between annual LAM MRP and TP loads with annual flow-weighted loads have R^2 values of 0.95 and 0.97 ($p < 0.01$), respectively, highlighting an effective validation of the overall total load estimation (Figure 4.5).







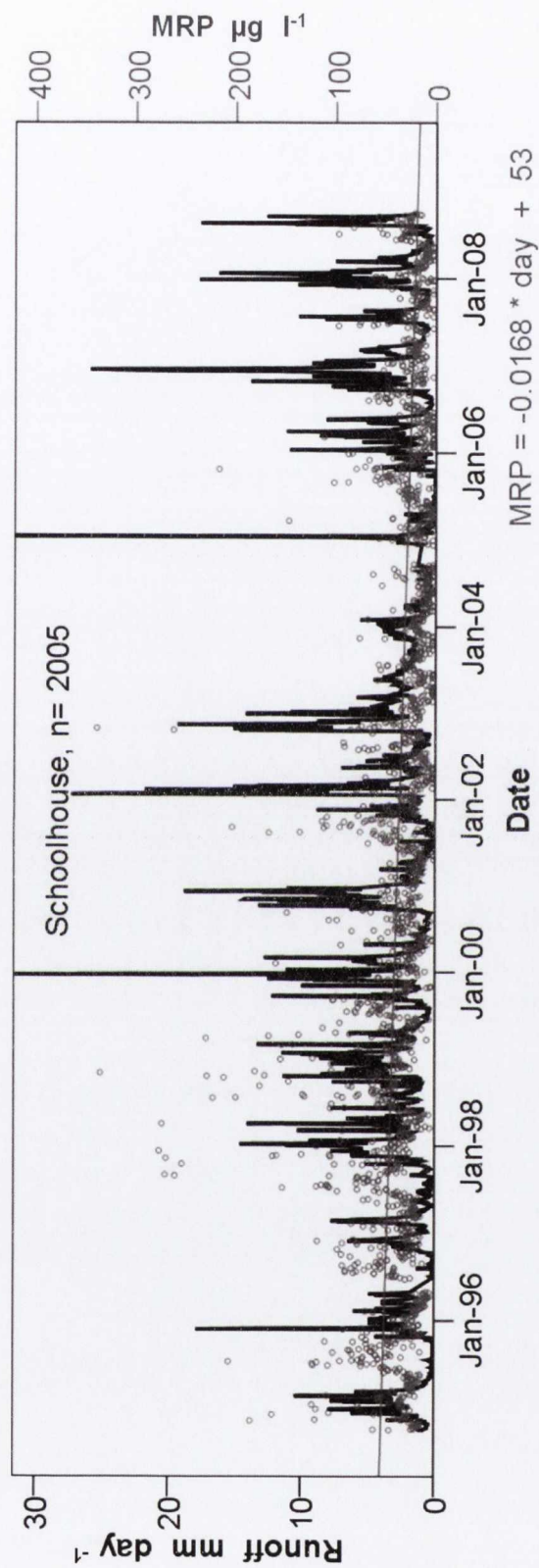
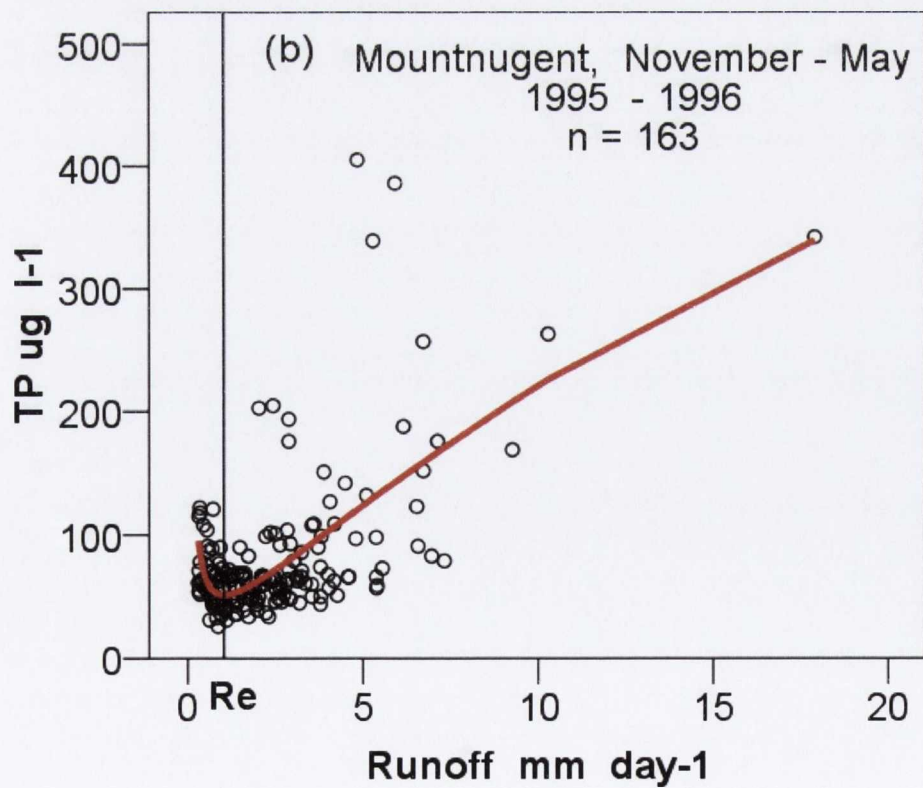
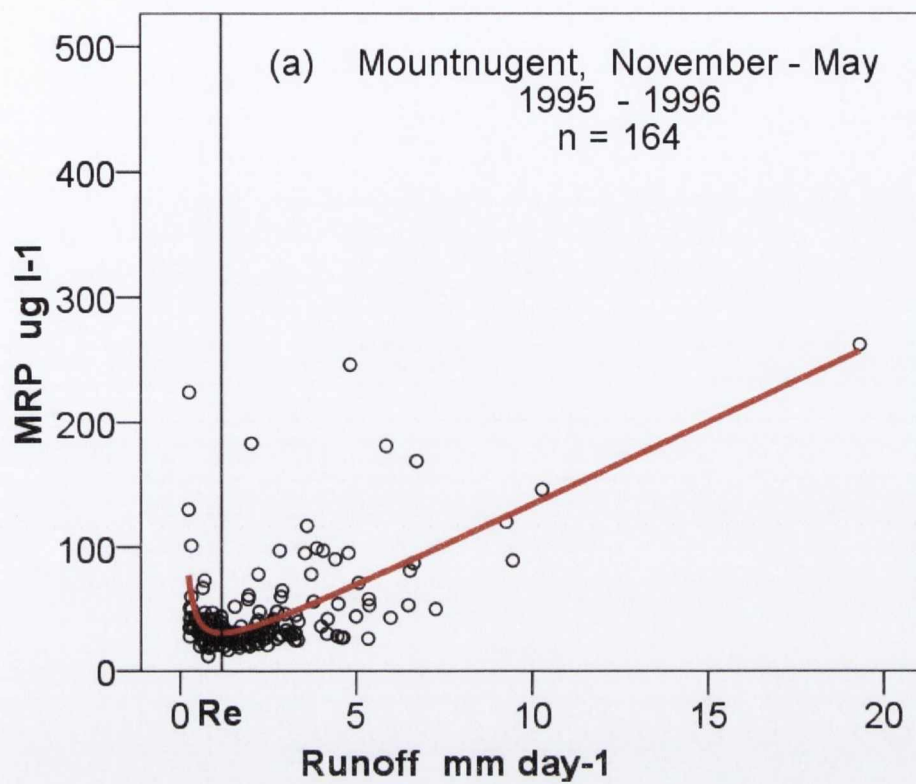


Figure 4.2. Measured runoff (mm day^{-1}) and MRP ($\mu\text{g l}^{-1}$) concentrations (1995–2008) with sample size (n) for the seven study rivers of subcatchments forming the Lough Sheelin catchment. The solid black lines represent measured runoff rates and the grey hollow circles indicate measured MRP concentrations. The simple linear equation for MRP trend is shown under the x axis



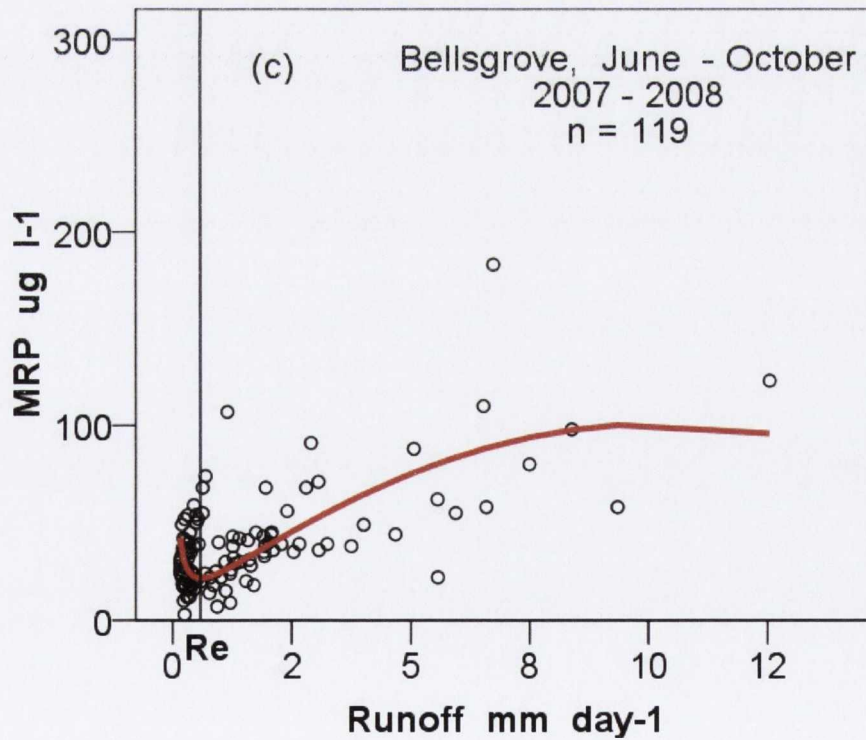
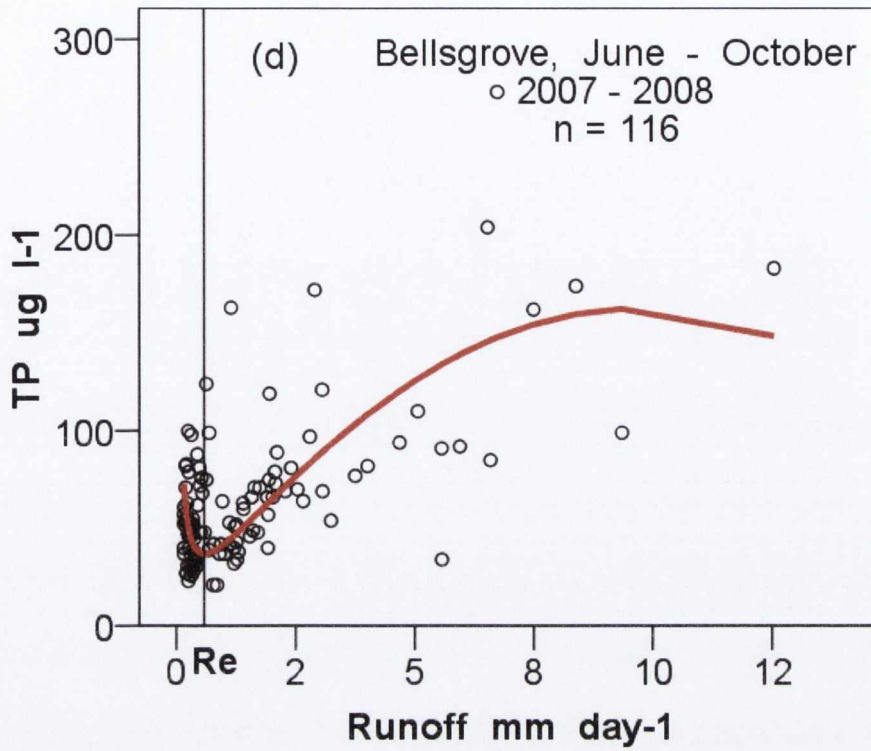


Figure 4.3. Examples of calibrated MRP ($\mu\text{g l}^{-1}$) and TP ($\mu\text{g l}^{-1}$) seasonal LAMs for the Mountnugent and Bellsgrrove subcatchments, showing sample size (n) and R_e position

Table 4.1a. TP and MRP loads ($\text{kg km}^{-2} \text{ yr}^{-1}$) estimated from LAMs for the seven study rivers in the Lough Sheelin catchment

Diffuse P load $\text{kg km}^{-2} \text{ yr}^{-1}$	Mountnugent		Ross		Bellsgrave		Halfcarton		Schoolhouse		Carrick		Crover	
	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP
95-96	49	24	20	9	40	23	11	5	32	18	34	13	42	25
97-98	39	23	8	4	36	24	9	3	60	45	21	11	22	14
99-00	45	28	12	8	48	36	15	12	77	61	15	9	32	26
01-02	50	25	10	1	55	24	9	2	38	33	29	10	61	29
03-04	40	14	8	3	44	28	4	2	47	30	20	11	33	19
05-06	33	14	2	1	39	17	14	4	29	16	35	11	28	18
07-08	66	36	35	11	57	31	17	7	72	33	50	23	30	16

Point P load $\text{kg km}^{-2} \text{ yr}^{-1}$	Mountnugent		Ross		Bellsgrave		Halfcarton		Schoolhouse		Carrick		Crover	
	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP
95-96	14	9	12	9	5	3	9	3	6	4	3	2	9	5
97-98	15	12	16	11	11	7	10	5	9	7	7	5	11	8
99-00	6	2	13	7	15	7	15	5	27	13	4	2	10	6
01-02	8	5	13	9	12	6	7	3	30	10	9	2	3	2
03-04	5	2	7	4	4	2	7	2	4	2	4	1	1	0
05-06	6	2	23	9	8	2	8	2	4	2	7	3	16	5
07-08	7	4	14	7	9	5	5	1	15	9	5	2	13	6

Table 4.1b. TP and MRP % seasonal point source duration estimated from LAMs for the seven study rivers in the Lough Sheelin catchment. (w) = winter and (s) = summer

Point time (w) %	Mountnugent		Ross		Bellsgrove		Halfcarton		Schoolhouse		Carrick		Crover	
	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP
95-96	31	36	26	35	28	25	31	25	20	20	15	17	25	23
97-98	37	42	42	41	33	35	44	30	19	23	24	24	30	27
99-00	20	20	28	29	35	21	42	34	30	16	33	31	21	15
01-02	37	49	41	63	42	39	64	62	61	48	49	24	15	15
03-04	16	22	33	36	11	11	70	65	4	4	35	23	15	15
05-06	17	16	60	17	1	0	55	18	28	25	29	28	13	33
07-08	22	23	36	36	32	32	39	28	25	23	43	39	43	38
Average	26	30	38	37	26	24	49	37	27	23	32	27	23	24

Point time (s) %	Mountnugent		Ross		Bellsgrove		Halfcarton		Schoolhouse		Carrick		Crover	
	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP	TP	MRP
95-96	60	54	46	35	57	47	60	63	69	70	63	61	61	75
97-98	27	31	70	81	40	42	34	59	28	31	58	64	36	48
99-00	38	31	76	57	60	58	49	46	51	52	67	61	49	56
01-02	35	50	79	83	54	59	11	88	51	51	50	56	33	26
03-04	57	64	65	71	54	58	81	86	30	22	77	81	70	48
05-06	57	48	85	83	75	60	55	57	42	34	71	58	33	NA
07-08	43	23	49	44	49	49	62	53	49	50	52	53	54	53
Average	45	43	67	65	56	53	50	65	46	44	63	62	48	51

Table 4.2. Ten-fold cross-validation results of LAM estimates (winter and summer) for the Lough Sheelin subcatchments

River	Validation %		RMSE $\mu\text{g l}^{-1}$		CV RMSE %		Average $\mu\text{g l}^{-1}$	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
Ross	78	39	8	16	41	52	19	30
Crover	47	36	20	45	52	68	38	66
Carrick	46	32	10	19	58	78	17	24
Halfcarton	72	57	5	20	58	110	9	18
Schoolhouse	46	46	32	34	94	69	34	49
Mountnugent	49	26	21	23	62	56	34	42
Bellsgrave	39	52	28	25	78	51	36	48

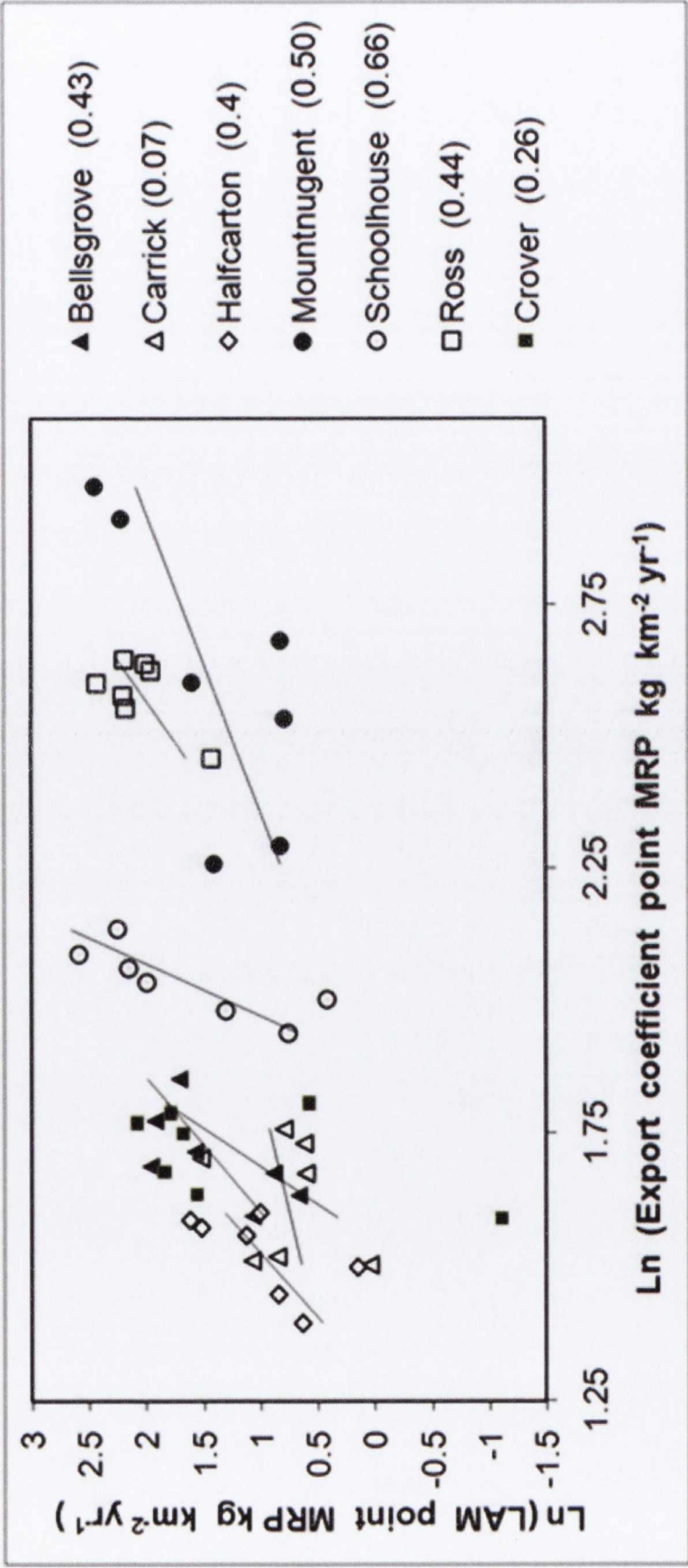


Figure 4.4. Linear relationships between MRP loads ($\text{kg km}^{-2} \text{ yr}^{-1}$) from point sources estimated by the LAM and export coefficients (log transformed) for the seven study subcatchments of the Lough Sheelin catchment. R^2 values ($p < 0.01$) are in brackets after the subcatchment name

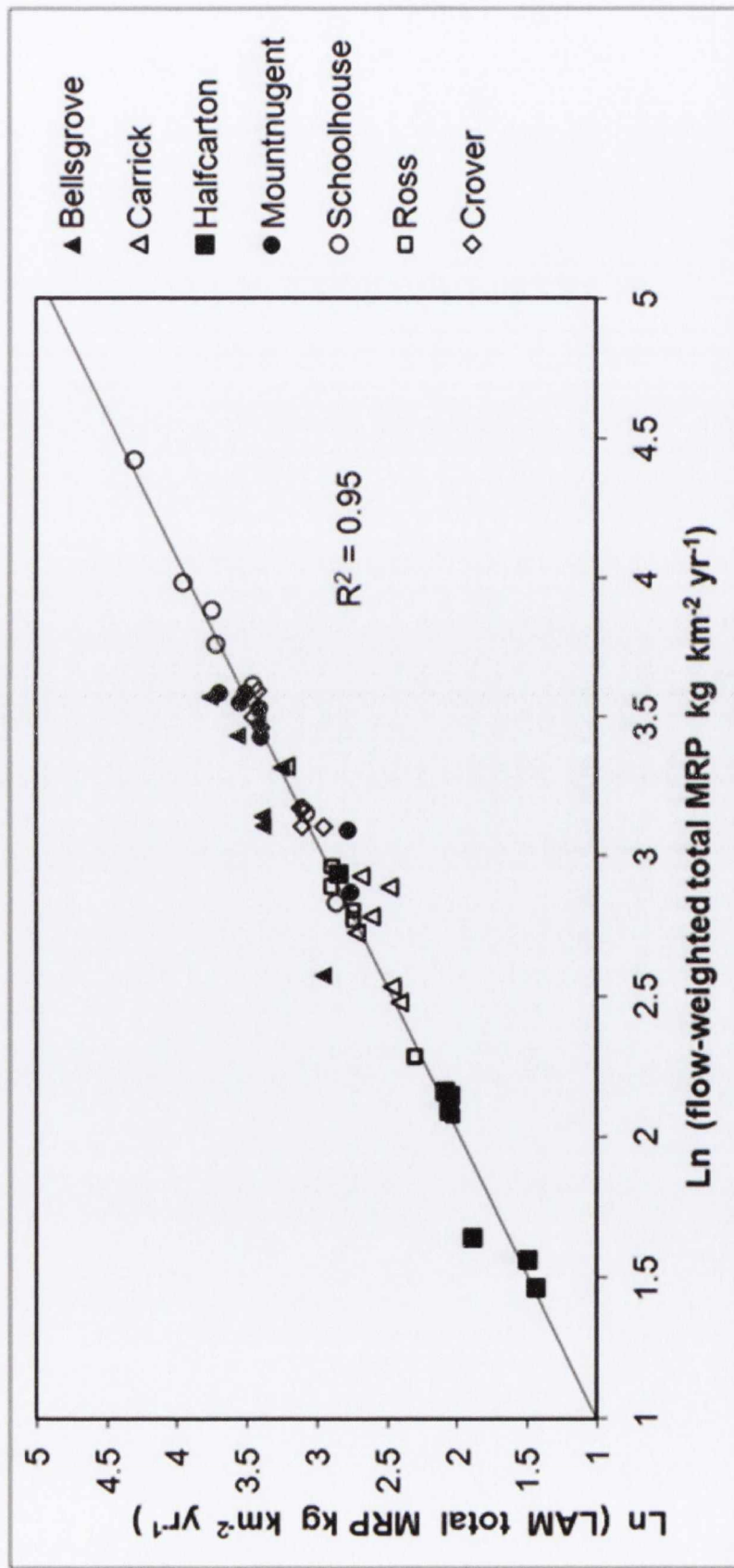


Figure 4.5a. Linear relationship ($p < 0.01$) between annual total (point and diffuse) MRP loads ($\text{kg km}^{-2} \text{ yr}^{-1}$) estimated by the LAM and flow-weighting (log transformed) for the seven study subcatchments that in part comprise the Lough Sheelin catchment

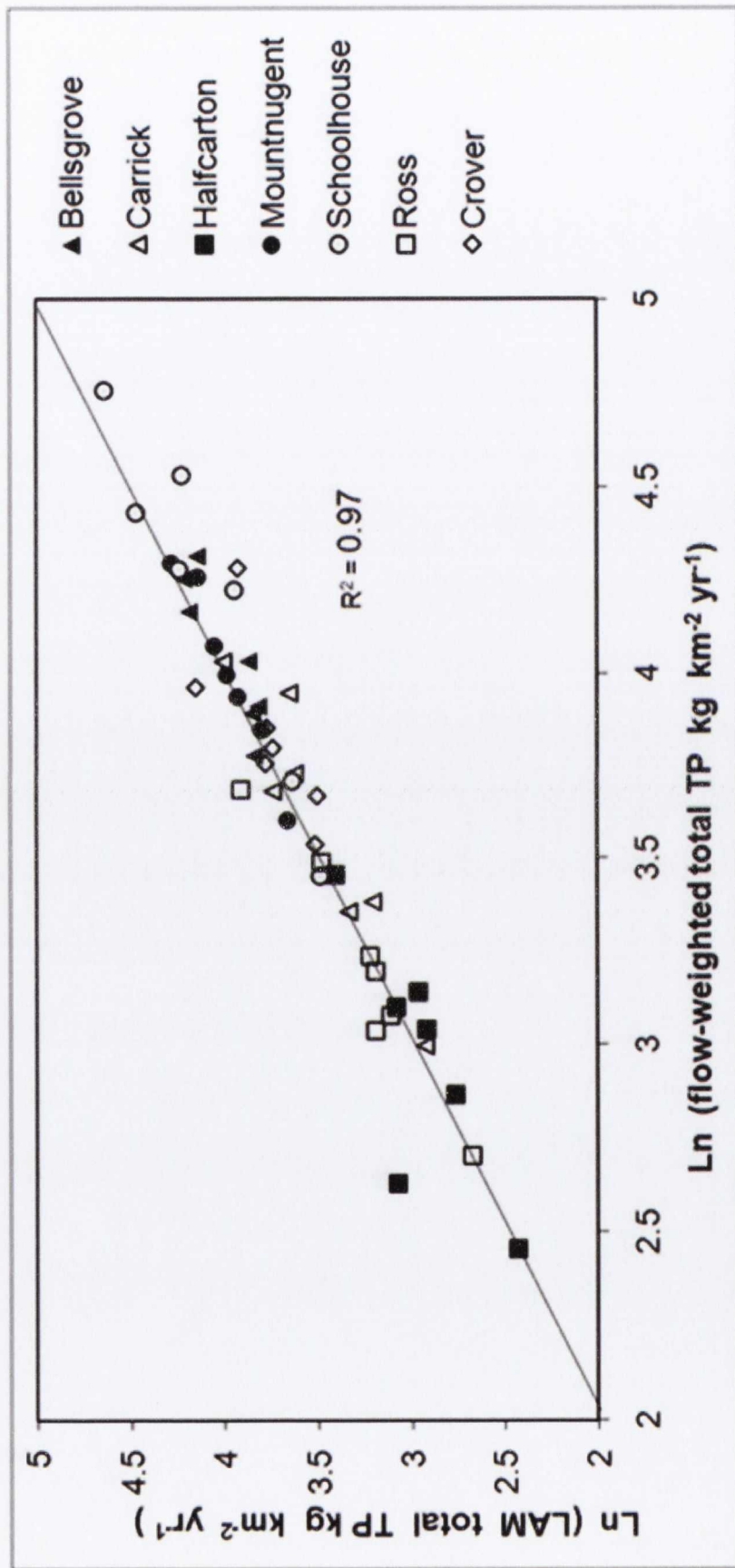


Figure 4.5b. Linear relationship ($p < 0.01$) between annual total (point and diffuse) TP loads ($\text{kg km}^{-2} \text{ yr}^{-1}$) estimated by the LAM and flow-weighting (log transformed) for the seven study subcatchments that in part comprise the Lough Sheelin catchment.

4.3.4. P export

There was substantial variation between years and between subcatchments in the rates of TP and MRP exports (Table 4.1a). Normalised to catchment area, the highest annual point and diffuse exports of both TP and MRP loads were delivered to the Schoolhouse river. In 1999-2000 the TP diffuse export was $77 \text{ kg km}^{-2} \text{ yr}^{-1}$, of which 79% was in the form of MRP ($61 \text{ kg km}^{-2} \text{ yr}^{-1}$). In these years the point source TP and MRP export rates (respectively, TP $27 \text{ kg km}^{-2} \text{ yr}^{-1}$ and MRP $13 \text{ kg km}^{-2} \text{ yr}^{-1}$) were also higher than in any other subcatchment. During the subsequent two year period point source TP and MRP inputs to this river remained high, but point source export rates did not remain high for the remainder of the study period, so that, for example, subsequently the point TP and MRP exports were 4 and $2 \text{ kg km}^{-2} \text{ yr}^{-1}$, respectively. The small Crover subcatchment produced low point source exports of both TP and MRP, which in 2003-2004 were only 0.7 and $0.3 \text{ kg km}^{-2} \text{ yr}^{-1}$ for TP and MRP, respectively. The large Ross subcatchment produced the lowest diffuse export rates of both TP and MRP with notably low rates in 2005-2006 of 1.8 and $1.2 \text{ kg km}^{-2} \text{ yr}^{-1}$, respectively. During this period diffuse sources were estimated to contribute only 8% and 18%, respectively, to the MRP and TP exports from this subcatchment.

Time series data were categorised into two distinct stages according to the timing of implementation of P-related POMs: Stage 1 (1995 to 1998, pre-implementation of P mitigation) and Stage 2 (1999 to 2008, during and post-implementation of P mitigation). Generally, annual diffuse source P loads exceeded point loads in terms of magnitude, except in certain periods in the Halfcarton and Ross rivers (Table 4.1a). The magnitude of point source P loads in Halfcarton dominated annual P load in 1997-1998 (TP and MRP), 2001-2002 (MRP) and 2003-2004 (TP). However, the R_e values in Table 4.1b showed that point source P had much greater dominance, in terms of flow duration, over diffuse source than the load magnitude values indicated. This was especially evident in the summer months when point sources dominated more than 50% of the time in a majority of the rivers.

Reductions of TP (60%, $p < 0.05$) and MRP (80%, $p < 0.05$) from point sources in Mountnugent 1999-2000 are attributed to increased P removal at the Ballyjamesduff WWTP from 1999. The R_e values indicated that the reduction of delivery of P to the river in 1999-2000 had a similar affect on MRP and TP point source dominance; the duration of dominance of MRP from point sources decreased in winter and increased in summer. However, a second attempt at point source P removal (55% point load MRP reduction from 2001-2002, $p < 0.05$) in 2003-2004 decreased both winter dominance of point source MRP and TP but had an increasing affect on point source dominance the summer months. Attempts at point source P remediation in Ross during 1999-2000 (38% MRP load reduction, $p > 0.05$) and 2003-2004 (53% MRP load reduction, $p < 0.05$)

generally decreased of length of time that P from point source predominated throughout the year (Table 4.1b). In 2003-2004 there was a general large reduction in the time duration dominance of point source P, except in Halfcarton. These reductions resulted from a number of statistically significant declines in point source TP and MRP from the subcatchments.

Accumulated loads (point, diffuse and total) and cattle stocking densities per unit area for each subcatchment for the period following implementation of measures aimed at abating P impacts are listed in Table 4.3. Overall, Schoolhouse contributed the greatest levels (per km²) of TP from point sources, and MRP and TP loads from diffuse sources, whereas the Ross subcatchment supplied the highest MRP loads from point sources. Lowest TP and MRP loads from point sources were from Carrick; Ross contributed the lowest MRP load from diffuse sources and Halfcarton the lowest TP load from diffuse sources. Point and diffuse sources in the Schoolhouse subcatchment contributed large loads of P during 1999-2000. A similar large peak in P from diffuse sources but not in point sources occurred in Crover during 2001-2002. Correlations between accumulated loads of MRP and TP from point and diffuse sources and accumulated cattle stocking density, human population density and the percentage of grasslands that underwent fertilisation application are detailed in Table 4.4. Notably, the highest significant relationships are between point sources of P and human population density. Furthermore, according to R² values, cattle stocking density appears to more strongly influence point sources of P rather than diffuse.

Extreme runoff events contributed a large proportion of annual P load to rivers. In 2007-2008, runoff greater than 10 mm day⁻¹ delivered 35% of annual loads over 20 days to Mountnugent. The sources and direction of change in P loads appear to have been altered in 2007-2008: P from diffuse sources in the Bellsgrave, Mountnugent, Ross and Schoolhouse subcatchments declined substantially from 1999-2000 to 2005-2006, but a high P load in 2007-2008 altered the downward trend and led to an overall increase between 1999 and 2008. The total rainfall over both hydrological year periods of 2007-2008 and 1999-2000 were similar (2264 and 2224 mm, respectively). There were, however, more extreme flows (≥ 10 mm day⁻¹) in each subcatchment in 2007-2008, and these were responsible for delivering a large proportion of the annual P load. Increased P loads from point sources were also registered for the Mountnugent ($p > 0.05$), Bellsgrave and Schoolhouse ($p < 0.05$) subcatchments in 2007-2008. Conversely, P loads from point sources decreased ($p > 0.05$) in Halfcarton and Ross ($p > 0.05$) during the same period.

Table 4.3. Accumulated estimated TP and MRP loads for the P mitigation stage (1998-2008) from LAMs for the Lough Sheelin subcatchments. Cattle and human population densities are also shown

River	Point MRP kg km ⁻²	Point TP kg km ⁻²	Diffuse MRP kg km ⁻²	Diffuse TP kg km ⁻²	Total MRP kg km ⁻²	Total TP kg km ⁻²	Cattle density LU km ⁻²	Rural human density km ⁻²
Bellsgrove	43	95	272	486	316	581	1094	98
Carrick	21	60	127	299	148	358	1050	86
Crover	38	84	215	368	253	452	1078	94
Halfcarton	26	82	55	119	81	201	892	78
Mountnugent	32	62	234	468	266	530	1381	148
Ross	73	139	50	133	123	272	1207	66
Schoolhouse	70	161	344	528	414	688	1531	134

Table 4.4. Strength (R^2) and statistical significance (p) of the linear regression relationships of accumulated loads of P (MRP and TP for 1998-2008 estimated from LAMs) with (i) rural human population densities, (ii) cattle stocking densities and (iii) % of fertilised grassland in the seven study rivers and their catchments for the large scale component of the research. Relationships between point sources of P with (i) and (ii) omit data for the two subcatchments (Mountnugent and Ross) that contain WWTPs. The values in bold highlight the R^2 values that are not significant

P source	Point MRP	Point TP	Diffuse MRP	Diffuse TP
Rural human population density (person km ⁻²)	$R^2 = 0.93, p < 0.05$	$R^2 = 0.88, p < 0.05$	$R^2 = 0.62, p < 0.05$	$R^2 = 0.68, p < 0.05$
Cattle stocking density (LU km ⁻²)	$R^2 = 0.85, p < 0.05$	$R^2 = 0.81, p < 0.05$	$R^2 = 0.69, p < 0.05$	$R^2 = 0.67, p < 0.05$
Fertilised grassland (%)	$R^2 = 0.020, p > 0.05$	$R^2 = 0.048, p > 0.05$	$R^2 = 0.64, p < 0.05$	$R^2 = 0.51, p < 0.05$

4.4. Discussion

This component of the research tested the H_0 that there is no relationship between environmental conditions at the level of subcatchment, sources of P and the effectiveness of measures aimed at reducing P inputs in the context of a river system. The results presented here have provided sufficient evidence to permit rejection of the H_0 with some confidence. Data for the period 1995-2008 indicated a trend of declining concentrations of P in all rivers, while significant temporal changes in P source loading as a result of P mitigation in the catchment (WWTP increased P removal, septic tank bye-laws, industrial discharge licensing and agricultural bye-laws) were detected near the time of implementation. These results imply that, to a certain extent, the policies introduced were effective in reducing P. However, inputs of P from diffuse sources in rural areas were found to be heavily influenced by land use and soil cover (poorly drained soils generally delivered the highest loads of P). The extent of human population and cattle population densities and soil type in rural areas had impacts on the amount of P from point sources delivered to rivers. The effectiveness of some POMs appears to have also been moderated by factors such as high rainfall and accidental pollution events; relatively short-duration events outside the control of mitigation management may have attenuated a signal of improving water quality. The following sections discuss these results in more detail.

4.4.1. Point sources of P

In addition to confirming the *a priori* expectation of a large point P source from the subcatchments containing urban areas, river data for the Lough Sheelin catchment also provide evidence of a point source influence in rural subcatchments. Evidence from the literature show that point sources of P detected in rural catchments have been attributed to cattle access points (Sharpley and Syers, 1979; Jarvie *et al.*, 2010), farmyard leaks (Edwards *et al.*, 2008; Edwards and Hooda, 2008), artificial land drains (Kurz, 2000; Withers and Jarvie, 2008) and malfunctioning septic tank systems (Arnscheidt *et al.*, 2007; Jarvie *et al.*, 2010). While the sample size is relatively small to make certain confirmations ($n = 5$) in the current research, the human population of the rural subcatchments, rather than cattle stocking density, appears to exert greater influence on point-sourced MRP loads (Table 4.4). Septic tanks are the main method of disposal of human waste in rural areas of the Lough Sheelin catchment. Each septic system is an individual proxy for larger, collective WWTPs, with the effluent from tanks draining to a soak-away trench in which nutrients are dissipated into the soil (Harper, 1992). Septic tank systems are thought to be more efficient at attenuating nutrients than larger WWTPs. However, Carvalho *et al.* (2005) and LLCMMS (2000), showed that P loads from septic tank systems to water bodies may be higher than expected, owing to poor design, maintenance or position of the system, or low possibilities

for the dilution of cumulative flows. Low soil permeability restricts dispersion and attenuation of nutrients owing to a high water table, therefore nutrients can by-pass soak-aways and exert an immediate impact on the trophic status of nearby watercourses, particularly during low flow conditions (Withers *et al.*, 2011).

Data from the Ross river showed the largest accumulated point source MRP loading per unit area, even following implementation of P mitigation at the WWTP (Table 4.3). Ross has a relatively low rural population density, a lower urban population than Mountnugent but the highest MRP:TP ratio (0.53). A high proportion of soluble P contained in TP indicates that the WWTP is a dominant contributor of MRP. In addition to source load magnitude, the estimation of R_e values showed that temporal dominance is also an important issue. For example, in summer 2001-2002, MRP and TP loads from point sources contributed, 49% and 57%, respectively, to annual P loads, but the R_e value indicates that loads from point sources dominated annual flows (79% TP and 83% MRP). This suggests that the river was at a much higher risk of eutrophication in the ecologically sensitive low-flow summer period than indicated by levels of P from point sources alone. Mountnugent had the second highest MRP:TP ratio (0.51), which was expected because of contributions from the WWTP. However, the overall magnitude of contributions of P from point sources in Mountnugent was relatively low (Table 4.3). The seasonal R_e values for the Mountnugent rivers indicated that although time duration of point loads of P were also more important than indicated by the magnitude of loads, diffuse sources of P were still the dominant origin of P in both winter and summer models. Therefore, the time dominance of diffuse source loads indicated that although there is point source P pressure in the subcatchment, mitigation of P should focus on reducing inputs of P from diffuse sources in the Mountnugent subcatchment. The Bellsgrove and Schoolhouse subcatchments contributed some of the highest MRP and TP loads from point sources to annual loadings of P, indicating the presence of constant sources of P in these rural subcatchments.

4.4.2. Diffuse sources of P

Soils in the Crover and Mountnugent subcatchments are predominately poorly drained gleys (Figure 3.13, Table 3.3). Well drained brown earths cover the Ross, Halfcarton and Schoolhouse subcatchments, whereas Bellsgrove and Carrick have a mixture of both soil types. Previous studies have found that poorly drained soils have the highest Q5:Q95 ratios and can help transfer high loads of P that show a diffuse-sourced behavior (Jordan *et al.*, 2005a), and this is evident from data presented here. Outputs of the LAMs estimated that the overall highest accumulated P loads from diffuse sources were from the Bellsgrove, Crover, Mountnugent and Schoolhouse

subcatchments (Table 4.3). These subcatchments contain the highest percentage of fertilised (improved) grasslands compared to the remaining subcatchments in the study (Table 3.3).

Previous studies have shown that runoff from grasslands generally carries little sediment and that the TP load is mainly dominated by soluble P (Heathwaite *et al.*, 1997). The strengths of the regression relationships between diffuse-sourced MRP and TP loads in Table 4.4 reflect this, with the occurrence of grassland fertilisation having a greater impact on MRP loads. Recently applied, inorganic fertilisers that are not incorporated into the soil, therefore remaining on the land surface, are a major source of MRP (Torbert *et al.*, 1999, Withers *et al.*, 2001; Kleinman *et al.*, 2002). The rapid increase in P loads associated with high rainfall levels in 2007-2008 are likely to have led to eutrophication observed at Lough Sheelin in 2008. Increases in P transfers in association with high levels of runoff have been reported elsewhere (Webb *et al.*, 1997; Tunney *et al.*, 2000; Shigaki *et al.*, 2007). Phosphorus, largely in the form of MRP, i.e. the most bioavailable form of P, can have major impacts on aquatic ecology (Wetzel, 2001). Given that agriculture is usually the main contributor to diffuse sources of P (Jennings *et al.*, 2003), implementation of measures targeting fertiliser use and slurry spreading, such as those being reviewed in the Nitrates Directive NAP (Fealy *et al.*, 2010), could reasonably be expected to facilitate recovery of Lough Sheelin.

Aside from agricultural-related diffuse sources of P, Table 4.4 shows a significant relationship between human population densities and P loads from diffuse sources ($n = 7$). Loads of P delivered to rivers from septic tanks may show diffuse-source characteristics owing to extreme runoff events flowing into and through tanks, producing a P-runoff relationship typical of the linear or exponential curve used in the LAM. Research by Neal *et al.* (2005) suggested that septic systems respond to both low and high flows, displaying the characteristics typical of both diffuse and point sources of P.

4.4.3. Appraisal of P mitigation

Variations in export rates of P were recorded during the period following implementation of mitigation measures in all subcatchments, although loads of MRP and TP declined overall. The significant decline in loads of P from point sources in Mountnugent and Ross is likely to reflect increased removal of P at WWTPs and restrictions on industrial discharges. However, despite the large decreases in P from point sources in Mountnugent in 1999-2000, MRP from point sources increased the following year. This increase may have reflected the continued occurrence of several point sources of P in the subcatchment. Nevertheless, loads of MRP from point sources

declined in 2003-2004, despite a rapidly growing population (a 30% increase from 2000 to 2004) in the catchment. The decline coincided with the implementation of septic tank systems and agricultural bye-laws. Phosphorus from point sources also declined in 2003-2004 in the rural subcatchments that underwent the implementation of both byelaws (Bellsgrrove, Carrick, Crover and Schoolhouse). However, extreme runoff events during 2007-2008 reversed this decreasing trend. Halfcarton and Ross, the subcatchments with rivers displaying lower Q5:95 ratios, free draining soils and lower P desorption indices, are less susceptible to high surface runoff. The R_e values support this evidence; point sources in the Ross subcatchment have greater dominate of both load magnitude and annual flow duration owing to the smaller influence of diffuse sources. However, diffuse sources of P tend to have more importance in subcatchments where gley soils are extensive (e.g. Mounthugent and Crover). A decrease in P from point sources in Halfcarton and Ross during 2007-2008, while increases occurred in other subcatchments, is indicative of a link between runoff and the magnitude of P load from point sources where soils are frequently waterlogged.

Using data from the Ross river, the R_e value showed that P loads from point sources had the greatest dominance of flows during the five-month summer season. Ross does not contribute excessive loadings of P to the annual catchment budget for P to the lake but high concentrations and dominance of MRP from point sources during the summer have a localised eutrophication effects in the river (Jordan *et al.*, 2005b). The installation of temporary facilities for removal of P from discharges at the WWTP in 2003-2004, and the control of industrial discharges, reduced the percentage of times that summer flows were dominated by P from point sources, thereby reducing the risk of eutrophication. Increased loads of P from point sources in 2005-2006 can be attributed to a large accidental spillage from the WWTP during August 2005 (Kerins *et al.*, 2007) that effectively masked any improvements that might otherwise have occurred following implementation of measures aimed at mitigating P inputs.

Lough Sheelin was reclassified from mesotrophic to eutrophic in 2008. Implementation in 2003 of restrictions on the spreading of slurry on land after the end of September of each year, aimed at reducing P transfers from diffuse sources, appears to have little overall positive impact on lake water quality. This may have been because unusually high rainfall rates in June-July 2007 increased surface runoff rates and led to the mobilisation of relatively high concentrations of newly applied fertilizers and slurry.

Chapter 5

Modelling the response of an eutrophic shallow lake to catchment-scale mitigation of P losses

5.1. Introduction

The impact of P in freshwaters is likely to be different owing to the nature of the waterbody (i.e. whether it is lentic or lotic, water residence time, depth of water etc.), loading of P (e.g. external or internal) and the organism(s) within the waterbody (Hillbricht-Ilkowska ; 1999; Hilton *et al.*, 2006; Schippers *et al.*, 2006; Ibelings *et al.*, 2007; Jeppesen *et al.*, 2007; Honti *et al.*, 2010; Meals *et al.*, 2010). This is particularly significant in the current research, specifically in terms of providing sufficient evidence to test the H_0 for both of the types of waterbody (rivers and lakes) typically found in a freshwater catchment. The research described in this chapter, therefore, aims to address this by extending the study of the effectiveness of P Reg POMs at reducing P loss in the Lough Sheelin catchment to examine the impact of environmental processes acting in the lake. Again, this research is carried out using a methodological framework based on mathematical modelling.

The research that underpins this chapter tests the H_0 that there is no relationship between conditions in the environmental setting of a lake, sources of P and the effectiveness of measures aimed at reducing P inputs. Testing this objective involved the following steps:

- Reconstruction of the long-term TP budget for Lough Sheelin for the time before, during and after the P Regs
- Calibration of published TP loading-response models using P data measured in Lough Sheelin and its contributing rivers
- Examination of changes in chlorophyll a - TP relationships in Lough Sheelin during the P Regs

These three steps aimed to address the H_0 in a collective manner. The lake TP budget was calculated to approximate retention/release of TP from lake bed sediment, thereby identifying

the key components of the P cycle driving the concentration of TP in the lake. The ability of a series of widely used TP loading-response models to describe the relationship between TP sources (lake TP loading) and TP response (lake TP concentration) were tested. The relationship between chlorophyll a and TP was examined to test for changes in the ecological sensitivity of the lake during the P mitigation programme.

Zebra mussel (*Dreissena polymorpha* Pallas) populations were established in Lough Sheelin by 2004 (Kerins *et al.*, 2007), with initial colonisation presumably commencing after implementation in 1998-1999 of the P Regs. As a consequence, the impacts of changes in TP loading and zebra mussel activity on water quality in Lough Sheelin are likely to have been combined. In an attempt to distinguish the actual impacts of implementing P Regs, monitoring data from before the onset of zebra mussel colonisation (1990-1999) were used as a control reference against which to compare TP dynamics post zebra mussel establishment (2004-2008). The period 1990-1999 contains an earlier attempt of P mitigation in the catchment (1990-1992) that comprised the implementation of policy to limit the spreading of livestock manure over the winter months and other circumstances likely to lead to excessive runoff of the applied wastes.

5.2. Materials and methods

The H_0 that shaped this study was tested using TP ($\mu\text{g l}^{-1}$), chlorophyll a ($\mu\text{g l}^{-1}$) and secchi depth (m) data from Lough Sheelin and TP ($\mu\text{g l}^{-1}$) loading data from the contributing catchment for the period 1990-2008. The sections that follow describe assembly of the research database, comprising data for 1990 to 2008, together with the steps involved in reconstructing the TP budget for Lough Sheelin. The calibration of several published TP loading-response models and examination of changes in the relationship between chlorophyll a and TP in the water column of the lake are also outlined.

5.2.1. Assembly of the research database

Mid-lake water samples from Lough Sheelin were taken monthly and analysed for TP ($\mu\text{g l}^{-1}$), chlorophyll a ($\mu\text{g l}^{-1}$) and secchi depth (m) during 1990 to 2008. Water samples from the seven tributaries studied in Chapter 4 were tested for TP three times a week for the same period. The sampling regime and analytical methods are described in full in Chapter 3. Total rainfall (mm) data for the catchment were sourced from Met Eireann. Information describing zebra mussel invasion of the lake was obtained from Millane *et al.* (2008) and Kerins *et al.* (2007).

Manipulation of the data was carried out using Microsoft Excel software. First, the TP, flow, chlorophyll a and secchi depth data were divided according to hydrological year (1st October – 30th September). Exploratory data analysis of the full data set showed that the data for 2000 and 2001, which contained large omissions of entries owing to lack of sampling or analyses of samples, were not appropriate and these were excluded from the analysis.

5.2.2 Reconstruction of the TP budget of Lough Sheelin

A TP budget for Lough Sheelin was reconstructed using data for the hydrological years 1990-2008. The annual net retention of TP (t yr^{-1}) in the lake (TP_{net}) was calculated according to the mass-balance equation adopted from Gibson *et al.* (2001) and Coveney *et al.* (2005):

$$\text{TP}_{\text{net}} = (\text{TP}_{\text{end}} - \text{TP}_{\text{start}}) - (\text{TP}_{\text{load}} - \text{TP}_{\text{out}}) \quad [5.1]$$

where:

TP_{net} = Net TP uptake (+) or release (-) (t yr^{-1})

TP_{end} = Lake water TP mass at end of year (t yr^{-1})

TP_{start} = Lake water TP mass at beginning of year (t yr^{-1})

TP_{load} = External TP load (t yr^{-1})

TP_{out} = TP load at lake outflow (t yr^{-1})

The annual TP load (t yr^{-1}) entering the lake from the catchment was calculated as the cumulative total TP_{load} (t yr^{-1}), comprising loads from: (i) tributaries; (ii) ungauged tributaries; and (iii) direct runoff. These steps are explained in the following sections:

- (i) Annual TP_{load} (t yr^{-1}) entering the lake from each of the seven gauged tributaries was calculated using the load estimation method in equation 5.2:

$$\text{TP}_{\text{load}} (\text{t yr}^{-1}) = \left[\sum_1^n (\text{TP}) * (\text{dmf}) / \sum_1^n (\text{dmf}) \right] * \left(\sum_1^{365.25} \text{dmf} \right) \quad [5.2]$$

where:

TP is the measured TP concentration ($\mu\text{g l}^{-1}$) from each sampled river

dmf is the measured daily mean flow ($\text{m}^3 \text{sec}^{-1}$) from each sampled river

n is the number of days in the hydrological year that TP samples were taken

Annual TP_{load} (t yr^{-1}) entering the lake from the stretch of river before a gauged monitoring point was calculated by a conversion factor for TP load derived from the corresponding gauged data.

(ii) Annual TP_{load} (t yr^{-1}) for tributaries draining the three rural subcatchments that had insufficient monitoring data (Maughera, Moneybeg and Rusheen) was estimated by application of a conversion factor for TP load derived from rural tributaries (with similar soil types and land uses) that were monitored (Bellsgrrove, Carrick, Crover, Halfcarton and Schoolhouse).

(iii) Annual TP_{load} (t yr^{-1}) from direct runoff to the lake was estimated from a TP export coefficient derived from a combination of data measured at the seven gauged catchments.

The TP_{out} parameter describes the TP load leaving the lake at the Inny outlet and was calculated using the TP flow-weighted method described in equation 5.2. The result of TP_{end} minus TP_{start} , otherwise known as the change in storage of TP_{lake} (t yr^{-1}), was calculated from the difference between the lake TP concentrations (TP_{lake}) from year to the year (e.g. the difference from October 1997 and October 1996). To convert to metric tonnes of TP in the entire lake, the calculated difference in TP ($\mu\text{g l}^{-1}$) was multiplied by the lake volume (m^3) and divided by a conversion factor.

The TP sedimentation coefficient, σ (yr^{-1}), was calculated as the net uptake of TP (TP_{net}) divided by the average annual lake TP mass (t yr^{-1}) (i.e. the fraction of TP in the water column that enters the lake bed sediment per year). The retention coefficient of TP (R_{cal}) was calculated as the net uptake of TP (TP_{net}) divided by TP load (TP_{load}) (i.e. the fraction of TP load that gets retained in the sediment per year).

5.2.3 Calibration of TP loading - response models

The five TP loading-response models listed in Table 2.2 were calibrated (annual models from 1990 to 2008) using the study dataset to predict annual average TP ($\mu\text{g l}^{-1}$) concentrations in the lake. Calibration required the calculation of model parameters and TP retention coefficients listed in Table 2.1.

Model parameters were classified into three generic groups: morphological parameters, TP derivatives and hydrological parameters:

- Information on the hydromorphology of Lough Sheelin was known from previous studies: A_L (lake surface area, 18.08 km^2), V_L (lake volume, $81.5 \times 10^6 \text{ m}^3$) and z (mean lake depth, 4.5 m).
- Hydrological characteristics were estimated using lake morphological data and cumulative 12-month hydrological load ($Q \text{ m}^3 \text{ yr}^{-1}$), which was calculated using gauged flow data and a conversion factor for TP load at ungauged sites. Annual lake flushing rates ($\rho \text{ yr}^{-1}$), a metric of the frequency of lake water renewal, were determined by dividing the cumulative hydrological load ($Q \text{ m}^3 \text{ yr}^{-1}$) by lake volume (V_L). Lake water residence time (τ_w), the average time that water spends in a lake, was calculated as the inverse of the flushing rate, ρ . Lake areal hydraulic loading rate ($q_s \text{ m yr}^{-1}$), the inflow water volume applied over the surface area of Lough Sheelin, was the equivalent of multiplying lake depth (z) by lake flushing rate (ρ).
- Derivatives of TP were calculated from manipulations of the original measured data. The annual flow-weighted TP concentration, $TP_{in} (\mu\text{g l}^{-1})$ entering the lake from the catchment was calculated as the cumulative total $TP_{load} (\text{t yr}^{-1})$ (calculated from equation 5.2) divided by the cumulative annual hydrological flow, $Q (\text{m}^3 \text{ yr}^{-1})$. Lake TP concentration, TP_{lake} , was calculated from an annual average of measured TP concentrations in the lake. The final TP parameter, L (areal TP loading rate $\text{g m}^2 \text{ yr}^{-1}$), was calculated using the formula:

$$L = (Q * TP_{in}) / A_L \quad [5.3]$$

The R coefficients, derived from the retention models in Table 2.3, were estimated using various combinations of the lake areal hydraulic loading rate ($q_s \text{ m yr}^{-1}$) and TP settling

velocities for the lake. The estimated R coefficients were applied to the theoretical equation of Dillon and Rigler (1974) to give predictions of TP_{lake} .

The accuracy of predictions from models was evaluated by RMSE analysis, comparing predicted values with measured values, described in equation 5.4.

$$RMSE = \sqrt{\sum_{i=1}^n (TP_{lake} - TP_{pred})^2 / n} \quad [5.4]$$

where:

TP_{lake} is the measured TP concentration in Lough Sheelin averaged over a year

TP_{pred} is the predicted lake TP concentration for the same year

n is the number of years of data in the study

A second method to test the more accurate models as indicated by RMSE was applied: estimation of an R^2 value ($p < 0.05$) for linear regression plots between predicted and measured TP_{lake} concentrations.

A priori, the TP loading-response model that showed the highest prediction accuracy in the years prior to zebra mussel invasion (1990-1999) was used to represent the long-term TP loading-response relationship in the lake system before establishment of the zebra mussels, and thus for predicting TP_{lake} concentrations for the period 2004-2008 in the absence of zebra mussels. The assumption that zebra mussel activity would affect the relationship between TP_{in} and TP_{lake} concentration by the process of altering TP sedimentation action could then be tested based on whether predicted concentrations were significantly different than the measured TP concentrations. If the measured TP_{lake} was typically greater than predicted concentrations then enhanced internal TP loading had occurred, and the zebra mussels had led to increased TP concentrations in the lake. Conversely, if the opposite occurred and TP concentrations decreased, then greater quantities of TP were likely to have been retained in the sediments as an indirect result of zebra mussel activity.

5.2.4 Examination of chlorophyll a - TP relationships

The strengths of linear relationships between chlorophyll a and TP concentrations in Lough Sheelin, based on averaged summer (June – October) and annual monthly data, were determined for pre (1983-1999) and post (2004-2008) establishment of zebra mussels. The general regression equation used was:

$$\log \text{Chl } a = a + b * \log \text{TP} \quad [5.5]$$

where:

$\log \text{Chl } a$ is the log of chlorophyll a

$\log \text{TP}$ is the log of TP

a and b are estimated model coefficients for the regression intercept and slope, respectively.

A test of parallelism was applied to the regression models to assess significant ($p < 0.05$) changes in slope and intercept between the two time periods (Kleinbaum *et al.*, 1998; Qualls *et al.*, 2007). The statistical analysis was implemented in PRISM 5 Graphpad software (Motulsky, 2007).

5.3 Results

5.3.1 Trends followed by TP, chlorophyll a and secchi depth from 1990 to 2008

Annual flow-weighted TP concentrations (TP_{in}) entering Lough Sheelin and TP concentrations in the lake (TP_{lake}) for 1990-2008 are shown in Figure 5.1. The effects of restrictions on the spreading of livestock manure during winter months, introduced in the early 1990s, are evident. The relationship between TP_{in} and TP_{lake} shows a marked change following the 2000-2001 gap in the data, after which there was much greater variability in the response of TP lake concentrations to TP loading compared with previously. Results from the application of ANOVA shows a significant decrease ($p < 0.05$) in TP_{in} from 1990-1997 (average TP $95 \mu\text{g l}^{-1}$) to 1998-2008 (average TP $66 \mu\text{g l}^{-1}$), i.e. following implementation of P Regs in the catchment. Despite this fall in TP load entering the lake, average TP_{lake} increased between the periods 1990-1997 ($25 \mu\text{g l}^{-1}$) and 1998-2008 ($31 \mu\text{g l}^{-1}$), although the increase ($6 \mu\text{g l}^{-1}$) was not statistically significant ($p > 0.05$).

Annual average of TP_{lake} ($\mu\text{g l}^{-1}$), chlorophyll a ($\mu\text{g l}^{-1}$) and secchi depth (m) for 1990-2008 are summarized in Figure 5.2 and Table 5.1. The relationships between the three parameters

followed a similar trend from 1990 to 1999. However, the chlorophyll a - TP ratio altered post-2004: a decline in chlorophyll a concentrations did not correspond with similar declines in TP. As such, the situation post-2004 was different from 1991-1993. During the latter period low levels of TP were associated with low concentrations of chlorophyll a. According to the available data, the lake was eutrophic until 2005 and then varied between eutrophic and mesotrophic states until 2008. Mesotrophic characterisation was based upon a combination of low chlorophyll a and high secchi depth levels, and contrasted with characterisation based on TP concentrations alone, which remained consistently in the eutrophic range.

5.3.2 Outputs of the TP budget

The TP budget for Lough Sheelin (1990-2008) comprises inflow TP (TP_{load}), change of TP storage in the water column, outflow TP (TP_{out}) and net TP retained/released by sediment dynamics (TP_{net}) (Table 5.2). Annual net TP sedimentation actions were positive (i.e. the sediments functioned as a net sink for TP) in all years except 2004, when net TP release to the water column occurred (1.76 t yr^{-1}). This negative value was removed from the analysis because it was considered an outlier. The greatest retention of TP (26 t yr^{-1}) by sedimentation took place in 1994 and the lowest (4.77 t yr^{-1}) occurred in 1997. Values for σ and R_{cal} , calculated by dividing TP_{net} by the average annual TP mass of the lake and TP_{load} , respectively, are also listed in Table 5.2. Variations in L , areal TP sedimentation, and R_{cal} are shown in Figure 5.3. Total P loading showed substantial annual fluctuations owing to variations in rainfall. Although interannual variability is evident, overall the rate of TP sedimentation appears to have declined since 1990 (Figure 5.4).

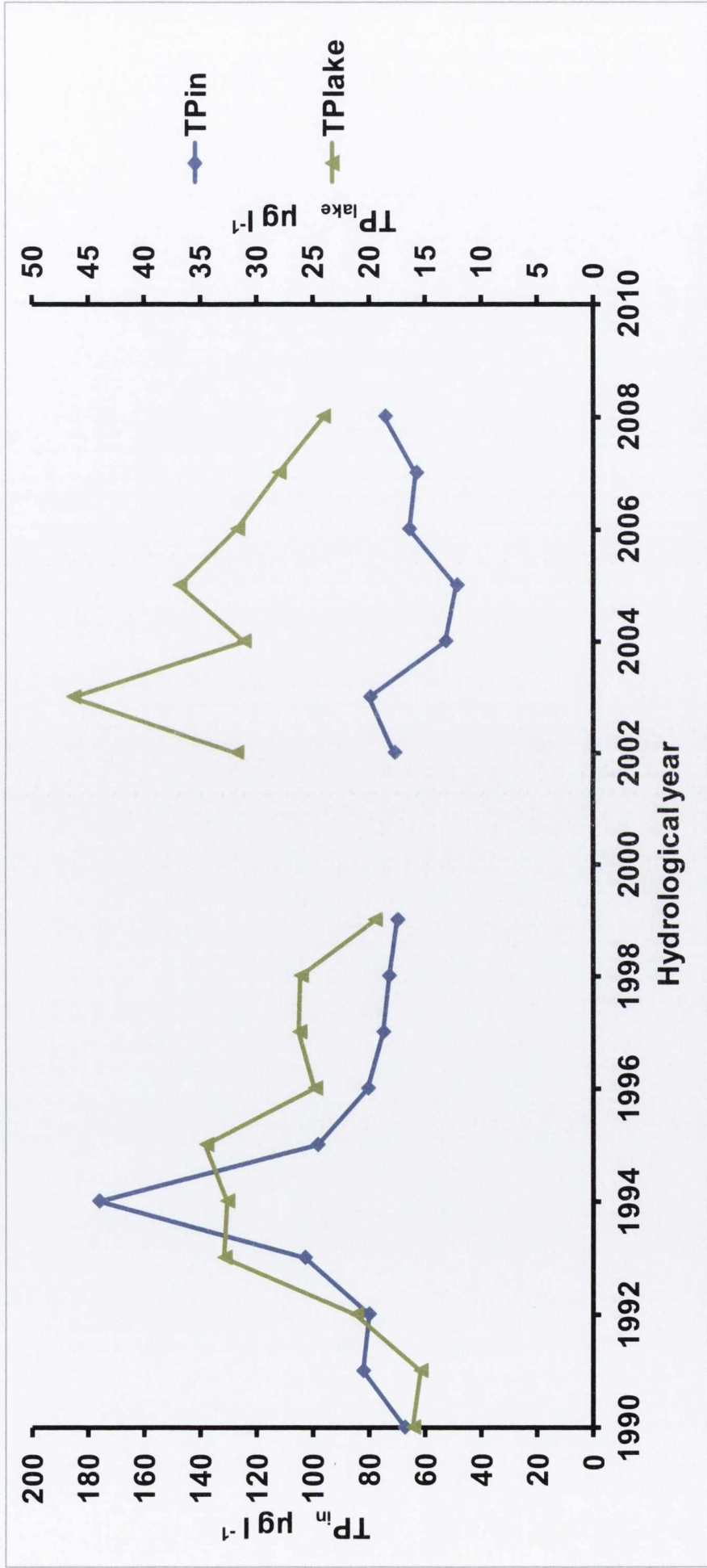


Figure 5.1. Timeseries plot showing annual flow-weighted TP loading concentration to Lough Sheelin (TP_m) and average annual TP concentration of the lake (TP_{lake}) for the hydrological years 1990 -2008

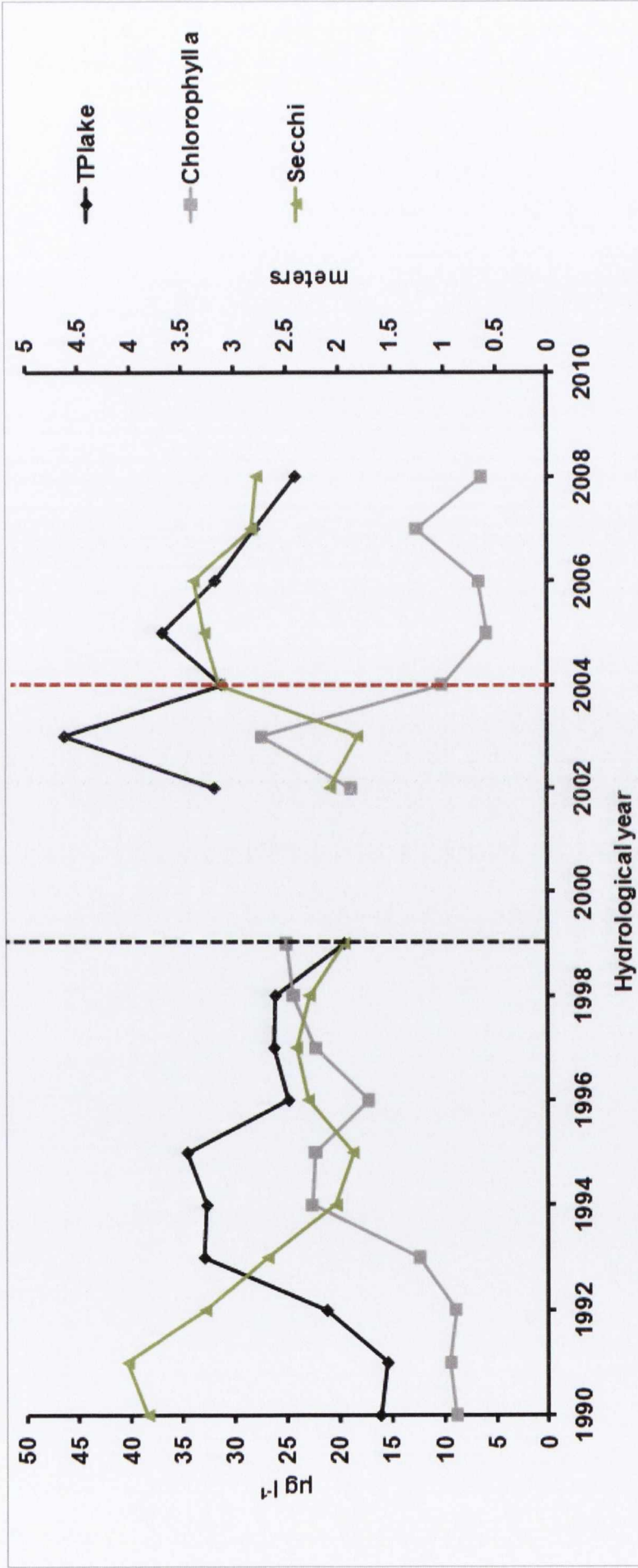


Figure 5.2. Timeseries plot of annual average TP concentration (TP_{lake}), chlorophyll a concentration and secchi depth in Lough Sheelin for the hydrological years 1990-2008. The black vertical line at 1999 indicates the onset of the P Regs POMs. The red vertical line at 2004 signifies the establishment of zebra mussel in the lake

Table 5.1. Trophic status for Lough Sheelin during implementation of the P Regs (1998-2008). The standards for TP, chlorophyll a and sechii depth in the bottom table are based on EPA classification for lakes which, in turn, is derived from a scheme proposed by the OECD (OECD, 1982)

Hydrological Year	Average TP (µg l ⁻¹)	Average chlorophyll a (µg l ⁻¹)	Secchi depth (m)	Trophic status
1998	26.06	24.38	2.28	Eutrophic
1999	19.47	25.02	1.94	Eutrophic
2000	No Data	No Data	No Data	No Data
2001	No Data	No Data	No Data	No Data
2002	31.79	18.82	2.08	Eutrophic
2003	46.31	27.36	1.82	Eutrophic
2004	31.13	10.11	3.14	Eutrophic
2005	36.83	5.82	3.28	Mesotrophic
2006	31.71	6.62	3.38	Mesotrophic
2007	28.00	12.53	2.83	Eutrophic
2008	24.06	6.32	2.78	Mesotrophic

Parameter	Mesotrophic	Eutrophic
Average TP (µg l ⁻¹)	>10 <20	>20 <50
Average chlorophyll (µg l ⁻¹)	2.5 - 8	8 - 25
Average secchi depth (transparency m)	3 - 6	3 - 1.5

Table 5.2. Parameters for the TP budget and TP sedimentation derivatives for Lough Sheelin during the hydrological years 1990-2008

Hydrological Year	TP _{in} t yr ⁻¹	TP _{out} t yr ⁻¹	TP _{lake} change in storage t yr ⁻¹	TP _{net} t yr ⁻¹	Sediment action	Sedimentation coefficient σ yr ⁻¹	Average TP mass t yr ⁻¹	Areal TP sedimentation m ⁻² yr ⁻¹	R _{cal} (dimensionless)
1990	10.35	2.41	-0.33	8.26	Net TP uptake	6.31	1.31	0.35	0.80
1991	12.46	3.83	-0.20	8.84	Net TP uptake	7.05	1.25	0.39	0.71
1992	9.91	2.33	-0.12	7.70	Net TP uptake	4.47	1.72	0.25	0.78
1993	13.77	4.11	1.24	8.42	Net TP uptake	3.15	2.68	0.17	0.61
1994	32.73	6.08	0.64	26.01	Net TP uptake	9.80	2.66	0.54	0.79
1995	13.71	5.03	0.21	8.47	Net TP uptake	3.02	2.81	0.17	0.62
1996	11.43	3.75	-1.44	9.12	Net TP uptake	4.52	2.02	0.25	0.80
1997	10.04	3.27	1.99	4.77	Net TP uptake	2.24	2.13	0.12	0.48
1998	11.02	3.61	-2.85	10.27	Net TP uptake	4.84	2.12	0.27	0.93
1999	13.39	3.54	0.56	9.29	Net TP uptake	5.87	1.58	0.32	0.69
2000	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
2001	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
2002	11.43	3.05	2.58	5.80	Net TP uptake	2.24	2.59	0.12	0.51
2003	12.00	4.29	-2.16	9.86	Net TP uptake	2.62	3.77	0.14	0.82
2004	5.04	3.25	3.54	-1.76	Net TP release	-0.69	2.53	-0.04	0.35
2005	6.50	2.69	-3.46	7.27	Net TP uptake	2.43	3.00	0.13	1.12
2006	8.79	2.99	0.41	5.39	Net TP uptake	2.09	2.58	0.12	0.61
2007	13.54	4.86	2.20	6.49	Net TP uptake	2.85	2.28	0.16	0.48
2008	14.96	3.47	-2.42	13.91	Net TP uptake	7.10	1.96	0.39	0.93

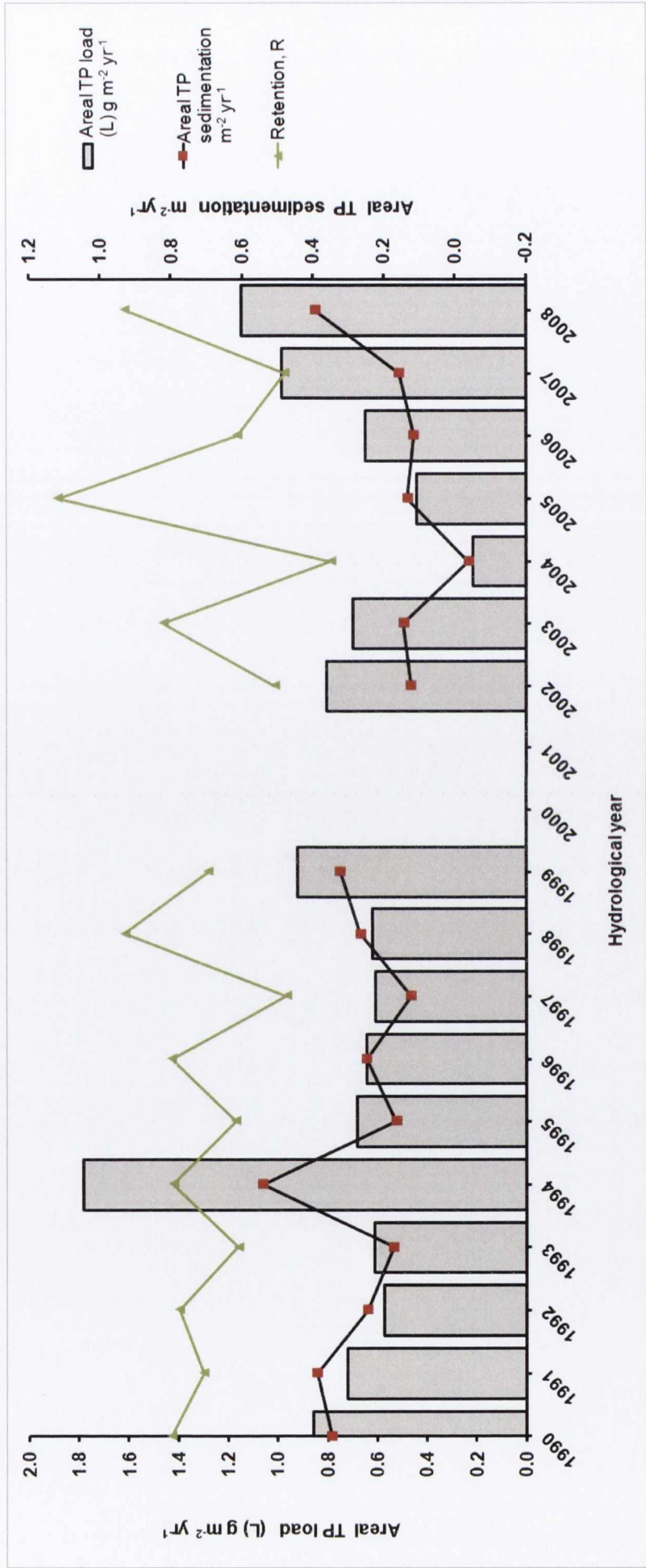


Figure 5.3a. Timeseries plot of annual areal TP load $\text{g m}^{-2} \text{yr}^{-1}$ (L, left vertical axis), annual areal TP sedimentation $\text{m}^2 \text{yr}^{-1}$, (right, vertical axis) and the calculated TP retention coefficient (R_{cal} , right vertical axis) for Lough Sheelin for the hydrological years 1990-2008. The annual areal TP load was calculated as the flow-weighted concentration of TP entering the lake divided by the surface area of the lake. Net TP sedimentation and estimated R values were calculated directly from the TP mass balance budget (Table 5.2)

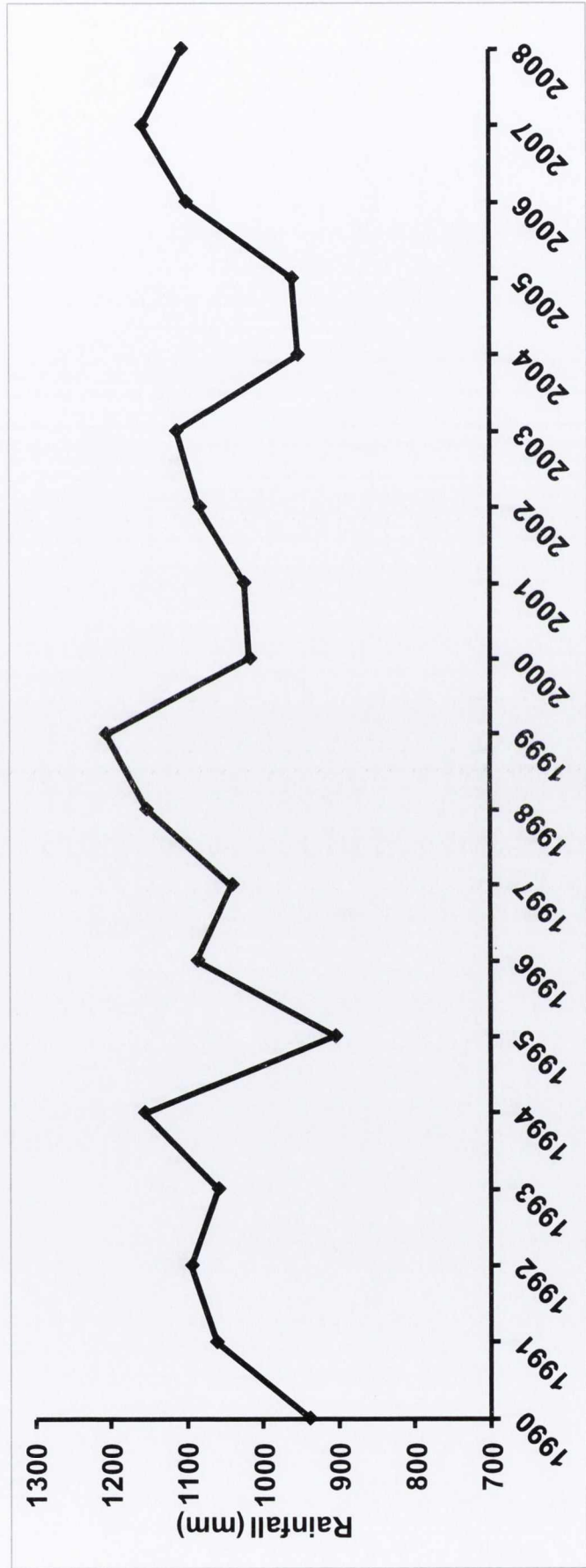


Figure 5.3b. Timeseries plot of annual rainfall (mm) in the Lough Sheelin catchment for the hydrological years 1990-2008

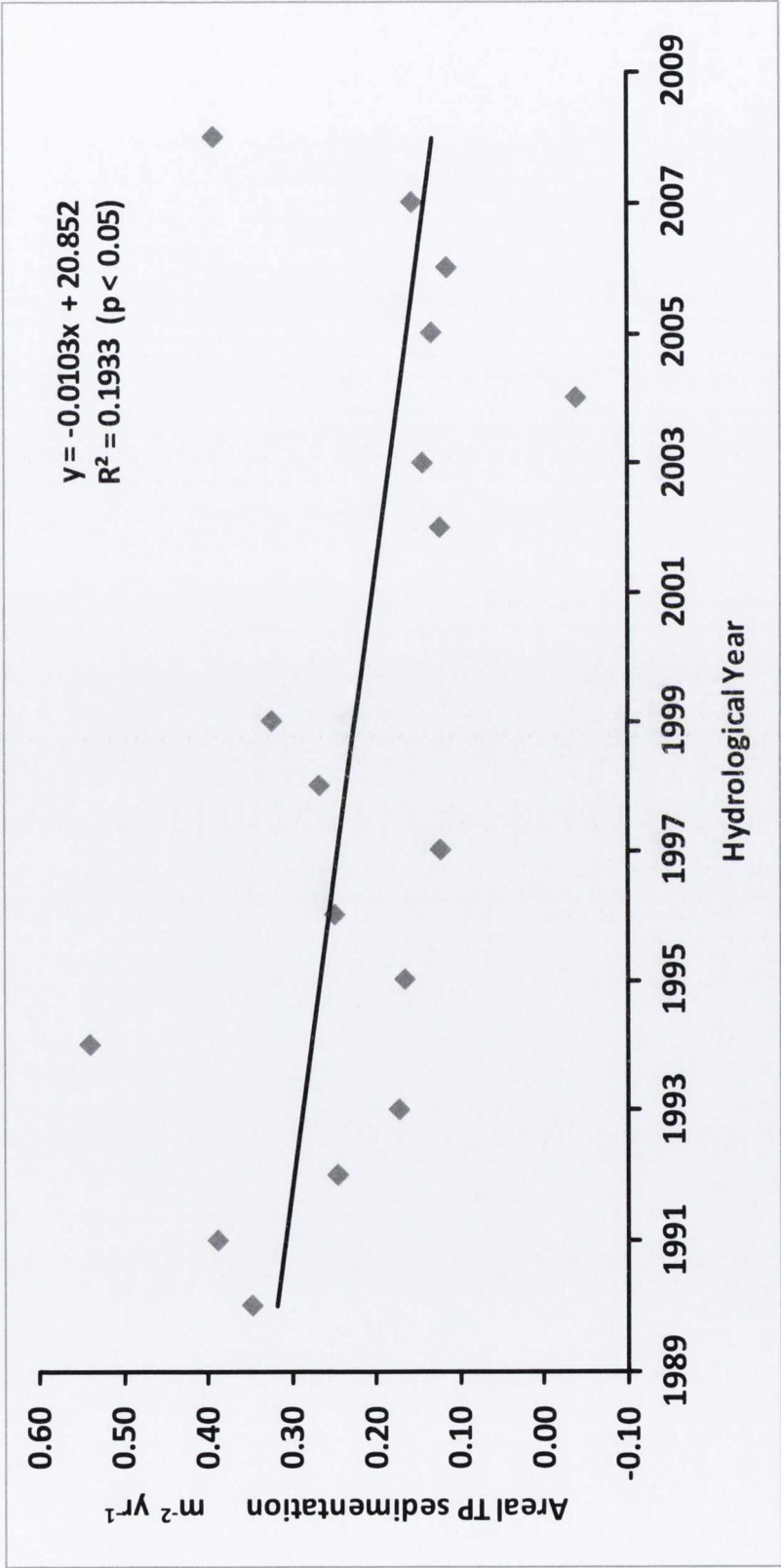


Figure 5.4. Timeseries plot of areal TP sedimentation (m⁻² yr⁻¹) for Lough Sheelin covering the hydrological years 1990 to 2008

5.3.3 Results of TP loading - response models

Initial model parameters used to calibrate the TP loading-response models for 1990-2008 are provided in Table 5.3. The predicted R values, derived according to the TP retention models specified in Table 2.3, are shown in Table 5.4, while Figures 5.5 and 5.6 illustrate predictions of TP_{lake} based on the TP loading-response models, together with corresponding values of measured TP_{lake} .

Figure 5.5 compares measured TP_{lake} concentrations for 1990-2008 with the TP_{lake} values predicted from the three TP loading models that use τ_w as a scaling factor for σ (Foy, 1992; OECD 1982 - general and shallow lakes models) and the Prairie (1989) model that uses a combination of estimations of σ and R. The RMSE values of predictions for the three time periods (overall - 1990-2008; pre zebra mussel establishment - 1990-1999 and; post zebra mussel establishment - 2004-2008) are shown in Table 5.5. Output from the OECD (1982) shallow model had the lowest overall RMSE ($24.5 \mu g l^{-1}$), i.e. the smallest deviation from observed concentrations of TP in the lake, therefore being the next efficient model to use σ . The model proposed by Foy (1992) produced very similar predicted values to the OECD (1982) shallow model and notably, predictions from the OECD (1982) general model and Prairie (1989) deviated most from measured values, consistently over-predicting.

Figure 5.6 compares measured TP_{lake} with levels of TP_{lake} predicted from models that use the retention coefficient, R, to describe the sedimentation of TP for the period 1990-2008. Corresponding RMSE values are listed in Table 5.5. The overall trends in the predicted TP_{lake} values were generally similar. However, the Larcen and Mercier (1976) model constantly predicted higher concentrations than the other models. The model derived by Ostrofsky (1978b) showed the lower overall RMSE ($11.9 \mu g l^{-1}$), whereas predictions by the Larcen and Mercier (1976) model had the highest overall RMSE ($25.2 \mu g l^{-1}$).

Overall, the models from the two different categories that best described the lake system (1990 - 2008) comprised: Ostrofsky (1978b) and OECD (1982) shallow. The second test of prediction accuracy, linear regression plots and R^2 values ($p < 0.05$) of predicted versus measured TP_{lake} concentrations for the overall period (1990-2008), are shown in Figure 5.7. All three regression lines for the long-term (1990-2008) showed relatively low R^2 values, but the separation of data for pre and post-zebra mussel establishment gave higher R^2 values.

The most accurate models of TP loading for 1990-1999 were used as a baseline against which to compare changes in TP_{lake} following establishment of zebra mussels in 2004. The Ostrofsky

(1978b) and OECD (1982) shallow models were selected as these had the lowest prediction errors (RMSE 10.70 and 36.40 $\mu\text{g l}^{-1}$, respectively). However, the relationships between measured and predicted TP_{lake} concentrations of these three models show a clear difference between times comprising pre and post-zebra mussel establishment (Figures 5.5 and 5.6). The Ostrofsky (1978b) model under-predicted TP_{lake} for the period 2004-2008 when compared with measured TP_{lake} for the period 1990-1999. Linear regression plots and R^2 values of predicted versus measured TP_{lake} for 1990-2008, 1990-1999 and 2004-2008 are shown in Figure 5.7. The R^2 values are higher for the two separated time series plots than those of the full time series. Furthermore, a change in direction of trends in both predicted and measured TP_{lake} values is evident, with levels of both declining post 2004.

5.3.4 Outputs of chlorophyll a and TP relationships

Linear regression relationships for log chlorophyll a - log TP for the time prior to and post establishment of zebra mussels are shown in Figure 5.8. Table 5.6 summarises the results of the test of parallelism applied to examine a change in regression relationships. Relationships between annual and summer log chlorophyll a - log TP relationships were weak but significant ($p < 0.0001$) for 1990 to 1999. However, for the period 2004 – 2008, post establishment of zebra mussels, the relationships changed; both the R^2 values ($p < 0.0001$) and the slopes decreased, while the intercept values increased. The changes in slopes and intercepts were statistically significant ($p < 0.05$). However, the slopes for both the seasonal and annual regressions were no longer significantly different from zero in 2004-2008.

Table 5.3. Parameters for the TP loading-response models based on Lough Sheelin data for the hydrological years 1990-2008

Hydrological Year	ρ , lake flushing		L , TP areal loading		TP_{in}		τ_w , water residence time		TP_{lake}	
	yr		$g\ m^{-2}\ yr^{-1}$		$\mu g\ l^{-1}$		yr^{-1}		$\mu g\ l^{-1}$	
1990	1.89		0.57		67.34		0.53		16.09	
1991	1.86		0.69		82.17		0.54		15.40	
1992	1.52		0.55		80.12		0.66		21.18	
1993	1.64		0.76		102.87		0.61		32.89	
1994	2.28		1.81		176.15		0.44		32.63	
1995	1.71		0.76		98.34		0.58		34.50	
1996	1.75		0.63		80.39		0.57		24.80	
1997	1.65		0.56		74.89		0.61		26.18	
1998	1.86		0.61		72.84		0.54		26.06	
1999	2.36		0.74		69.78		0.42		19.47	
2000	No Data		No Data		No Data		No Data		No Data	
2001	No Data		No Data		No Data		No Data		No Data	
2002	1.99		0.63		70.77		0.50		31.79	
2003	1.85		0.66		79.60		0.54		46.31	
2004	1.18		0.28		52.58		0.85		31.13	
2005	1.65		0.36		48.53		0.61		36.83	
2006	1.65		0.49		65.58		0.61		31.71	
2007	2.64		0.75		62.97		0.38		28.00	
2008	2.48		0.83		74.10		0.40		24.06	

Table 5.4. Predicted TP retention (R) coefficients based on data from Lough Sheelin for the hydrological years 1990-2008

Hydrological Year	Nürnberg 1984	Dillon and Kirchner 1975b	Chapra 1975	Ostrofsky 1978a	Vollenweider 1975	Kirchner and Dillon 1975	Ostrofsky 1978b	Larzen and Mercier 1976
1990	0.57	0.61	0.65	0.62	0.54	0.57	0.66	0.42
1991	0.57	0.61	0.66	0.63	0.54	0.57	0.67	0.42
1992	0.60	0.66	0.70	0.65	0.59	0.60	0.68	0.45
1993	0.59	0.64	0.68	0.64	0.57	0.59	0.68	0.44
1994	0.53	0.56	0.61	0.60	0.49	0.54	0.65	0.40
1995	0.58	0.63	0.67	0.64	0.56	0.58	0.67	0.43
1996	0.58	0.63	0.67	0.63	0.56	0.58	0.67	0.43
1997	0.59	0.64	0.68	0.64	0.57	0.59	0.68	0.44
1998	0.57	0.61	0.66	0.63	0.54	0.57	0.67	0.42
1999	0.52	0.55	0.60	0.59	0.49	0.54	0.64	0.39
2000	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
2001	No Data	No Data	No Data	No Data	No Data	No Data	No Data	No Data
2002	0.56	0.60	0.64	0.62	0.53	0.56	0.66	0.42
2003	0.57	0.61	0.66	0.63	0.55	0.57	0.67	0.42
2004	0.64	0.71	0.75	0.68	0.65	0.64	0.70	0.48
2005	0.59	0.64	0.68	0.64	0.57	0.59	0.68	0.44
2006	0.59	0.64	0.68	0.64	0.57	0.59	0.68	0.44
2007	0.50	0.53	0.57	0.57	0.46	0.53	0.63	0.38
2008	0.51	0.54	0.59	0.58	0.47	0.53	0.64	0.39

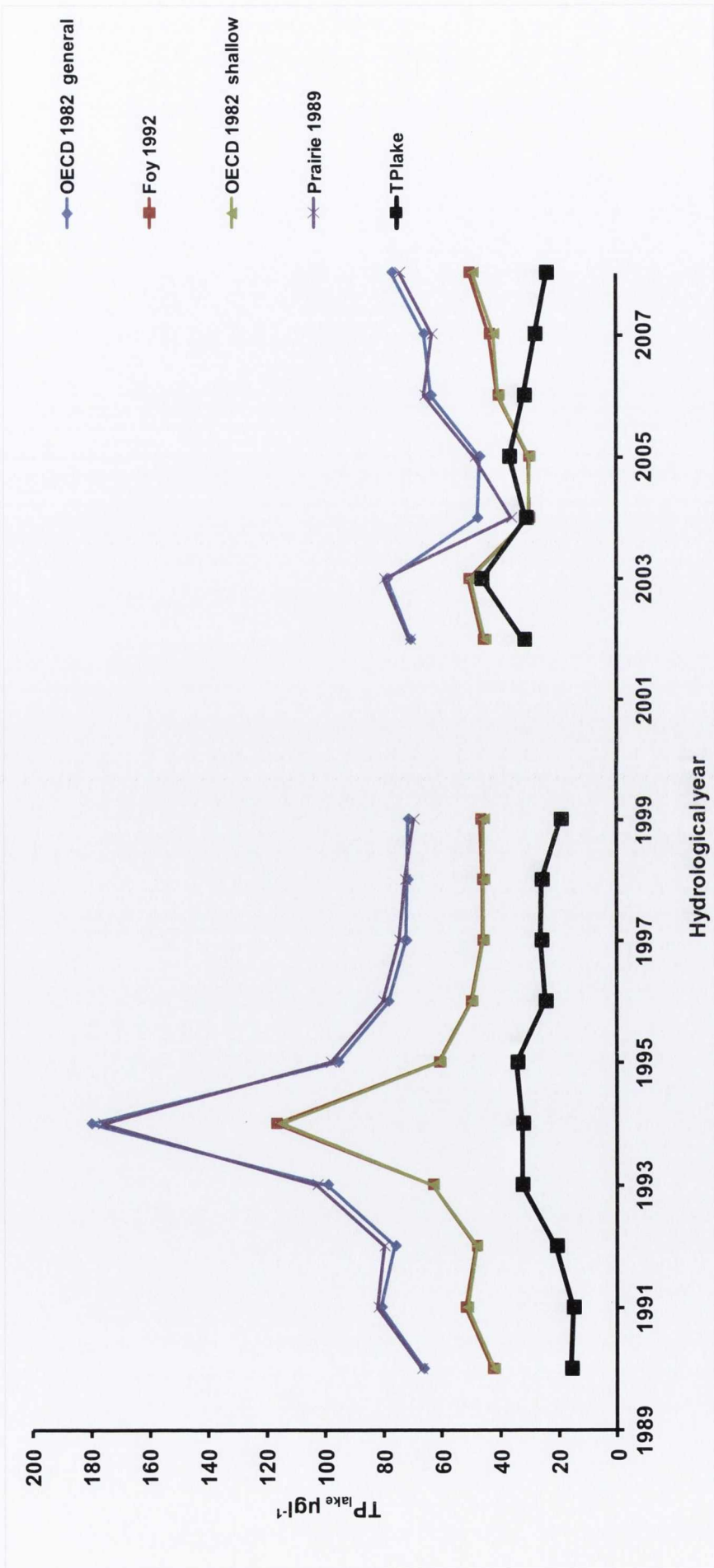


Figure 5.5. Timeseries plot showing measured TP_{lake} (red line) and predicted TP_{lake} concentrations (µg l⁻¹) in Lough Sheelin for (i) the three TP loading models that use τ_w as a scaling factor for σ (OECD general 1982, OECD shallow 1982 and Foy 1992) and (ii) the Prairie 1989 model that uses a combination of estimates of σ and R. The RMSE of predictions for 1990–2008, 1990–1999 and 2004–2008 are shown in Table 5.5.

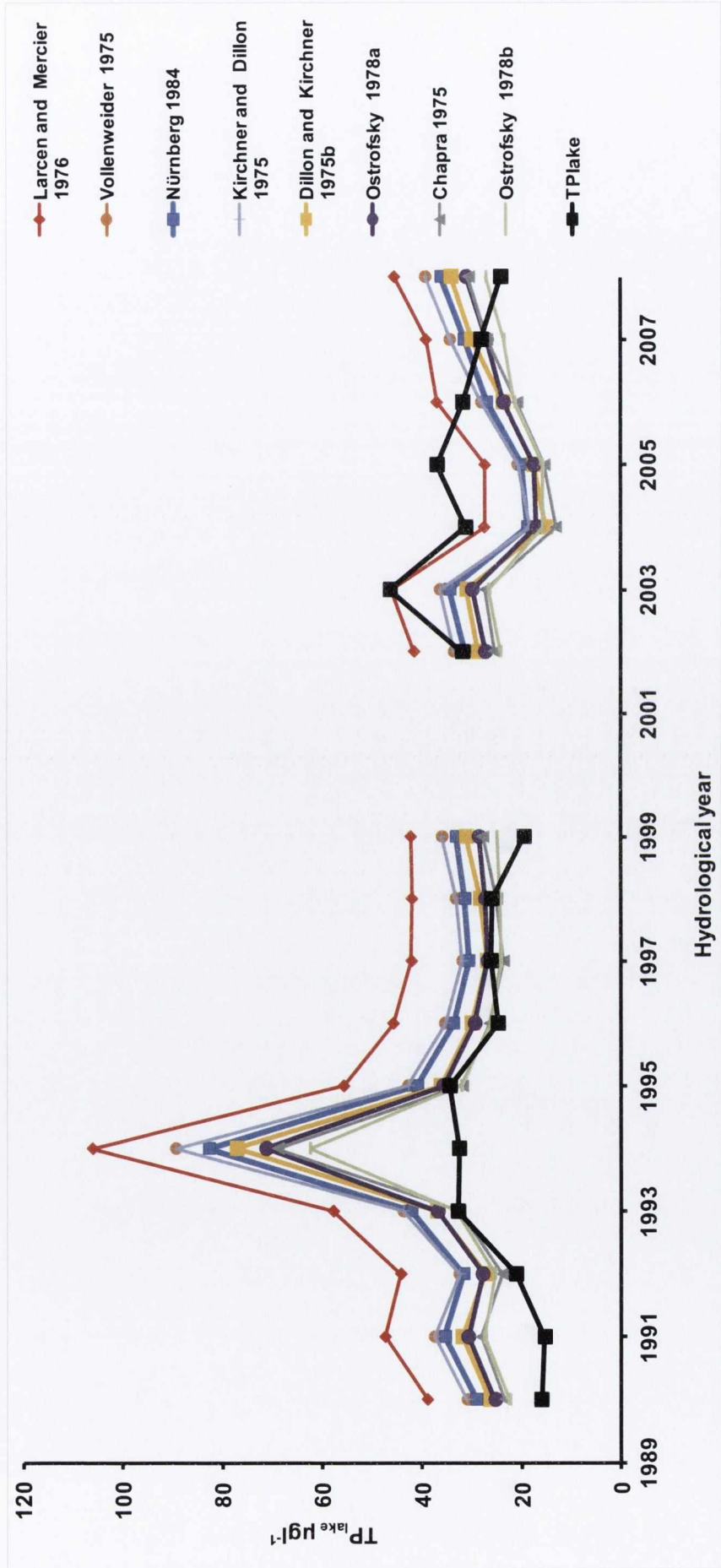


Figure 5.6. Timeseries plot showing measured TP_{lake} (red line) and predicted TP_{lake} concentrations ($\mu\text{g l}^{-1}$) in Lough Sheelin for the Dillon and Rigler (1974) TP loading-response model. The model used 8 different estimations of R to describe the sedimentation of TP (Table 2.2). The associated RMSE of prediction for 1990-2008, 1990-1999 and 2004-2008 are shown in Table 5.5.

Table 5.5. RMSE values for TP_{lake} predictions from TP loading-response models for the hydrological years 1990-2008

Model	RMSE $\mu\text{g l}^{-1}$		
	1990-2008	1990 – 1999	2004-2008
OECD 1982 shallow	24.50	26.60	13.8
OECD 1982 general	49.10	52.40	33.4
Foy 1992	25.1	27.00	14.6
Larcen and Mercier 1976	25.20	31.60	11.9
Chapra 1975	13.20	12.80	13.8
Dillon and Kirchner 1975b	14.60	16.10	12.7
Kirchner and Dillon 1975	15.50	18.40	10.7
Nürnberg 1984	16.10	19.10	11.1
Ostrofsky 1978a	13.20	14.10	11.8
Ostrofsky 1978b	11.90	10.70	12.8
Vollenweider 1975	18.00	21.70	11.9
Prairie 1989	49.10	52.80	31.70

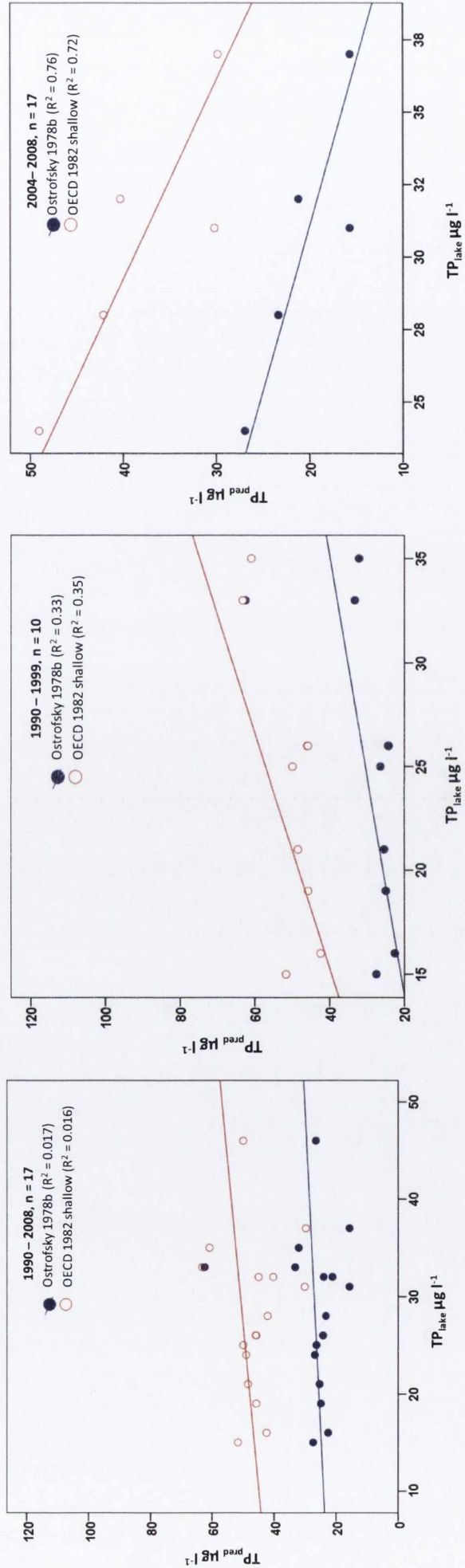


Figure 5.7. Linear regression relationships between measured TP_{lake} and predicted TP_{pred} in Lough Sheelin. Predictions are estimated from the Ostrofsky (1978b) and OECD (1982) shallow models for three time periods: (a) 1990–2008 data; and, (b) 1990–1999 data; and, (c) 2004–2008 data. R^2 values correspond to $p < 0.05$.

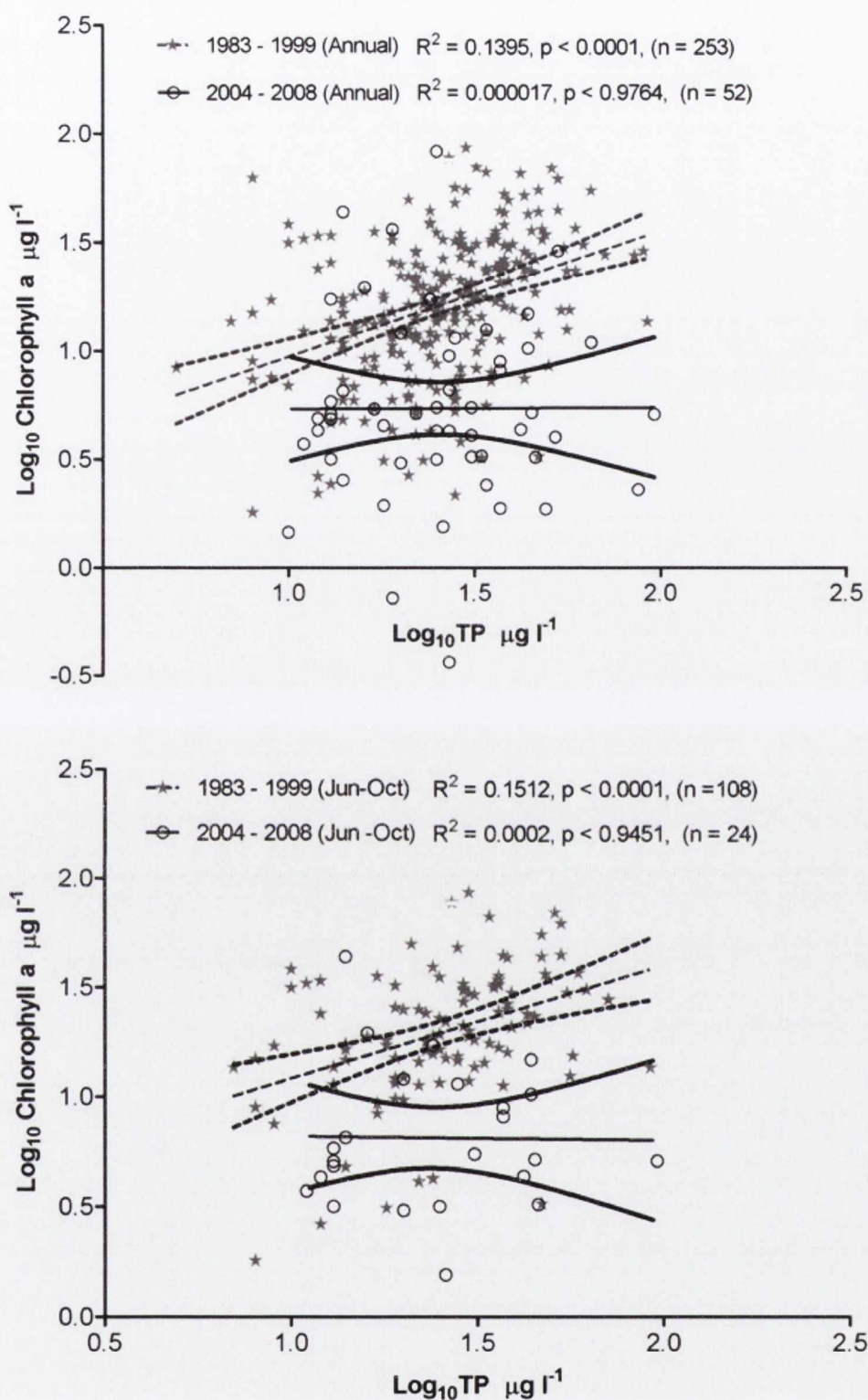


Figure 5.8. Relationship between $\log_{10}$ chlorophyll a and $\log_{10}$ TP concentrations in Lough Sheelin for the hydrological years 1983 to 2008. Data are divided into subsections: (a) June - October data and (b) annual data. The red regression line shows the long-term relationship between $\log_{10}$ chlorophyll a- $\log_{10}$ TP before the invasion of zebra mussels (1983-1999). The blue line shows the relationship between the two parameters after the establishment of zebra mussels (2004-2008). Data were $\log_{10}$ transformed to meet the assumption of statistical normality for regression analysis.

Table 5.6. Test of parallelism results for log₁₀ chlorophyll a and log₁₀ TP regression relationships for the period pre (1990-1999) and post (2004-2008) zebra mussel establishment in Lough Sheelin.

Mussel presence	Data type	df	Intercept (95 % CI)	Slope ± 95% CI	F value (p-value)	R ²	p-values of parallelism test
Pre - zebra mussels	Jun - Oct	106	0.5665 ± 0.1693	0.5164 ± 0.1188	18.88 (< 0.0001)	0.1512	0.04979
Post- zebra mussels	Jun - Oct	22	0.8387 ± 0.3832	-0.01903 ± 0.2731	0.004857 (0.9451)	0.0002207	
Pre - zebra mussels	Annual	251	0.3893 ± 0.1296	0.5815 ± 0.09116	40.69 (< 0.0001)	0.1395	0.00922
Post- zebra mussels	Annual	50	0.7239 ± 0.3658	0.007641 ± 0.2568	0.0008851 (0.9764)	0.0000177	

5.4 Discussion

The H_0 stated at the onset of this study can be rejected based on the results of this research; conditions within the environmental setting of Lough Sheelin significantly influenced the effectiveness of schemes aimed at mitigating concentrations of P in the lake. Available data suggest that external loadings of TP to Lough Sheelin fell following a peak in the early 1990s and remained relatively low to 2008, a period that includes implementation of two sets of measures aimed at mitigating inputs of P to waterbodies in the catchment. However, despite a declining trend in the external loadings of TP, TP concentrations in the lake remained at early 1990s and higher levels though to 2008. Zebra mussels have been shown to have contrasting effects on TP levels in lakes they invade, leading to reduced concentrations in some and increases in others. In the case of Lough Sheelin, one possibility is that the action of zebra mussels has led to enhanced internal loading of TP, thereby negating any ecological effects of reduced external loadings of TP. Therefore, the sediment bed of Lough Sheelin, thought to have been a sink for almost 75% of TP entering the lake since 1990, had the potential to provide enough TP to sustain the concentration of TP in the water column at a higher rate than assumed, based on the loads entering the lake. The following sections will discuss these results in detail, with reference to the published literature.

5.4.1 Response of Lough Sheelin to P mitigation efforts in the catchment

Data for 1990 to 2008 suggest that external loadings of TP to Lough Sheelin significantly declined ($p < 0.05$) following a peak in the early 1990s and remained relatively low until 2008.

Some inter-annual variability is apparent, however. Variability in annual P loads to Lough Sheelin has been attributed to unusually high levels of rainfall (EPA, 1994; Kerins *et al.*, 2007). Moreover, as is evident from the application of LAMs in this study, the presence of impermeable soils, WWTPs and septic tanks, and occasional associated leakages and spillages, in the catchment are all factors that are likely to have contributed to inter-annual variability in external loadings of TP.

Despite significant falling external TP loads overall, TP concentrations in the lake remained at early 1990s and higher levels though to 2008. However, the data also show that the response of TP in the water column to reduced TP loadings was not consistent throughout 1990-2008. For example, from 1990 to 1998, the response of TP concentrations in the lake to loadings of TP showed similarities to findings in published research: decreased loadings led to reduced lake concentrations (Jeppesen *et al.*, 2005; Köhler *et al.*, 2005; Søndergaard *et al.*, 2005). This loading-response relationship, apparently well established according to visual observation of the trend from 1990 to 1998, changed markedly after 2004. Despite an overall significant reduction of TP

loading in the period during which P Regs had been implemented, TP concentrations in the lake showed an overall increase, although this was not statistically significant ($p < 0.05$). The results of implementation of the first set of measures prior to the P Regs (restrictions on the spreading of manure during winter months) in 1990 to 1992 suggest that the change in the TP loading-response after 2004 was not a secondary impact of decreased TP load to the lake and must, therefore, be a result of some other factor, one which was not present in the early 1990s.

Observations of the chlorophyll a concentration and secchi depth responses to lake TP concentration reported in other research (e.g. Jeppesen *et al.*, 2005) is supported by data for Lough Sheelin from 1990 to 1999 in which TP is shown as a systematic driver that has positive impacts on concentrations of chlorophyll a, which in turn has a negative influence on the level of transparency depth (Wetzel, 2001). The TP remediation attempt in 1990-1992 possibly led to the expected decline in TP concentration, a fall in chlorophyll a concentrations and an increase in secchi depth. These short-term reductions in TP delivered to Lough Sheelin as a result of mitigation prior to the P Regs have been documented (EPA, 1994; Santillo and Pocock, 1995). The ratio of chlorophyll a to TP changed after 2004, however, with concentrations of chlorophyll a declining rapidly without a similar fall in TP concentrations. This would suggest that conditions within the lake underwent changes in the years following implementation of the P Regs, altering the response of lake TP concentrations to TP loadings and the influence lake TP concentrations exerted on chlorophyll a.

Loading-response models for TP in lakes have been used in many studies to predict the value of one of the model parameters from another or to examine the impact of proposed TP loading reductions (Søndergaard *et al.*, 1999; Convey *et al.*, 2005; Girvan and Foy, 2006). Here, the aim was to test a group of commonly used models with a view to identifying a particular model that would best describe the TP dynamics of Lough Sheelin, thus providing further information on sedimentation in the lake to support estimates from the TP budget. Zebra mussels can alter the concentration of TP in lakes (Qualls *et al.*, 2005), however, and because of this the models were re-tested on data from before and after the establishment of zebra mussels in Lough Sheelin. The Prairie (1989) model and Ostrofsky (1978b) model (calculating R to fit into the Dillon and Rigler (1974) theoretical model) both showed lowest RMSE values for the long-term data (Table 5.5), although substantial over prediction was observed in 1994. These models were also the most accurate for the pre-zebra mussel establishment years, 1990-1999. Notably, all models using L showed greater prediction accuracy than models using the mass of TP in the lake (i.e. OECD, 1982 and Foy, 1992). Furthermore, Ostrofsky (1978b) gave a better fit than other retention models

fitted to the loading-response model of Dillon and Rigler (1974) because it predicts the highest rate of TP retention for a given hydraulic load (average $R = 0.67$).

Adopting the Prairie (1989) and Ostrofsky (1978b) models as the most accurate, predictions of TP concentrations in the lake for 2004-2008 (post zebra mussel establishment) were examined for consistency. However, both models predicted markedly lower TP concentrations than measured concentrations (Figures 5.5 and 5.6). This observation may be due to increased release of TP from sediments to the water column, thereby leading to elevated TP concentrations in the lake that could not have been accounted for by the models (Søndergaard *et al.*, 2003). This explains the tendency of the models by Kirchner and Dillon (1975) and Nurnberg (1984) to most accurately predict TP_{lake} in the post-zebra mussel years; both of these models describe a lower coefficient for R than Ostrofsky (1978b). Models by OECD (1982) and Foy (1992) consistently overestimated TP_{lake} , possibly owing to the bias on hydraulic flushing and losses of TP mass in the lake through the outflow rather than sedimentation. The evidence provided here therefore implies that the recovery of Lough Sheelin was impacted by internal lake processes that were outside the control of measures implemented as part of the P Regs. The following section will discuss the constraints in the effectiveness of the P Regs measures as a result of TP sedimentation dynamics in the lake and the presence of zebra mussels.

5.4.2. Influence of environmental processes in Lough Sheelin on reduced loadings of P from the catchment

Lough Sheelin was characterised as mesotrophic in 2008 (Table 5.1). Owing to high transparency levels and low chlorophyll *a* concentrations, an improvement in trophic status of the lake was assumed, despite TP remaining in the eutrophic range. Zebra mussels were established in Lough Sheelin by 2004, around the same time large improvements occurred in secchi depth and chlorophyll *a* concentrations. Similar characterisation problems have been observed in Lough Key, a lake in the River Shannon catchment that was colonised by zebra mussels in 1998 (e.g. Lucy *et al.*, 2005). These initial data suggest that the effects of implementation of P Regs on TP concentration in Lough Sheelin were masked by the impacts of zebra mussel establishment in the lake.

The lake TP budget showed positive annual net TP sedimentation. Although sediment uptake and release of TP may have been occurring simultaneously in different parts of the lake, overall the lake sediment functioned as a net sink for TP in all years except 2004 (Table 5.2). The amount of TP incorporated into the lake bed sediment also appeared to be greater than TP lost to the

outflow, despite the estimated hydrological residence time being just six months. Compared with deep lakes, where a redox dependent accumulation of P occurs in the anoxic hypolimnion during stratification, shallow lakes are usually well mixed and oxidised throughout the water column, encouraging sediment retention (Søndergaard *et al.*, 2003). Lough Sheelin is a polymictic lake; the lake is too shallow for thermal stratification to develop (O'Sullivan and Reynolds, 2005). Therefore, TP retention by sediments was expected. Overall, an estimated 73% of TP load to the lake has been retained by sediments since 1990.

An overall decline in the rate of TP sedimentation in the lake bed sediment following establishment of zebra mussels is evident from the data in Figure 5.4. The reason for this may be increased release of TP into the water column or decreased incorporation of TP in the sediments. Results from Figure 5.1, showing increased TP concentrations in the lake despite reduced TP loading from the catchment, however, suggest that it is the former. Zebra mussel-induced alteration of P sedimentation rates in lakes has been reported (Bykova *et al.*, 2006; Turner, 2010). Adult zebra mussels recycle P in invaded lakes by filtering organisms and particles containing P from the water column. The P taken up is either assimilated into their biomass or excreted. This results in increased accumulation of organic matter, which increases microbial activity at the sediment-water interface, intensifies P remineralisation, decreases oxygen penetration into the sediments and releases Fe-P (Søndergaard *et al.*, 2003; Brönmark and Hansson, 2005; Bykova *et al.*, 2006). The overall increase in average TP and decrease in average chlorophyll *a* evident in the data for the period post-implementation of the P Regs may therefore be a result of zebra mussel establishment.

Overall interannual variations in net TP sedimentation in Lough Sheelin indicate changes in the net partitioning of external TP loads between the water column and the lake bed sediment. A constant sedimentation rate is essential for the TP concentration of a lake to change in proportion with TP loads to the lake (Coveney *et al.*, 2005). Areal TP loading also shows substantial interannual variation, partially owing to fluctuations in annual rainfall. The rates of TP sedimentation generally reflect these variations because TP load is a primary factor in the calculation of the sedimentation rate. Nevertheless, despite this dependency, TP sedimentation results are indicative of the general sediment TP dynamics in the lake. The long-term TP budget shows that the key factor driving TP dynamics in Lough Sheelin is TP loading from the catchment, most (73 %) of which is usually incorporated into the sediment, a process that has recently been altered by zebra mussel activity. Ultimately, the impacts of a reduction of TP loading from the Lough Sheelin catchment, following implementation of the P Regs, were not reflected in the

concentration of TP in the lake owing to increased internal TP loading from sediments induced by zebra mussel function.

Phytoplankton biomass, one of the four biological quality elements for lake ecological classification cited in the WFD, is typically quantified according to levels of chlorophyll a concentration (Kasprzak *et al.*, 2008). As concentrations of TP are an important determinant of aquatic productivity (Schindler *et al.*, 2008; Wang and Wang, 2009), understanding the relationship between chlorophyll a and TP concentrations is fundamental to establishing the range of concentrations of TP necessary to achieve or maintain good ecological status (Søndergaard *et al.*, 2011). Furthermore it is generally accepted that reduced concentrations of TP are expected to directly influence improved ecological status (OECD, 1982; Sas, 1989). A decoupling of the chlorophyll a -TP relationship following establishment of zebra mussels in Lough Sheelin is evident from the data presented here. Departures over time from a previously established relationship between these two parameters have been reported elsewhere (Kaiser *et al.*, 1994), including following invasion by zebra mussels (Mellina *et al.*, 1995; Nicholls *et al.*, 1999; Nicholls *et al.*, 2001; Hall *et al.*, 2003; Winter *et al.*, 2011). A reason for this disassociation may be attributed to mussel filtration reducing chlorophyll a concentrations but inadvertently increasing the release of TP from the lake bed sediment. This action would explain the data observed here; an overall decline in chlorophyll a concentration but an overall increase in TP concentration in the water column (Nicholls and Hopkins, 1993; Fahnenstiel *et al.*, 1995b; Effler and Siegfried, 1998).

Chapter 6

Quantifying the hierarchy of pressures on P water quality in rivers across the Irish Ecoregion using georeferenced landscape-scale environmental data

6.1. Introduction

The results presented in Chapter 4 have shown that the risk of subcatchments contributing disproportionate loads of P to freshwaters increases when high loads of P from point or diffuse sources are coupled with high P transport factors. The importance of targeting limited resources for P mitigation towards these critical areas is recognised across the Irish Ecoregion (Maguire *et al.*, 2009; Doody *et al.*, 2012). However, inadequate site-specific monitoring data and tools limit widespread identification of areas vulnerable to P pollution at the subcatchment scale (EHS, 2006; EPA, 2006). Understanding the main sources and environmental influences on the sensitivity of high concentrations of P in rivers and lakes at the landscape-scale, through their incorporation as predictors of pollution potential, offers on possible way of solving this problem.

Given the multiple potential sources and environmental drivers of high concentrations of P in rivers (Foy *et al.*, 2003; Jordan *et al.*, 2005a; Douglas *et al.*, 2007; Schulte *et al.*, 2010; Greene *et al.*, 2011; O'Driscoll *et al.*, 2011), any landscape-scale predictive model in this area has the potential to be highly complex. Previous studies of a similar context have often been limited in scope, focusing on the impact of changes in one particular sector (e.g. agriculture), excluding hydrological variables, using incomplete datasets or geographically-constrained by the international border that runs through the northern part of the Ecoregion of Ireland (e.g. Daly and Mills, 2006; Donohue *et al.*, 2006). The research described in this chapter combines a number of georeferenced spatial datasets relating to the main environmental conditions that exist in river catchments throughout the Irish Ecoregion to provide as complete an understanding of the determinants of P in rivers as possible at the landscape perspective. Significant relationships derived can be used to guide construction of a prediction model that can identify rivers with a high likelihood of being vulnerable to impairment by P or relatively resistant to recovery following reduced inputs of P.

The research that underpins this chapter tests the H_0 that there is no relationship between environmental conditions and P concentrations for river quality at the landscape-scale. The following steps were carried out in testing this objective:

- Exploring, quantifying and explaining the nature of statistical relationships between concentrations of P in rivers and the environmental conditions (sources and stressors of P) within 72 river catchments across the Irish Ecoregion
- Exploring, estimating and explaining the spatial variation of concentrations of P in rivers that is unaccounted for by the environmental conditions assessed

Where strong relationships were found, multiple regression models to predict P were constructed and validated with data external to the calibration database. Furthermore, by merging a spatial model (quantifying dependence between concentrations of P at river monitoring points) with the regression models, a geospatial model employing environmental conditions and spatial dependence to predict areas vulnerable to P impairment was developed.

6.2. Materials and methods

Testing the H_0 underpinning this component of the research utilised river water quality and georeferenced catchment attribute data from 72 (49 RoI (EPA) and 23 NI (NIEA)) independent (i.e. not nested in another catchment) river monitoring points (Table 3.1; Figure 3.2). An additional five sites in the RoI were subsequently used for validation purposes. Information on the water sampling and analytical procedure carried out to gain these data is provided in Chapter 3. The 72 study monitoring points/catchments were selected using data obtained from several governmental bodies in the RoI and the NI under academic license. Data for P and flow were collated in Microsoft Excel format and spatially represented in ArcGIS using the easting and northings coordinates of the river monitoring points. Digital spatial data relating to surface water bodies and environmental conditions in the study catchments were acquired in the format of ESRI raster and vector shapefiles. Human and cattle population densities, obtained in Microsoft Excel format, were spatially referenced to DED boundaries in ArcGIS. All data were projected according to the Irish National Grid.

The methodological framework utilised to test the H_0 and apply the results to construct a prediction model comprised three main steps, which are illustrated in Figure 6.1 and described in detail in following sections of this chapter. First, the data used and the processes by which the

primary data were combined, manipulated (creating secondary data) and explored in a GIS framework are outlined. Second, the application of regression analysis between (flow-weighted) concentrations of P in rivers and environmental variables in their relative catchments, together with PCA, is explained. Finally, descriptions of the examination of spatial dependence (geospatial analysis) between concentrations of P at river monitoring points and the application of RK are provided.

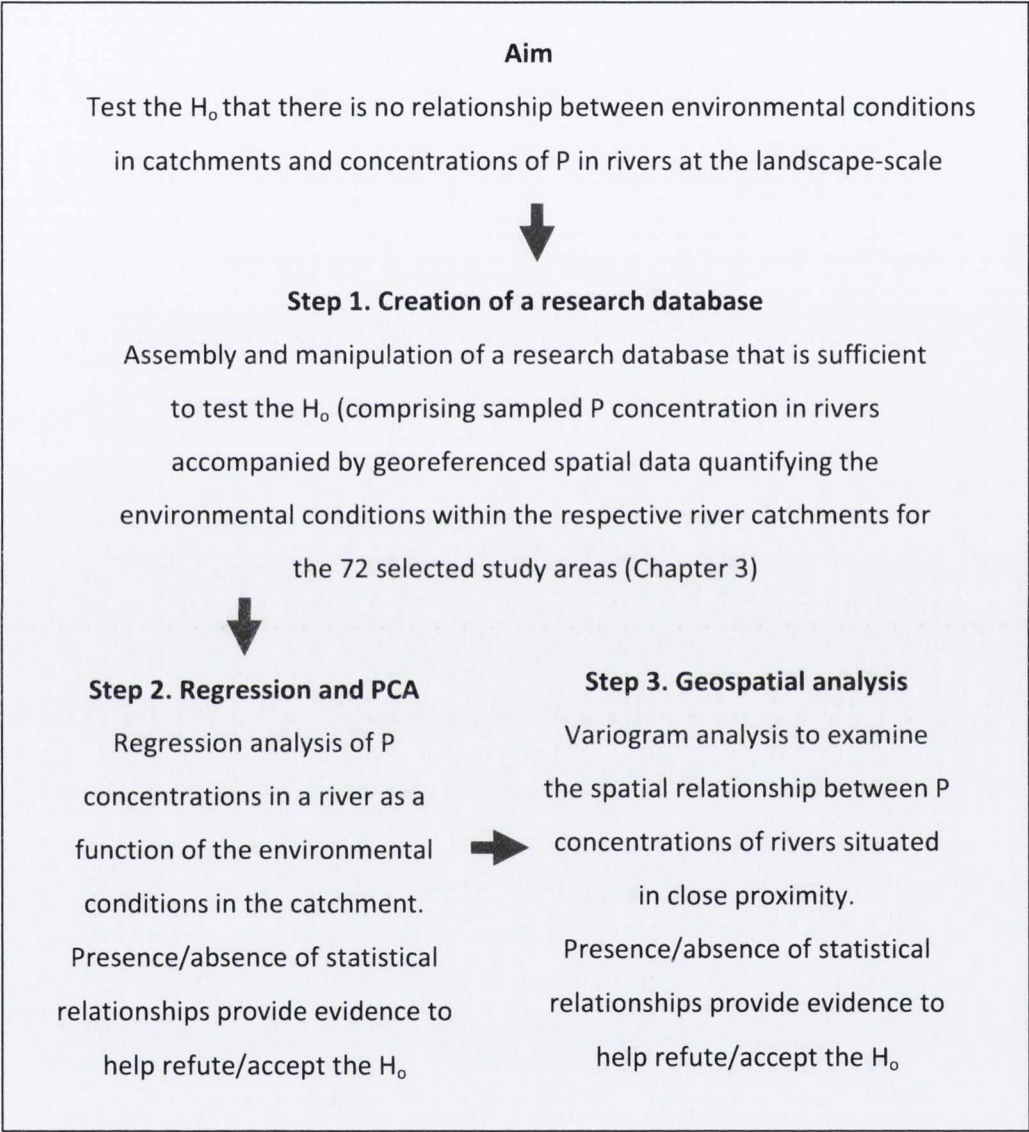


Figure 6.1. Flow chart of the methodological framework applied to test the H_0 underpinning the research study at the small scale. First the H_0 to test is identified; a research database is then created for the study sites that have been selected as suitable for this component of the research (see Chapter 3 for details); regression and PCA are applied to assess the concentration of P in rivers as a function of environmental conditions in their respective catchments; then, variogram analysis is conducted to account for any spatially-related variation in P that has been unaccounted for by regression/PCA. The outputs of these last two steps supply evidence to refute or accept the proposed H_0 .

6.2.1. Creation of the research database

6.2.1.1. Assembly of georeferenced P water quality and environmental data

Georeferenced water quality data comprising unfiltered MRP (RoI) and filtered SRP (NI) $\mu\text{g l}^{-1}$ values were available for river monitoring points in the RoI and NI for the years 2006 to 2008. Daily mean flows ($\text{m}^3 \text{sec}^{-1}$) for the 77 river monitoring points were available via internet download: RoI data from the *Hydronet* (EPA, 2011) and the *Hydro-Data* (OPW, 2011), and NI data from the *National River Flow Archive* (CEH, 2011). Flow data for some NIEA outlet points were interpolated by applying a conversion factor on the dmf of a neighbouring monitoring point. Data on land elevation (DEM) for the Irish Ecoregion were acquired from OSI and OSNI as raster grid files, based on 1:50,000 contour lines digitally transformed to 20m x 20m (OSI) and 50m x 50m (OSNI) resolution. Digital representations of the river and lake network in the Irish Ecoregion were sourced from the EPA and NIEA in the form of vector polyline shapefiles. The river and lake outlines were produced by extraction from the OSI and OSNI 1:50,000 DEM and contained information on river length, Strahler stream order, lake area and lake perimeter.

Digital geological bedrock data, comprising vector polygons at a scale of 1:100,000 were acquired from the GSI and GSNI. Digital data describing forestry cover was obtained from the RoI Forestry Service, DAFF (RoI) and AFBI (NI). Forestry data were acquired in spatial polygon format and included information on the extent of forest cover for the year 2007. Information on urban land cover for the RoI (2006) and NI (2001) was attained from the CSO and AFBI, respectively. The EPA and AFBI provided spatial information on CLC at a scale of 1:100,000, and on soils (both in shapefile vector polygon format). Total cattle densities (RoI 2000, 2006-2008) and (NI 2006-2008) were downloaded from the CSO (RoI), DAFF (RoI) and NISRA (NI) websites. Levels of human population (RoI 2002 and 2006; NI 2001) were also downloaded from the CSO and NISRA websites. Cattle density and human population datasets were acquired at DED (RoI) and ward (NI) levels. Digital spatial data for DED and ward boundaries in polygon format were sourced from the EPA and AFBI.

6.2.1.2. Manipulation of P and environmental data

Data for P and flow

In NI, P data are routinely analysed in a different form (SRP) than in the RoI (MRP) and therefore a means of harmonising data was required before any Ecoregion-wide analysis could take place. Harmonisation of data first comprised compilation of a dataset consisting of corresponding MRP and SRP concentrations (60 samples), sourced from AFBI (data not shown). This dataset was used

to determine the relationship between the two P fractions as measured on the same water sample that could then be used as a factor applied to SRP data to convert to MRP. The relationship showed high significance (R^2 of 0.99) and a linear regression of MRP as a function of SRP was therefore applied to the 23 NIEA sites to convert SRP to MRP. The resulting combined MRP data (72 monitoring) were seasonally (summer (May – October) and winter (November – April)) flow-weighted to estimate a mean concentration ($\mu\text{g l}^{-1}$) of fwMRP using the following equation:

$$\text{fwMRP } (\mu\text{g l}^{-1}) = [\sum_1^n (\text{MRP} (n)) * (\text{dmf} (n)) / \sum_1^n (\text{dmf})] \quad [6.1]$$

where:

MRP (n) is the empirical MRP ($\mu\text{g l}^{-1}$) for the number of days (n) samples were taken

dmf (n) is the daily mean flow ($\text{m}^3 \text{sec}^{-1}$) for n days

The fwMRP data were divided into variables '**MRP_sum**' and '**MRP_win**' (dependent variables) that consisted of a single fwMRP value for each river monitoring site for both summer and winter.

Potential environmental predictors of P

The *hydrology* function in ArcMap's *Spatial Analyst Tools* was used to prepare the DEM data for analysis. Catchment delineation was carried out to develop digital catchment boundaries for each monitoring point; the sub-functions, *fill*, *flow accumulation* and *flow direction* were applied to the DEM to create a layer approximating the extent of drainage so the 72 monitoring points could be used as *pour points* by the *watershed* function to create the catchment boundary. Topographical attributes for each catchment were estimated using digital river, lake and DEM data. The *Clip* function in ArcToolbox was used to extract the information for characterisation of each catchment. Potential explanatory predictors of fwMRP are listed in Table 6. 1 and were calculated as follows:

- '**Catchment_Area**' (km^2) was derived by GIS geometric areal calculation of each catchment represented by the delineated polygon shapefile.
- '**95_percentile**': The 95th percentile flow value (the flow rate ($\text{m}^3 \text{sec}^{-1}$) that was equalled or exceeded for 95% of the flow record), was calculated from the three year dmf record (2006 – 2008) for each river monitoring point.

- **'River_Length'**: The total length (km) of the rivers in each catchment was obtained using the *calculate geometry* function in the attribute table of the clipped river network of each catchment.
- **'Drainage_Density'**: The extent of the drainage capacity of the catchment was calculated from the division of length (km) of rivers in each catchment divided by the catchment area (km²).
- **'Catchment_Lake_Ratio'**: The ratio of catchment area (km²) to the area of lakes in the catchment (km²).
- **'River_Order1 (2, 3, 4, 5)'**: The Strahler stream order of the river that contains the monitoring station.
- **'Mean_Slope'**: The mean slope (degrees) of the catchment was calculated from the DEM layer using the *slope* function in ArcMap's Spatial Analyst Tools. Catchment slope is the maximum rate of change in the elevation between each cell and the neighbouring cell. The mean slope of each catchment was determined by tabulating descriptive statistics using the *zonal statistics* command.
- **'TWI'**: a proxy index of the degree of surface saturation and soil water content (Beven and Kirkby, 1979) , determined by mathematical calculation through the application of *Raster Calculator* (function of *Spatial Analysis Tools*) to the DEM derived layers of flow accumulation and degree slope as in equation 6.2:

$$[TWI] = \ln([flowacc_flow1] * 400 / \tan([SlopeDegrees] * 3.1416 / 180)) \quad [6.2]$$

Accumulated flow equated to the cumulative flow into each downslope cell. Degree slope represents the maximum rate of change (degrees) in the elevation between a cell and neighbouring cells. A low TWI indicated dryness: a high TWI indicated wetness (Barling *et al.*, 1994).

- Landuse in the 72 study catchments were classified. CLC Level 1 categories were tabulated as percentages of **'Semi_Natural'**, **'Arable_Mix'**, **'Pasture'** and **'Artificial_Surfaces'** in each catchment. Spatial representation of forestry cover, a dataset independent of CLC, was used to quantify the variable **'Forest'**, the percentage composition of forest cover (public

and private) in each catchment. The percentage of urban settlement, '**Urban %**' in each catchment was also determined using CSO data that were independent of the CLC data.

- Digital data on bedrock geology was reclassified to produce three categories of bedrock that are vulnerability to weathering (Selby, 1980; Goudie, 2006):
 - **Bedrock_1**: Susceptible to weathering
 - **Bedrock_2**: Intermediate vulnerability to weathering
 - **Bedrock_3**: Resistant to weathering

Table 6.2 shows the geological composition of each of the above categories.

- '**Runoff_Risk**': The potential predictor variable '**Runoff_Risk**', calculated through the method devised by Daly and Mills (2006), is the extent of gley soils in a catchment as a percentage of the total area of catchment multiplied by an assigned risk weight (Table 6.3). The risk weight increases with increased extend of gley soils and reflects the greater runoff risk associated with gleyed soils.
- '**Cattle**': Cattle stocking density was determined from several sources of data. For study catchments in the RoI, estimates of cattle stocking densities were based on CSO data from 2000. Cattle densities were assumed to have an overall even distribution in each DED were used to estimate the total density of cattle in a catchment for 2000 through area-weighting by GIS. Estimates of stocking densities for the period 2006 to 2008 utilised county-level data from the AIM database (formally the CMMS). A mean value (2006-2008) of the estimated cattle stocking density (cattle km⁻²) for each catchment was established. A mean value for cattle stocking densities in study catchments in NI for the period 2006-2008 was attained using annual data from the DARD (via NISRA) annual agricultural census at ward resolution.
- '**Humans**': Human population densities for study catchments in the RoI were estimated by area-weighting census data for 2006. These data were then assumed to be representative for the 2006-2008 study period. For study catchments in NI, human population densities were derived from an area-weighting of data from the 2001 census. A conversion factor, based on population growth rates in the RoI from 2002 to 2006, was applied to the 2001 NI data to estimate 2006-2008 population densities.

Table 6.1. Potential predictors (environmental conditions in river catchments, independent variables) of fwMRP concentrations (dependent variable) in the 72 study rivers their respective catchments for the small scale component of the research (Irish-Ecoregion wide)

Potential predictor (environmental condition in river catchment)	Description	Data type
95_percentile	95 percentile flow value of sample river ($\text{m}^3 \text{sec}^{-1}$)	Continuous
Arable_Mix	CLC class - % of arable and mixed agriculture in catchment	Continuous
Artificial_Surfaces	CLC class - % of artificial surfaces in catchment	Continuous
Bedrock_1 (2,3)	% of bedrock type in catchment	Continuous
Catchment_Area	Area of catchment (km^2)	Continuous
Catchment_Lake_Ratio	Ratio of catchment area (km^2) to lake area (km^2)	Continuous
Cattle	Cattle density in catchment (cattle unit km^2)	Continuous
Drainage_Density	Length of catchment river (km) network per unit area (km^2)	Continuous
Forest	% forestry in catchment	Continuous
Humans	Human population in catchment (person km^2)	Continuous
Mean_Slope	Mean slope of catchment (%)	Continuous
Pasture%	CLC class - % of pasture in catchment	Continuous
River_Length	Length of all rivers in catchment (km)	Continuous
River_Order1 (2,3,4,5)	Indicator variable of Strahler stream order of sample river	Binary
Runoff_Risk	P runoff risk index applied to % gley soils in catchment	Continuous
Semi_Natural%	CLC class - % of semi-natural areas in catchment	Continuous
TWI	Topographic Wetness Index (dimensionless)	Continuous
Urban%	% of urban area (km^2) in catchment	Continuous

Table 6.2. Geological composition of the reclassified bedrock types (based on weathering potential) to serve as potential predictors (environmental condition in river catchments) of concentrations of fwMRP in the 72 study rivers for the small scale component of the research (Irish-Ecoregion wide)

Bedrock	Reclassified type	Weathering potential
Limestones, Mudstone, Shales, Metasediments	1	Vulnerable to weathering
Interbedded/Conglomerated Type 1 and Type 2 bedrock, Undifferentiated Argillaceous rocks, Bauxitic Clay,Psammite and Semi-Pelite	2	Intermediate vulnerability to weathering
Andesite, Basalt, Sandstone, Diorite, Gabbro, Granite,Granodiorite, Undifferentiated Igneous rock, Psammite, Quartzite, Rhyolite, Gneisses & Schists	3	Resistant to weathering

Table 6.3. Assigned runoff risk weights of gley soil (from Daly and Mills, 2006) to estimate the potential predictor variable (Runoff_Risk) of concentrations of fwMRP in the 72 study rivers for the small scale component of the research (Irish-Ecoregion wide)

% gley soil in catchment	Risk weight
<10	1
11-25	2
26-75	3
>76	4

6.2.1.3. Exploratory data analysis

The dependent data (MRP_win and MRP_sum) and corresponding environmental attributes of a catchment (independent data) were divided into two geodatabases – one comprising data pertaining to the 49 study river monitoring points/catchments in the RoI (EPA) database, the other combining data from both the RoI and NI, totaling 72 sites (EPA_NIEA database). All variables were analysed for normality to meet the statistical requirements of regression analysis using histograms, normal Q-Q plots and the Sharpiro-Wilk test for normality. All non-normal data were log (x+1) transformed. A paired t-test was applied to the fwMRP data in each database to test the hypothesis that the means of both P datasets were equal ($p < 0.05$).

6.2.2. Regression and PCA

6.2.2.1. Regression analysis

Simple linear regression analysis was applied to explore fwMRP as a function of the individual environmental conditions of the river catchments in both databases. Significant predictors ($p < 0.05$) of fwMRP were retained and non-significant variables were deleted from the study databases. A correlation matrix was developed to show relationships between all variables for both databases. Initial multiple linear regression models were fit to describe fwMRP as a function of a combination of significant predictors. The resulting residual plots and VIFs of each regression model were examined to ensure that multiple regression assumptions were met and to identify multicollinearity amongst predictors. Multicollinearity exists when variables are auto-correlated. The VIF for a predictor, j , was calculated by:

$$VIF_j = \frac{1}{1 - R_j^2} \quad [6.3]$$

where:

R_j^2 is the coefficient of determination when a predictor X_j is regressed on the other covariates

The VIF is always greater than or equal to 1. Typically, a $VIF > 2.5$ indicates the presence of multicollinearity between two or more model predictors.

6.2.2.2. PCA

Principal component analysis, a means of reducing the complexity of data to enable identification of the main causes, or principal components (Field, 2009), of variation was applied to intercorrelated predictor variables to yield standardised, independent predictors of fwMRP. Typically, the first principal component accounts for the greatest variance with each subsequent component explaining progressively less. Two sets of three principal components were estimated for each of the two databases.

The two databases, comprising MRP_winx, MRP_sumx, easting and northing coordinates of the river monitoring points, and the corresponding principal components, were imported into the R computer programme v 2.12 (Venables and Smith, 2010). Stepwise multiple linear regression of fwMRP as a function of a combination of the principal components was carried out. Optimum combinations of the predictors were selected and four independent regression models were selected. The coefficient of determination (R^2 , $p < 0.05$) quantified the proportion of variation explained by the calibrated models and the VIFs explained the degree of multicollinearity between model predictors.

6.2.3. Geospatial analysis

6.2.3.1. Variogram modelling

Spatial correlation, based on straight-line or Euclidean distance (Webster and Oliver, 2007) between river monitoring points, was examined in the dependent variables (seasonal fwMRP) and residuals from the regression models that describe P as function of the three principal components. Isotropy was assumed. Spatial dependence was determined through variogram analysis and modelled using automatic fitting options in the gstat package of the R programme (Pebesma and Wesseling, 1998; Hengl *et al.*, 2007).

Variogram functions related the semivariance (half the expected squared difference between paired data values $z(x_i)$ and $z(x_i+h)$) to the lag distance h , by which sample points were separated (Webster and Oliver, 2007):

$$\gamma(h) = \frac{1}{2E[Z(x) - Z(x+h)]^2} \quad [6.4]$$

For discrete sampling sites, the function for the variogram was:

$$\gamma(h) = \frac{1}{2} m(h) \sum_{i=1}^{m(h)} [z(x_i) - z(x_i + h)]^2 \quad [6.5]$$

where:

$\gamma(h)$ is the experimental semivariance estimation at a lag distance h

$z(x_i)$ is the value of the measured samples at sample location x_i

$m(h)$ is the total number of sample points within the distance h

Sample (experimental) variograms were computed for the dependent data fwMRP in order to examine an initial spatial structure (see Chapter 2 for descriptive information on the variogram). The variogram models were fit to the dependent data with initial variogram parameters comprising nugget = 0, sill parameter = the overall variance in the dataset and the range = one-quarter of the diagonal of the bounding box (maximum distance of spatial autocorrelation). To develop the geospatial model, a variogram was then fitted to the residuals of the four seasonal regression models (based on principal components) from section 6.2.2.2. In all cases, the structure of data in the experimental variograms indicated that a spherical variogram model would best fit the residual variogram structures.

6.2.3.2. RK

In the RK procedure, instead of kriging $z(x_i)$ directly, a regression analysis was applied to $z(x)$ as a function of a group of the predictor variables (Principal components) $q_k(x)$:

$$z(x) = z^*(x) + \varepsilon(x) = \sum_{k=0}^n \beta_k q_k(x) + \varepsilon(x) \quad [6.6]$$

where:

$z(x)$ is the target variable; $x = (x,y)$ represents the two-dimensional spatial coordinates
 $z^*(x)$ is the spatial field that can be estimated for each point x where $q_k(x)$ is known
 β_k are fitted regression coefficients
 q_k are the external predictor variables
 $\epsilon(x)$ is a normally distributed residual with zero-mean

The regression models (based on principal components) developed in section 6.2.2.2 were combined with the corresponding variogram models from section 6.2.3.1 using a script command in the gstat package of R. A kriging function was then applied to these combined models using the *krige* function in the gstat package. Hybrid spatial prediction models (geospatial models) and corresponding models of estimated predicted variances (95% confidence interval) of the geospatial models were produced.

6.2.3.3. Validation of geospatial models

The geospatial models were examined for accuracy using two methods: cross-validation and prediction of P values for river monitoring sites that were not included in the calibration database ($n = 5$).

Cross-validation comprised an automated leave-one-out method, run using a script command in gstat, in which monitoring points were omitted in turn and values of fwMRP computed. This process was repeated until a complete subset of computed fwMRP values was produced. The observed and predicted fwMRP values were regressed and an R^2 value generated. In addition, the RMSE metric was used to examine prediction accuracy:

$$RMSE = \sqrt{\sum_{i=1}^n (Z(S_i) - \hat{Z}(S_i))^2 / n} \quad [6.7]$$

where:

$Z(S_i)$ is the observed value for monitoring point S_i

$\hat{Z}(S_i)$ is the predicted value for the same monitoring point as $Z(S_i)$

n is the number of monitoring points in the study.

The summer and winter geospatial models derived from the Rol database were used to predict fwMRP concentrations at five river monitoring points in the Rol (V1-5, Table 3.1). These catchments were external to the calibration dataset and fwMRP data from 2009-2010 were used to compare with the predicted values. Prediction accuracy was assessed using RMSEs.

6.3. Results

6.3.1. Results of exploratory data analysis

Flow weighted MRP concentrations in the Rol rivers ranged from $3 \mu\text{g l}^{-1}$ in winter to $134.7 \mu\text{g l}^{-1}$ in summer and values for the NI rivers ranged from $0.75 \mu\text{g l}^{-1}$ in summer to $442.93 \mu\text{g l}^{-1}$ in winter. Owing to a non-normal distribution of data, a $\log(x+1)$ transformation was applied to the fwMRP data. All potential predictor variables, except cattle density and % pasture, had a non-normal distribution and these were $\log(x+1)$ transformed also. The t-tests on fwMRP data showed that the means of the two populations were statistically different ($p < 0.05$).

6.3.2. Outputs of regression analysis

Results of the simple linear regression analyses showed 11 and 9 significant predictors of seasonal fwMRP in the Rol (EPA) database and the combined Rol-NI (EPA_NIEA) database, respectively (Figures 6.2 and 6.3; Table 6.4). The coefficient of determination (R^2) is reported with the individual regression plots. All relationships were found to be significant at $p < 0.05$. The dominant predictors of fwMRP concentrations in the study catchments in the Rol were catchment mean slope, TWI and human population. However, for the combined Rol-NI database, catchment mean slope was found to be a poor indicator of fwMRP. Moreover, although TWI was not a significant predictor, human population was a strong explanatory variable. Overall, the variables % pasture, cattle density, % urban, runoff risk, % artificial, human density, % bedrock type 1 and TWI were positively related to fwMRP. Furthermore, % bedrock type 3, catchment mean slope, drainage density and % forest were inversely related to fwMRP. Drainage density was significantly related to fwMRP in the Rol database but not in the combined Rol-NI database.

Initial multiple linear regressions of fwMRP as a function of a combination of all significant predictors yielded large VIFs, ranging from 1.5 to 20.8, indicating the presence of multicollinearity between predictor variables (Table 6.5). The correlation matrices and associated Pearson Correlation coefficients (r) are provided in Tables 6.6 and 6.7.

6.3.3. Results of PCA

The results of PCA are illustrated in Figures 6.4 and 6.5 and summarised in Tables 6.8 and 6.9. For both databases used in this study, the first three principal components have eigenvalues greater than 1. For the study catchments in the RoI (EPA) database, the first three components accounted for 74% of the total variation. The main component, Principal component 1, explained 37.5% of total variation and was mainly influenced by variation in drainage density, % forest cover, mean catchment slope and % of weather resistant bedrock (all drivers with negative influences on the concentration of P in the study rivers), while variation in % urban, % artificial areas and human population density largely explained Principal component 2, which accounted for 25% of total variation (all drivers with positive influences on the concentration of P in study rivers). Variations in cattle density, % pasture, P runoff risk and TWI were reflected in Principal component 3 (all drivers with positive influences on the concentration of P in the study river). A slightly different combination of principal components was generated for the combined RoI-NI (EPA_NIEA) database, with the three main axes explaining 73% of the total variation. Principal component 1, mainly influenced by cattle density, % pasture and bedrock vulnerable to erosion, explained 31% of total variation. Principal component 2 accounted for 30% of total variation and was largely explained by % urban, % artificial and human population density. Principal component 3 explained 12% of total variation and comprised mainly P runoff risk, mean catchment slope and % forest cover.

The optimal combination of environmental predictors (in the form of Principal components) of fwMRP was selected by stepwise multiple linear regression. Four regression models were produced: VIF analysis indicated that multicollinearity between predictor variables was not present ($VIF = 1.0$), while a normality test showed that the residuals did not significantly depart from a normal distribution in all cases. The intercepts, component coefficients, VIFs, R^2 values and significance levels for all four regression models with parameters based on PCA are listed in Table 6.10.

Table 6.4. Significant predictors (environmental conditions in river catchments, independent variables, $p < 0.05$) of MRPLX1 (dependent variable) in the 72 study rivers their respective catchments for the small scale component of the research (Irish-Ecoregion wide). The heading 'Database' indicates in which database (Rol (EPA) and/or the combined Rol-NI (EPA_NIEA) database) a particular predictor has shown a significant relationship with fwMRP

Predictor (environmental condition in river catchment)	Description	Database	Data type
ArtificialLX1	CLC class - % of artificial surfaces in catchment	Both databases	Continuous
Bed[1,2,3]LX1	% of bedrock type in catchment	Bed1LX1(EPA_NIEAdatabase), Bed3LX1 (EPA_database)	Continuous
Cattle	Cattle density in catchment (cattle km ²)	Both databases	Continuous
DrainageDensityLX1	Length of catchment river (km) network per unit area (km ²)	EPA_database only	Continuous
ForestLX1	% forestry land cover in catchment	Both databases	Continuous
HumansLX1	Human density in catchment (person km ⁻²)	Both databases	Continuous
MeanSlopeLX1	Mean slope of catchment (%)	Both databases	Continuous
Pasture	CLC class - % of pasture in catchment	Both databases	Continuous
RunoffRiskLX1	P runoff risk index applied to % gley soils in catchment	Both databases	Continuous
TWILX1	Topographic Wetness Index (dimensionless)	EPA_database only	Continuous
UrbanLX1	% of urban area in catchment	Both databases	Continuous

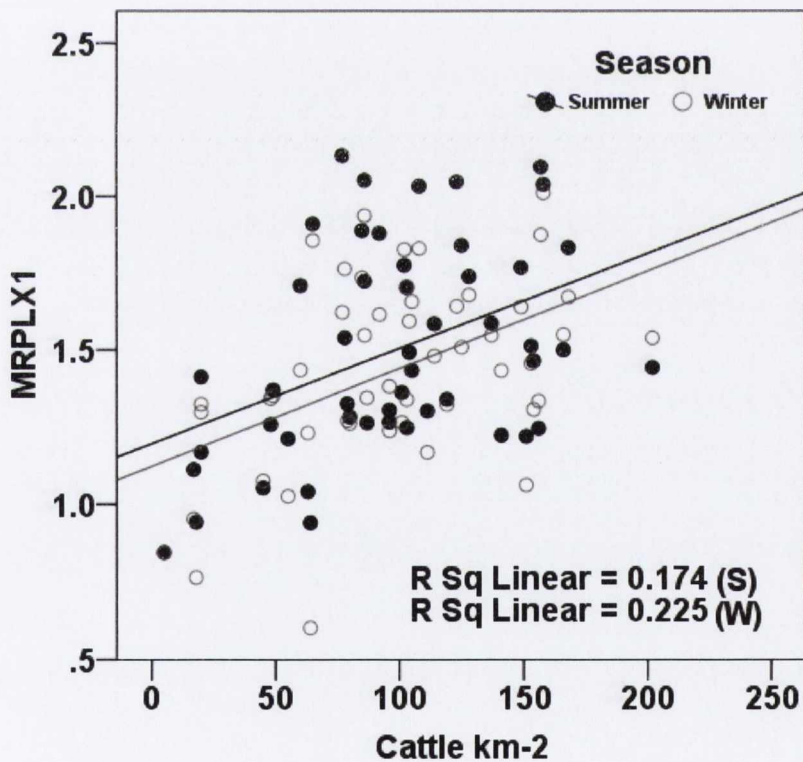
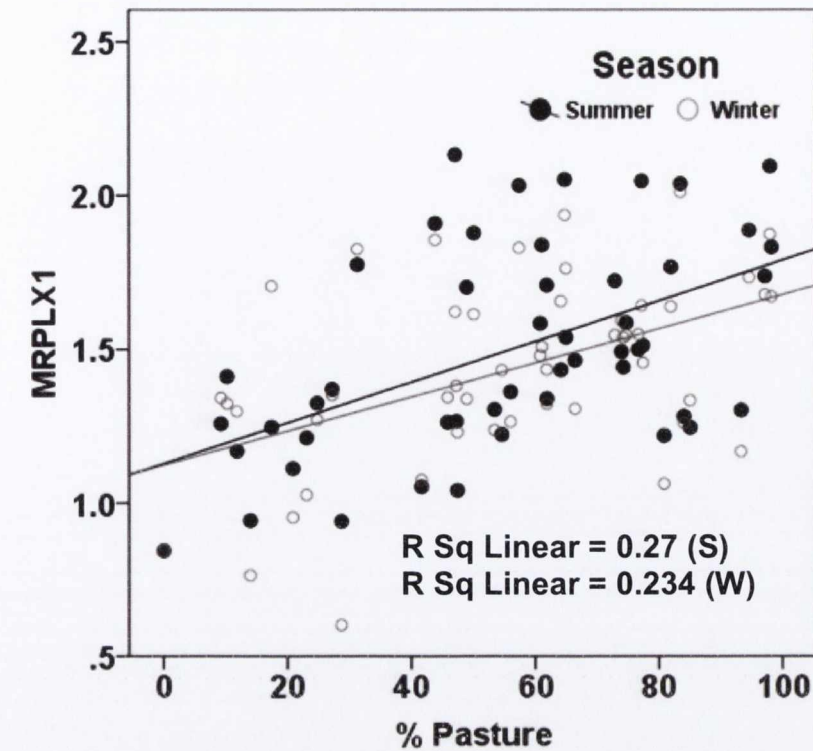


Figure 6.2a. Simple linear regression plots between variables (% pasture and cattle density) representing environmental conditions in river catchments and seasonal MRPLX1 (($\log(x+1)$) transformed mean flow weighted concentration of MRP ug l^{-1} in rivers). The relationships are statistically significant at $p < 0.05$. $n = 49$, RoI (EPA) database

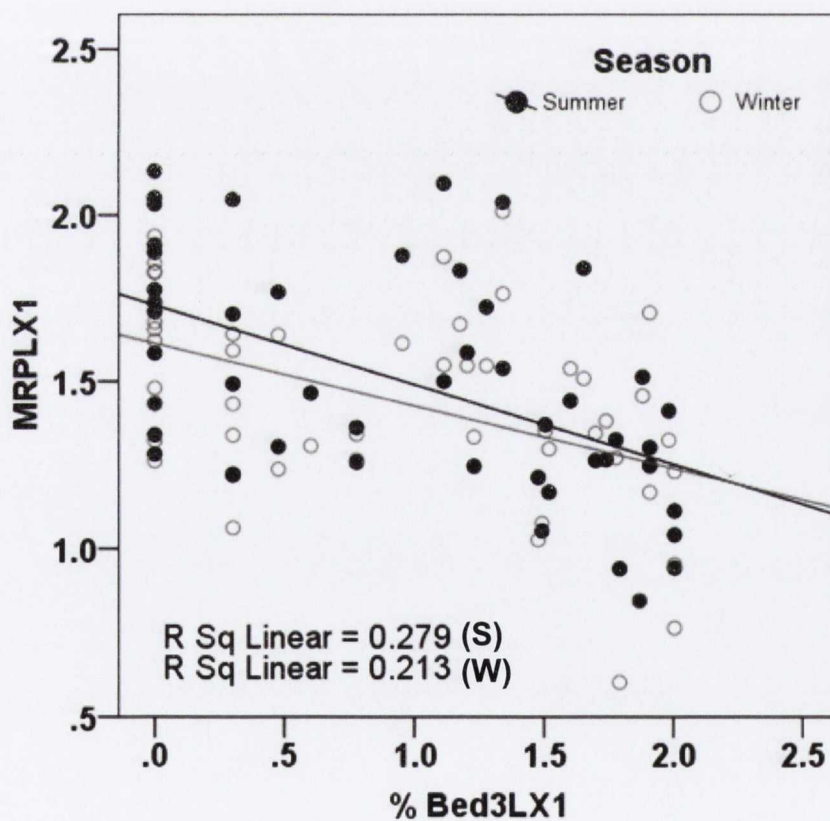
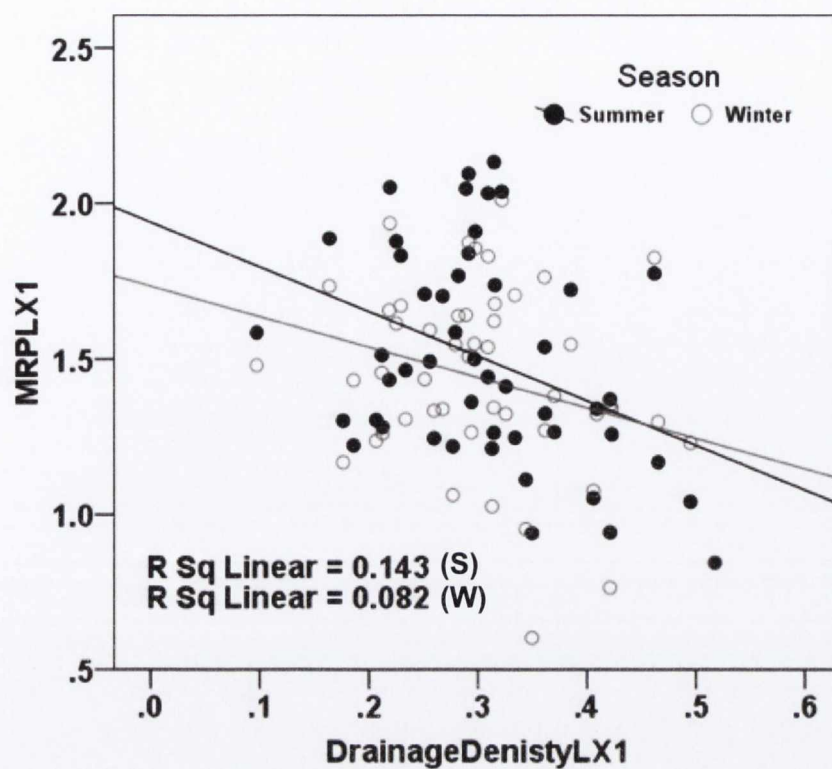


Figure 6.2b. Simple linear regression plots between variables (drainage density and the % of bedrock type 3) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ug l^{-1} in rivers (MRPLX1). All data was log (x+1) transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 49$, RoI (EPA) database

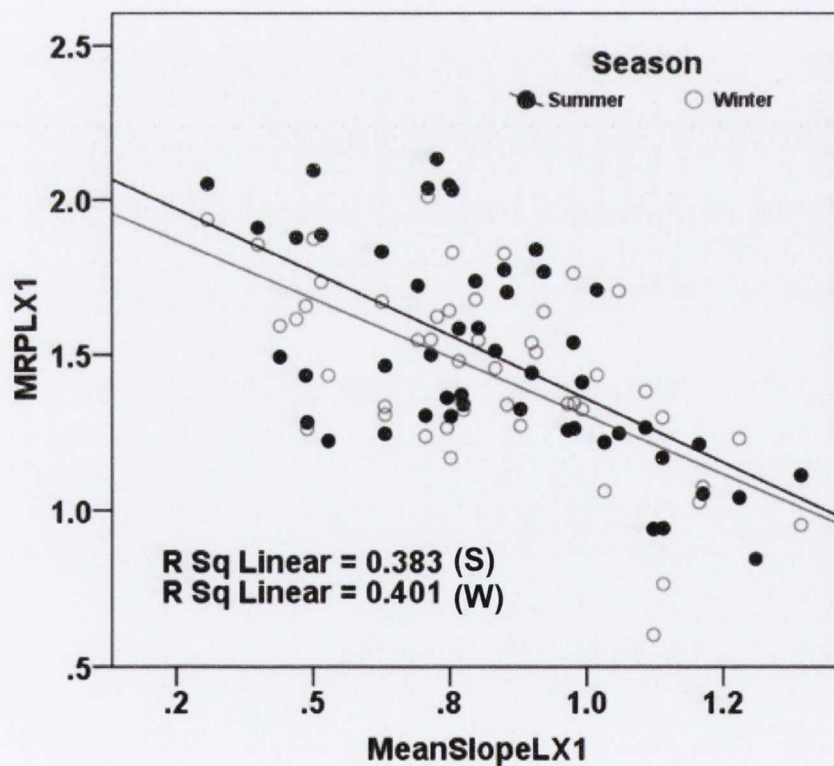
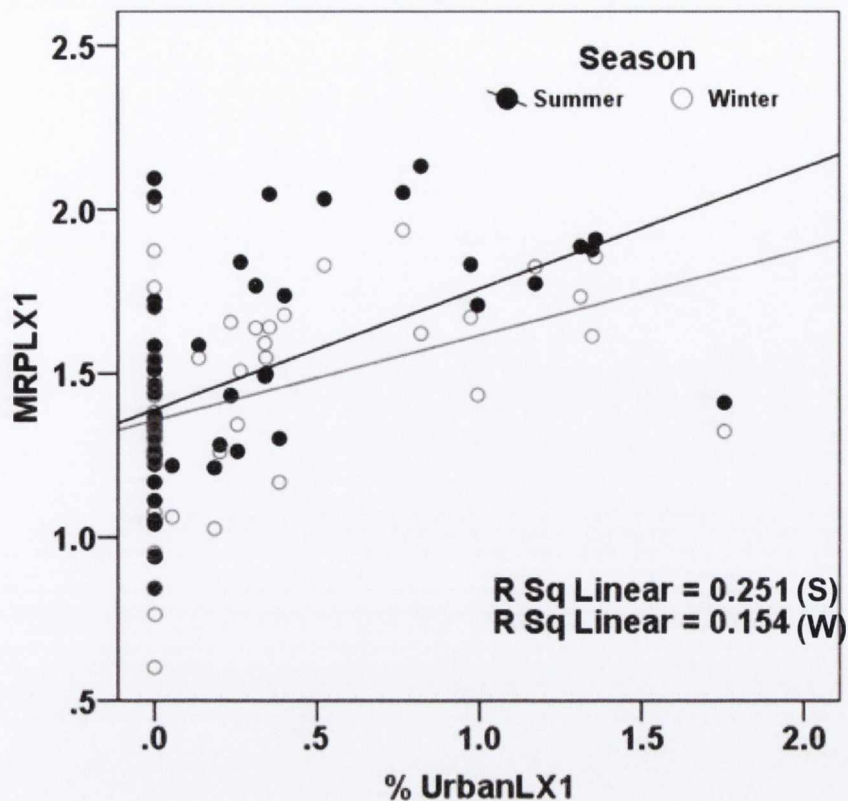


Figure 6.2c. Simple linear regression plots between variables (% urban land area and mean slope) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ug l^{-1} in rivers (MRPLX1). All data was $\log(x+1)$ transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 49$, RoI (EPA) database

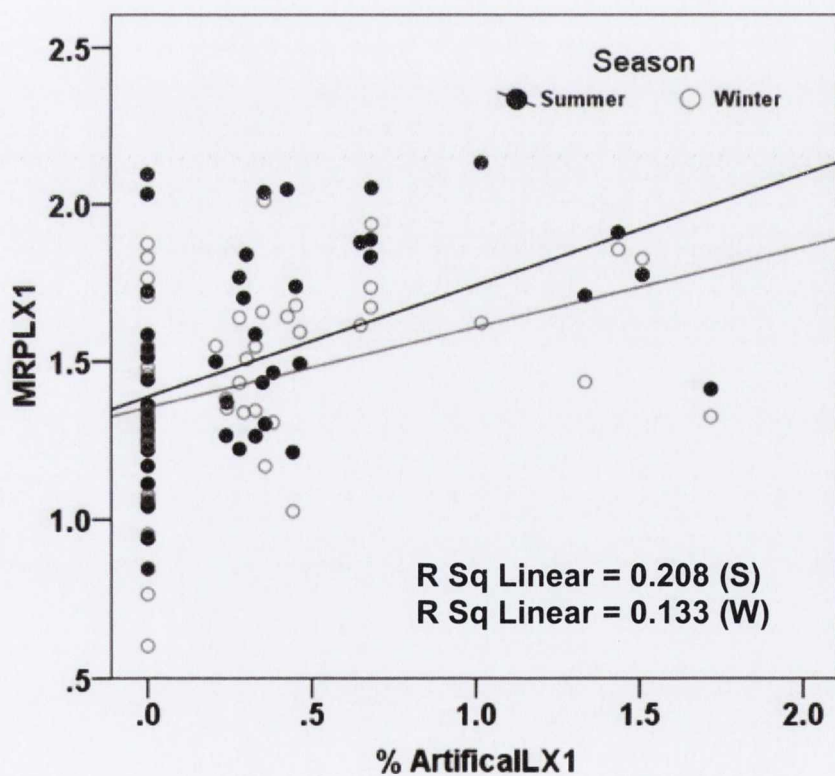
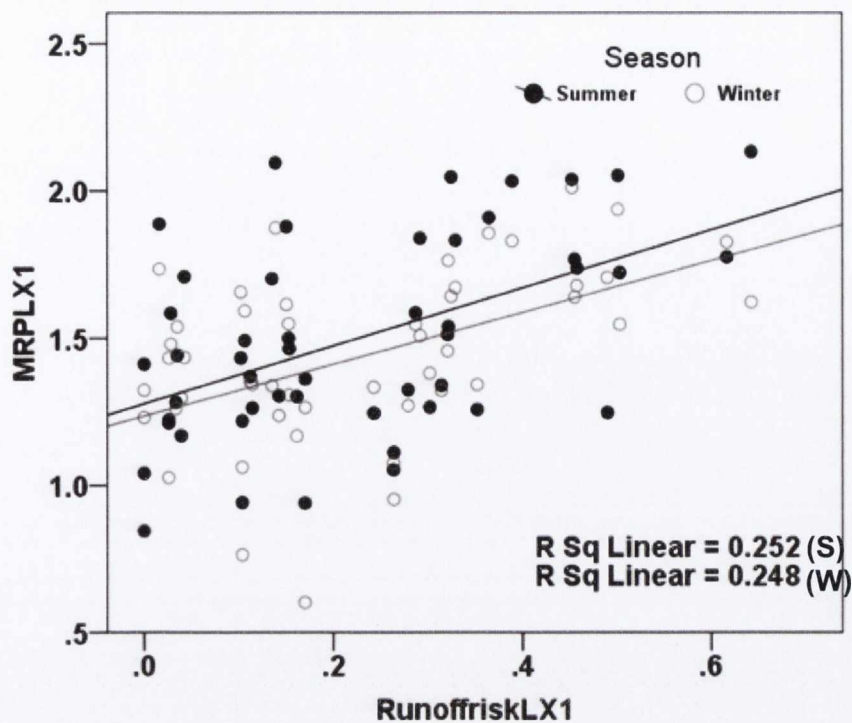


Figure 6.2d. Simple linear regression plots between variables (runoff risk of soils and % artificial land area) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was $\log(x+1)$ transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 49$, RoI (EPA) database

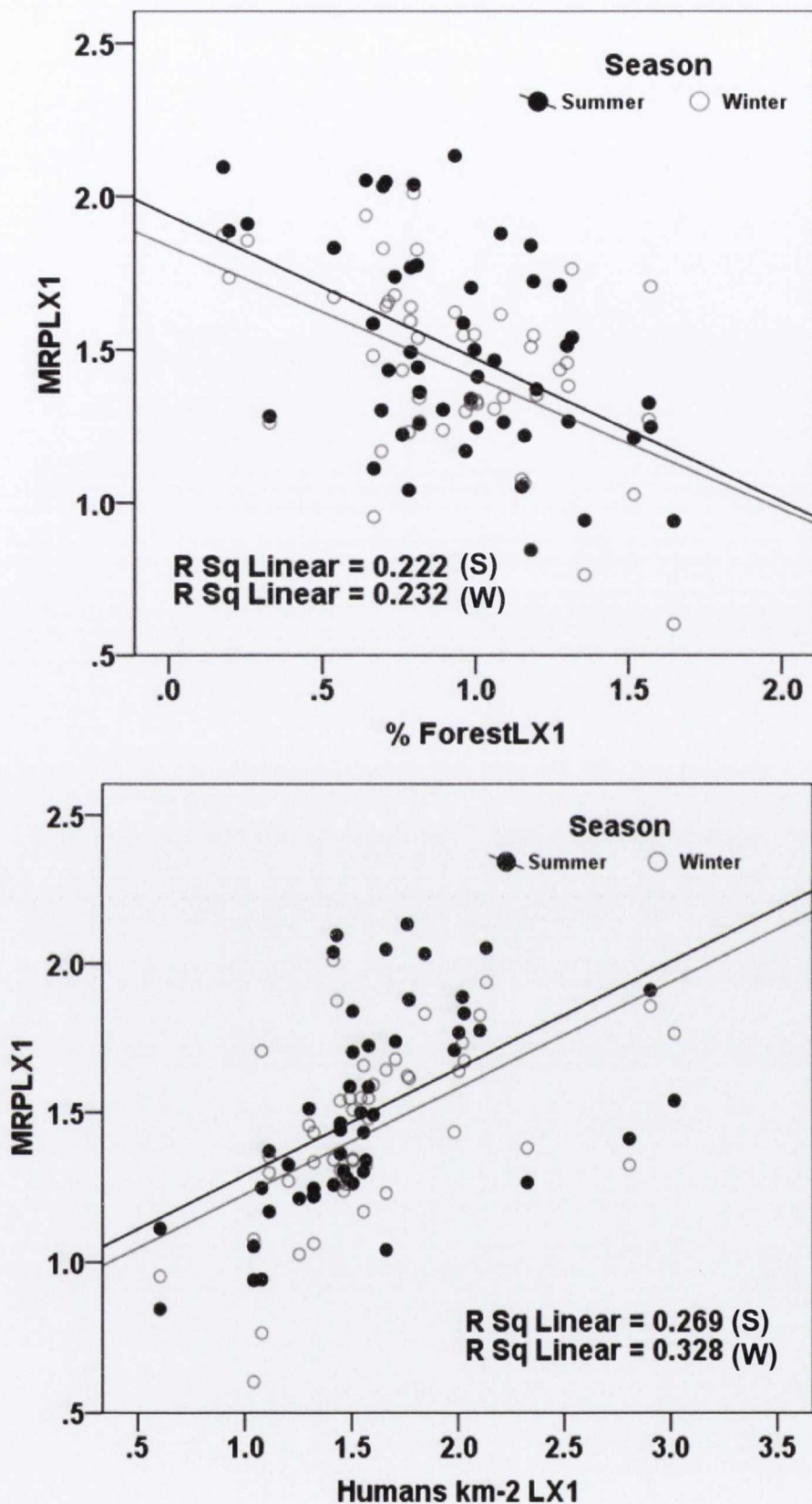


Figure 6.2e. Simple linear regression plots between variables (% forestry cover and human population density) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was $\log(x+1)$ transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 49$, RoI (EPA) database

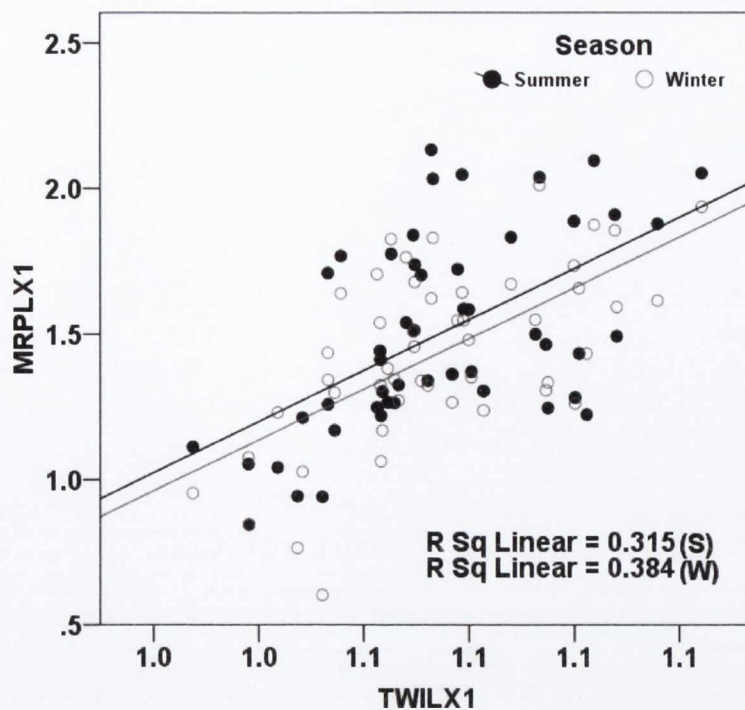


Figure 6.2f. Simple linear regression plots between TWI in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was $\log(x+1)$ transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n=49$, Rol (EPA) database.

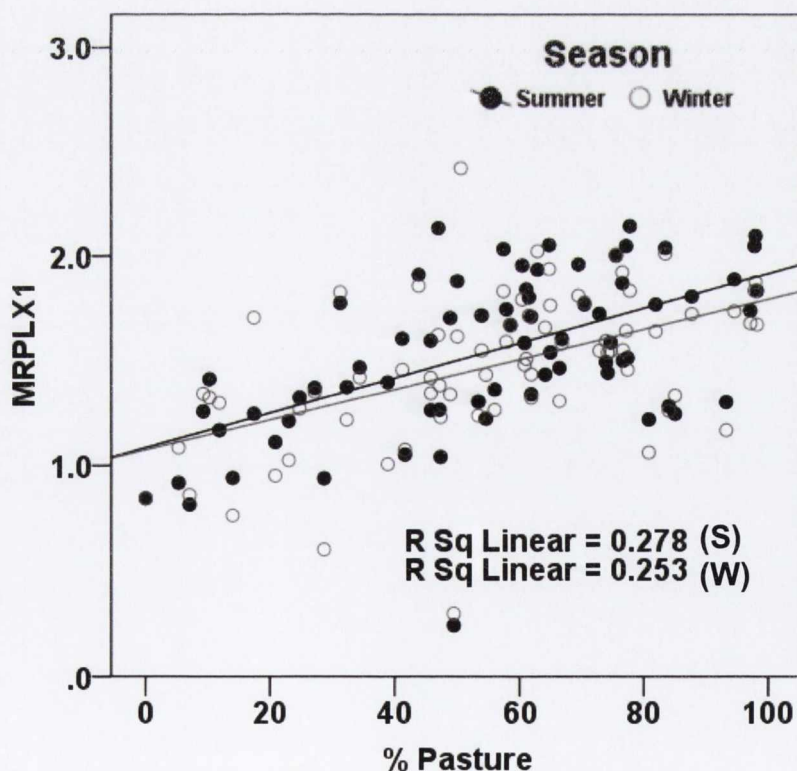


Figure 6.3a. Simple linear regression plots between % pasture land in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was $\log(x+1)$ transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 72$, combined Rol-NI (EPA_NIEA) database

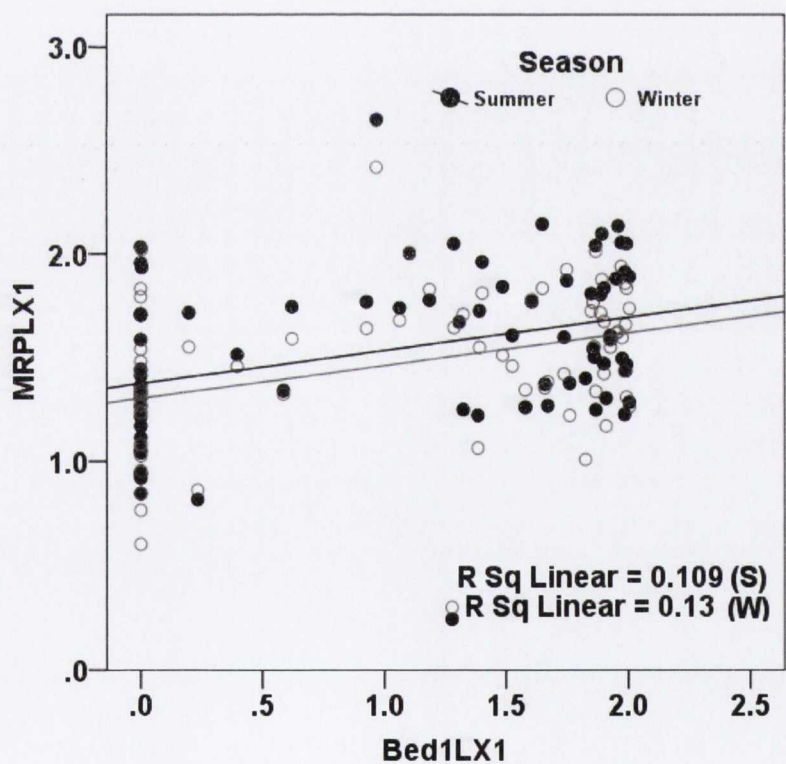
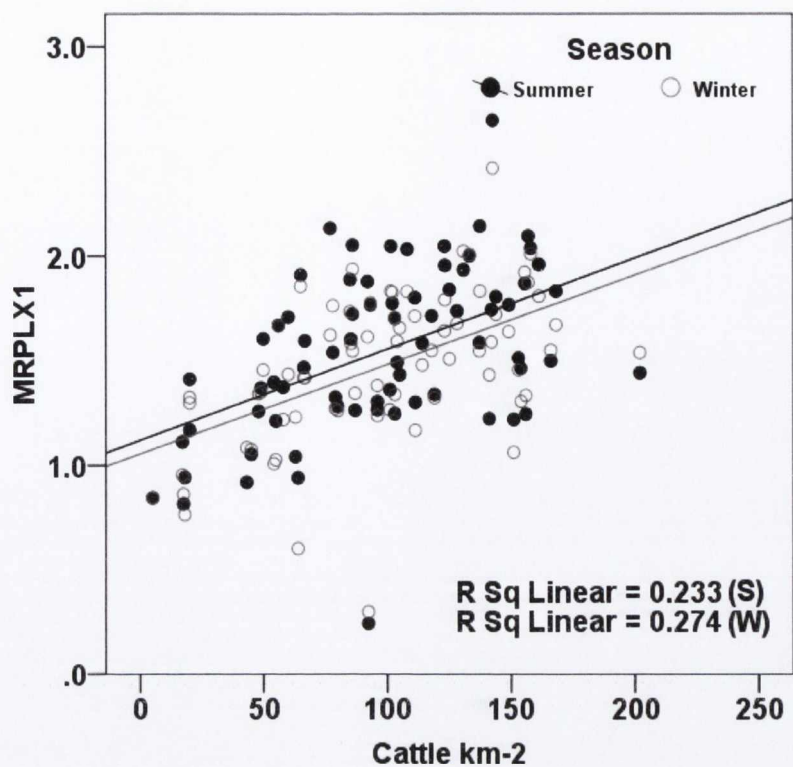


Figure 6.3b. Simple linear regression plots between variables (cattle stocking density and the % of bedrock type 1) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was $\log(x+1)$ transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 72$, combined RoI-NI (EPA_NIEA) database

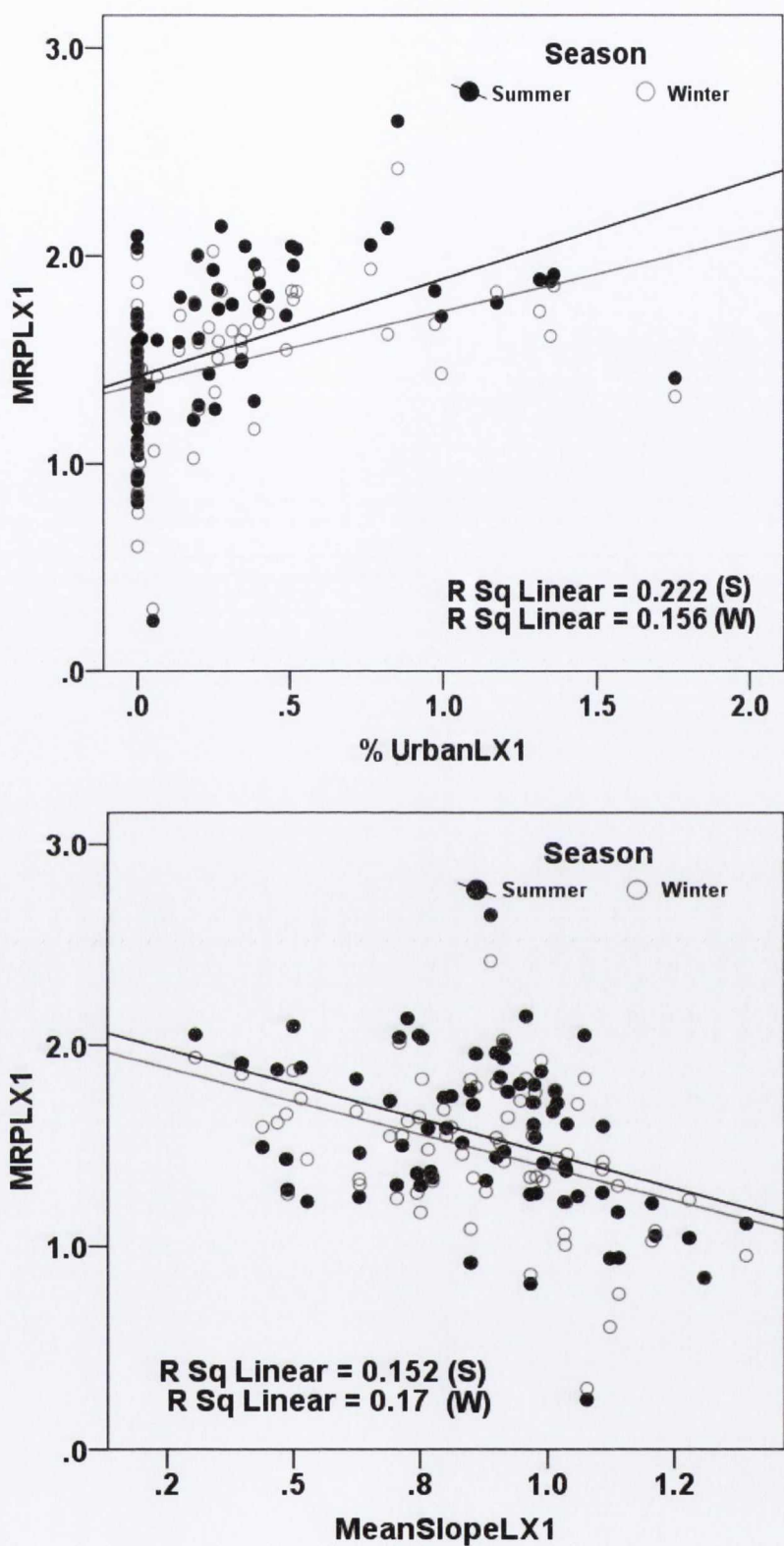


Figure 6.3c. Simple linear regression plots between variables (% urban land area and mean slope) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was log (x+1) transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 72$, combined RoI-NI (EPA_NIEA) database

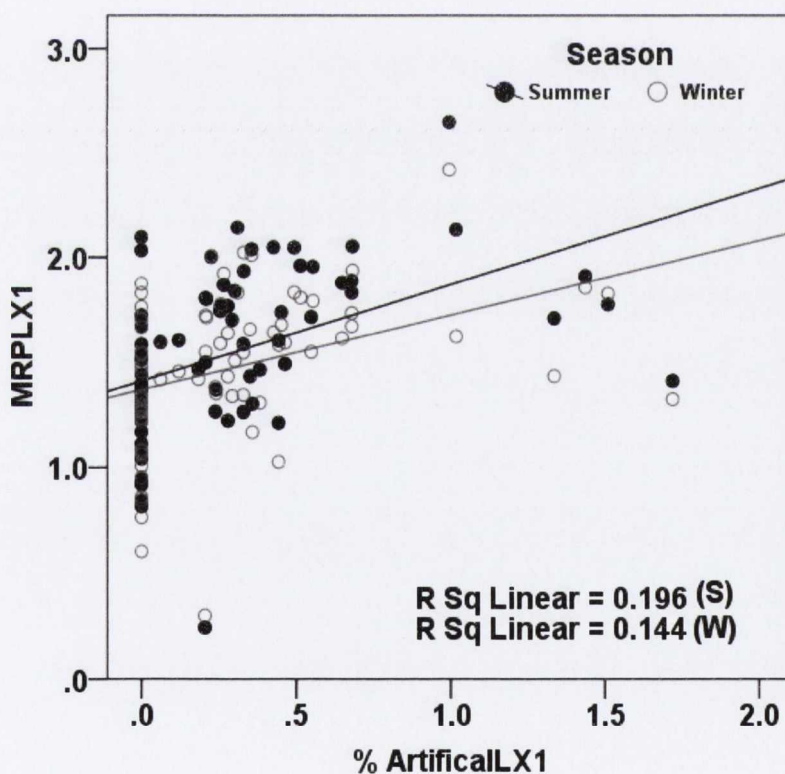
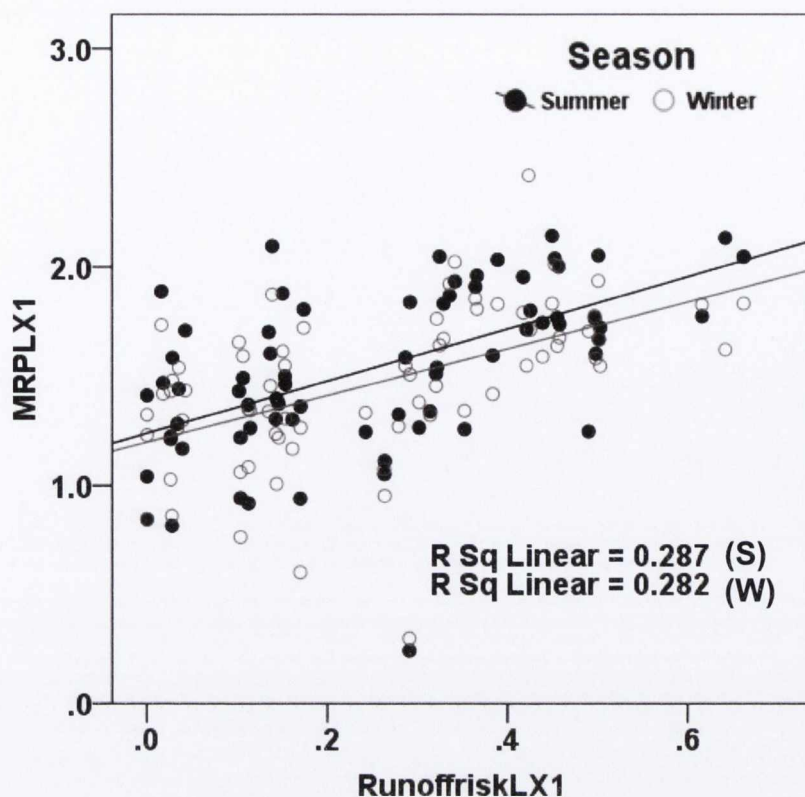


Figure 6.3d. Simple linear regression plots between variables (runoff risk of soils and % artificial land area) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was $\log(x+1)$ transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 72$, combined RoI-NI (EPA_NIEA) database

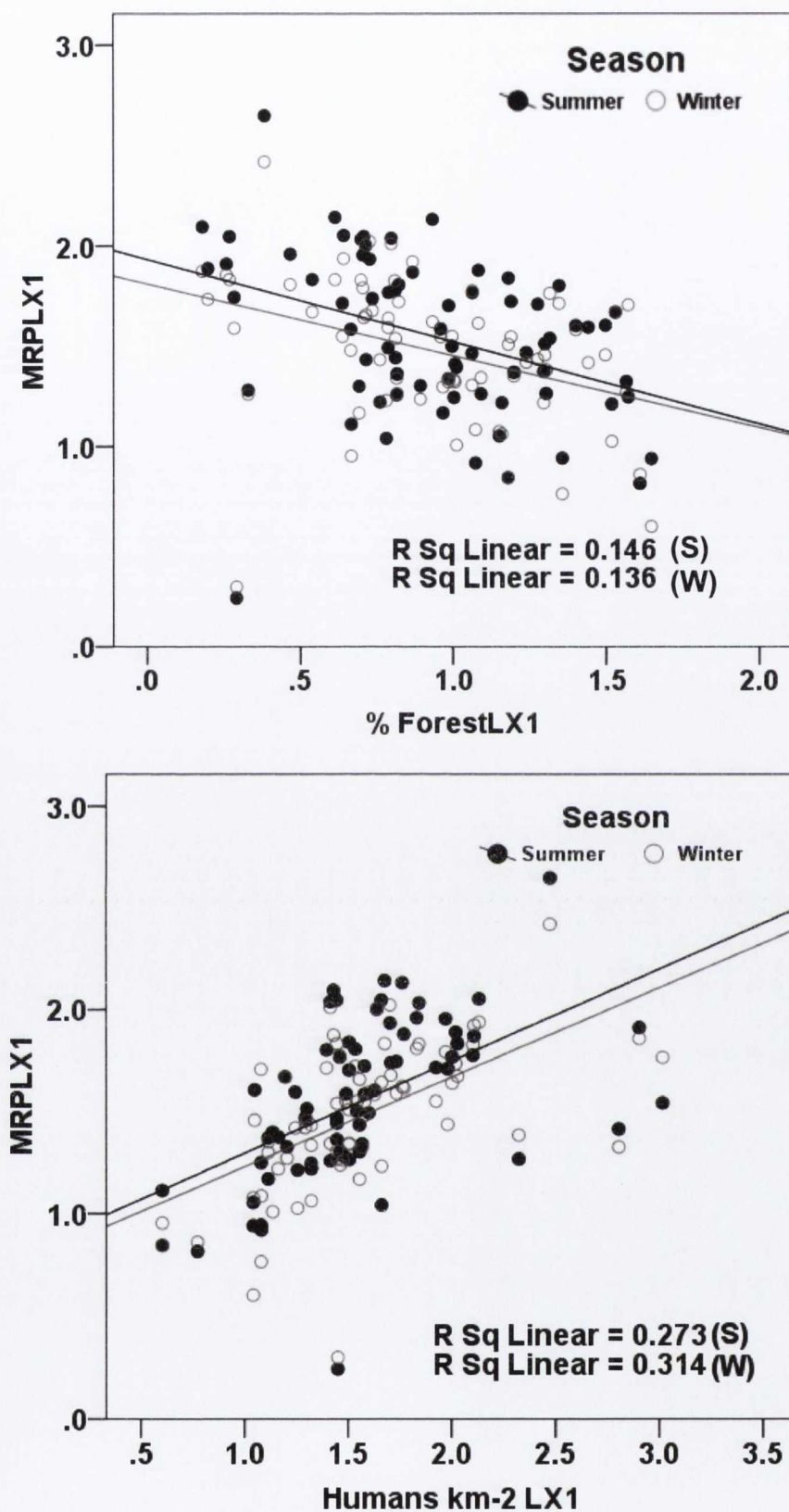


Figure 6.3e. Simple linear regression plots between variables (% forestry cover and human population density) representing environmental conditions in river catchments and seasonal flow weighted concentration of MRP ugl^{-1} in rivers (MRPLX1). All data was log (x+1) transformed for statistical normality before regression analysis. The relationships are statistically significant at $p < 0.05$. $n = 72$, combined Rol-NI (EPA_NIEA) database

Table 6.5. Variance inflation factors from initial linear regression relationships between concentrations of fwMRP (MRPLX1) as a function of environmental conditions in river catchments (significant predictors, $p < 0.05$). Data are based on the Rol (EPA) database and the combined Rol-NI (EPA_NIEA) database

Predictor (environmental conditions in river catchments)	VIF		
	EPA database		EPA_NIEA database
	WinMRPLX1	SumMRPLX1	WinMRPLX1 SumMRPLX1
Cattle	3.23	3.23	2.78 2.78
Pasture	4.18	4.18	3.33 3.33
DrainageDensityLX1	2.44	2.44	not significant not significant
UrbanLX1	5.89	5.89	5.73 5.73
MeanSlopeLX1	20.86	20.86	1.83 1.83
RunoffRiskLX1	1.54	1.54	1.29 1.29
ArtificialLX1	5.36	5.36	5.34 5.34
ForestLX1	2.06	2.06	1.59 1.59
HumansLX1	2.12	2.12	2.26 2.26
TWILLX1	15.89	15.89	not significant not significant
Bed3LX1	1.98	1.98	not significant not significant
Bed1LX1	not significant	not significant	1.60 1.60

Table 6.6. Pearson's correlation relationships between the independent (environmental conditions in river catchments) and dependent variables (SumMRPLX1 and WinMRPLX1 - concentration of fwMRP in rivers) of the Rol (EPA) database (n = 49) used for the small scale study

Correlations													
	SumMRPLX1	WinMRPLX1	Bed3LX1	Drainage DensityLX1	UrbanLX1	MeanSlope LX1	RunoffriskLX1	ArtificialLX1	Pasture	Cattle	ForestLX1	HumansLX1	TWILX1
SumMRPLX1	Pearson Correlation	1.000	.844**	-.529**	-.378**	.501**	.502**	.456**	.520**	.417**	-.471**	.519**	.561**
	Sig. (2-tailed)			.000	.007	.000	.000	.001	.000	.003	.001	.000	.000
WinMRPLX1	Pearson Correlation		1.000	-.461**	-.286**	.392**	.498**	.364**	.484**	.474**	-.481**	.573**	.619**
	Sig. (2-tailed)			.001	.046	.005	.000	.010	.000	.001	.000	.000	.000
Bed3LX1	Pearson Correlation			1.000	.424**	-.319*	-.185	-.317*	-.385**	-.242	.517**	-.340*	-.517**
	Sig. (2-tailed)				.002	.026	.203	.026	.006	.094	.000	.017	.000
DrainageDensityLX1	Pearson Correlation				1.000	-.215	.150	-.124	-.609**	-.500**	.365**	-.191	-.595**
	Sig. (2-tailed)					.138	.304	.394	.000	.000	.010	.189	.000
UrbanLX1	Pearson Correlation					1.000	.115	.882**	.049	-.125	-.329*	.643**	.306*
	Sig. (2-tailed)						.431	.000	.741	.391	.021	.000	.032
MeanSlopeLX1	Pearson Correlation						.49	.49	.49	.49	.49	.49	.49
	Sig. (2-tailed)						.017	.076	.000	.001	.000	.012	.000
RunoffriskLX1	Pearson Correlation						1.000	-.148	-.587**	-.474**	.567**	-.358*	-.957**
	Sig. (2-tailed)							.311	.000	.000	.000	.000	.000
ArtificialLX1	Pearson Correlation							1.000	.169	.188	.015	.236	.061
	Sig. (2-tailed)								.245	.195	.919	.103	.679
Pasture	Pearson Correlation								.49	.49	.49	.49	.49
	Sig. (2-tailed)								.000	.000	.000	.000	.000
Cattle	Pearson Correlation								1.000	-.125	-.209	.625**	.222
	Sig. (2-tailed)									.394	.150	.000	.125
ForestLX1	Pearson Correlation									.773**	-.491**	.251	.529**
	Sig. (2-tailed)									.000	.000	.082	.000
HumansLX1	Pearson Correlation									.49	.49	.49	.49
	Sig. (2-tailed)									.000	.000	.000	.000
TWILX1	Pearson Correlation									1.000	-.231	.094	.457**
	Sig. (2-tailed)										.111	.521	.001

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Table 6.7. Pearson's correlation relationships between the independent (environmental conditions in river catchments) and dependent variables (SumMRPLX1 and WinMRPLX1 - concentrations of fwMRP in rivers) of the combined Rol-NI (EPA_NIEA) database (n = 72) used for the small scale study

Correlations													
	SumMRPLX1	WinMRPLX1	Bed1LX1	Drainage DenistyLX1	UrbanLX1	MeanSlope LX1	RundrfrskLX1	ArtificalLX1	Pasture	Cattle	ForestLX1	HumansLX1	TWILX1
SumMRPLX1													
Pearson Correlation	1.000	.906**	.330**	.056	.472**	-.390**	.536**	.443**	.527**	.483**	-.382**	.522**	.153
Sig. (2-tailed)		.000	.005	.638	.000	.001	.000	.000	.000	.000	.001	.000	.199
N	72	72	72	72	72	72	72	72	72	72	72	72	72
WinMRPLX1													
Pearson Correlation	.906**		.361**	.085	.396**	-.412**	.531**	.379**	.503**	.523**	-.369**	.560**	.130
Sig. (2-tailed)	.000		.002	.585	.001	.000	.000	.001	.000	.000	.001	.000	.275
N	72	72	72	72	72	72	72	72	72	72	72	72	72
Bed1LX1													
Pearson Correlation	.330**	.361**		.000	.146	-.461**	.267**	.135	.471**	.295	-.185	.203	.307**
Sig. (2-tailed)	.005	.002		.996	.221	.000	.024	.258	.000	.012	.120	.088	.009
N	72	72	72	72	72	72	72	72	72	72	72	72	72
DrainageDenistyLX1													
Pearson Correlation	.056	.085	.000		-.163	.573**	.374**	-.106	-.198	-.207	.133	-.147	.340**
Sig. (2-tailed)	.638	.585	.996		.172	.000	.001	.378	.095	.081	.265	.218	.004
N	72	72	72	72	72	72	72	72	72	72	72	72	72
UrbanLX1													
Pearson Correlation	.472**	.396**	.146	-.163		-.344**	.149	.885**	.127	.022	-.370**	.670**	-.014
Sig. (2-tailed)	.000	.001	.221	.172		.003	.211	.000	.289	.853	.001	.000	.905
N	72	72	72	72	72	72	72	72	72	72	72	72	72
MeanSlopeLX1													
Pearson Correlation	-.390**	-.412**	-.461**	.573**	-.344**		-.021	-.263**	-.469**	-.416**	.435**	-.352**	-.080
Sig. (2-tailed)	.001	.000	.000	.000	.003		.000	.026	.000	.000	.000	.002	.504
N	72	72	72	72	72	72	72	72	72	72	72	72	72
RundrfrskLX1													
Pearson Correlation	.536**	.531**	.267**	.374**	.149	-.021		.1000	.207	.274*	-.143	.277*	.081
Sig. (2-tailed)	.000	.000	.024	.001	.211	.863		.081	.021	.020	.232	.019	.498
N	72	72	72	72	72	72	72	72	72	72	72	72	72
ArtificalLX1													
Pearson Correlation	.443**	.379**	.135	-.106	.885**	-.263**	.207		.1000	.047	-.288*	.660**	.022
Sig. (2-tailed)	.000	.001	.258	.378	.000	.026	.081		.697	.865	.014	.000	.855
N	72	72	72	72	72	72	72	72	72	72	72	72	72
Pasture													
Pearson Correlation	.527**	.503**	.471**	-.198	.127	-.469**	.272*	.047		.1000	-.480**	.319**	.005
Sig. (2-tailed)	.000	.000	.000	.095	.289	.000	.021	.697		.72	.72	.006	.969
N	72	72	72	72	72	72	72	72	72	72	72	72	72
Cattle													
Pearson Correlation	.483**	.523**	.295*	-.207	.022	-.416**	.274*	.020	.764**		-.397**	.284*	.005
Sig. (2-tailed)	.000	.000	.012	.081	.863	.000	.020	.865	.000	.001	.001	.016	.966
N	72	72	72	72	72	72	72	72	72	72	72	72	72
ForestLX1													
Pearson Correlation	-.382**	-.369**	-.185	.133	-.370**	.435**	-.143	-.288*	-.480**	-.397**		-.391**	-.019
Sig. (2-tailed)	.001	.001	.120	.265	.001	.000	.232	.014	.000	.001	.72	.001	.872
N	72	72	72	72	72	72	72	72	72	72	72	72	72
HumansLX1													
Pearson Correlation	.522**	.560**	.203	-.147	.670**	-.352**	.277*	.660**	.319**	.284*	-.391**	1.000	-.009
Sig. (2-tailed)	.000	.000	.088	.218	.000	.002	.019	.000	.006	.016	.001	.72	.940
N	72	72	72	72	72	72	72	72	72	72	72	72	72
TWILX1													
Pearson Correlation	.153	.130	.307**	.340**	-.014	-.080	.081	.022	.005	.005	-.019	-.009	1.000
Sig. (2-tailed)	.199	.275	.009	.004	.905	.504	.498	.855	.969	.966	.872	.940	.72
N	72	72	72	72	72	72	72	72	72	72	72	72	72

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

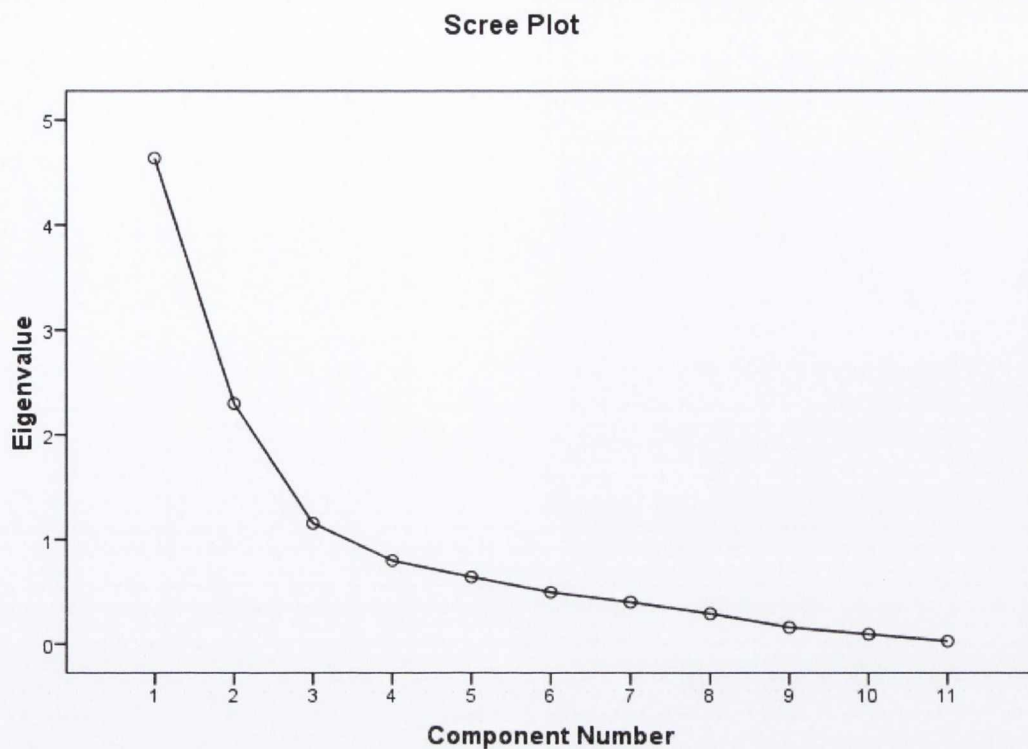


Figure 6.4a. Scree plot from PCA of the significant predictors (environmental conditions in river catchments) of concentrations of fwMRP in rivers using data from the RoI (EPA) database (n = 49, 11 variables)

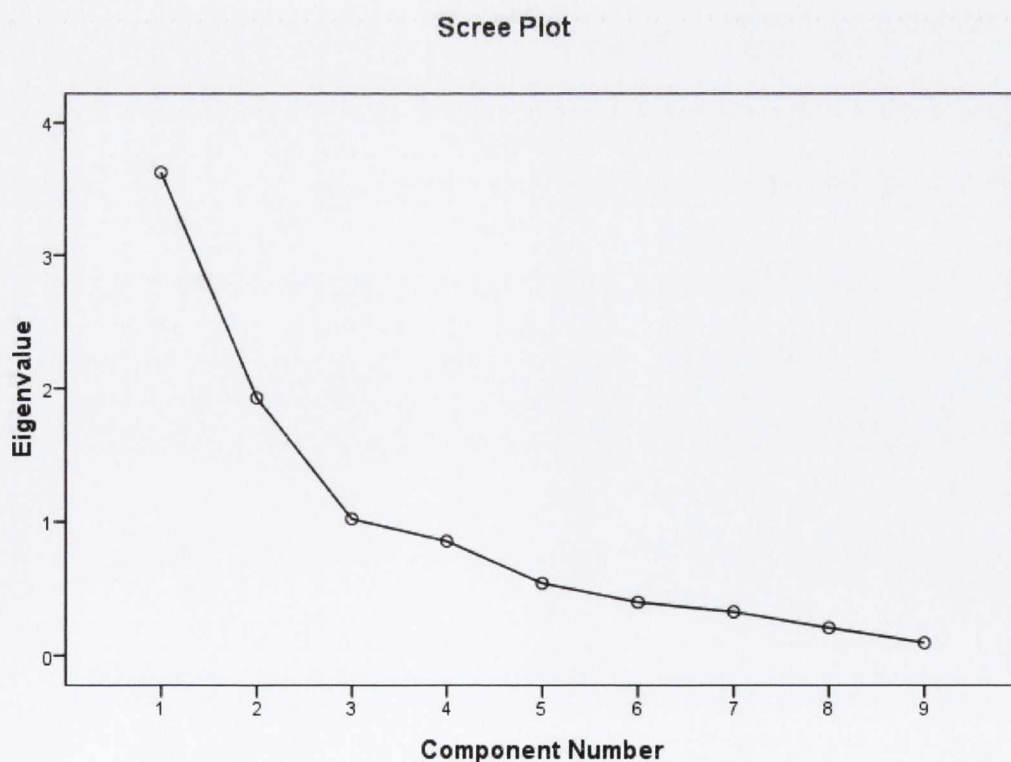


Figure 6.4b. Scree plot from PCA of the significant predictors (environmental conditions in river catchments) of concentrations of fwMRP in rivers using data from the RoI-NI (EPA_NIEA) database (n = 72, 9 variables)

Component Plot in Rotated Space

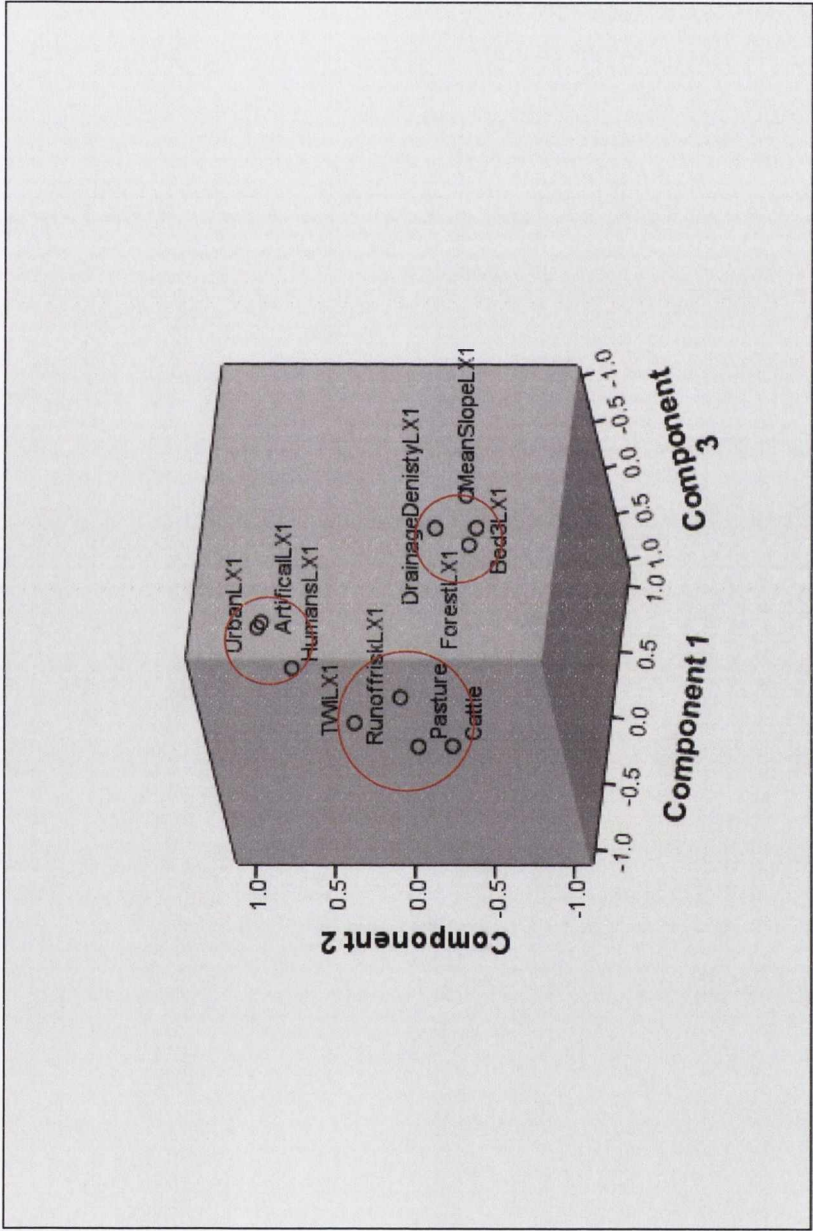


Figure 6.5a. Principal component analysis plot in rotated space (varimax rotation) showing significant predictors (environmental conditions) of concentrations of fwMRP in rivers. Data used are from the Rol (EPA) database (n = 49, 11 variables). Three Principal components were extracted (shown in the red circles)

Component Plot in Rotated Space

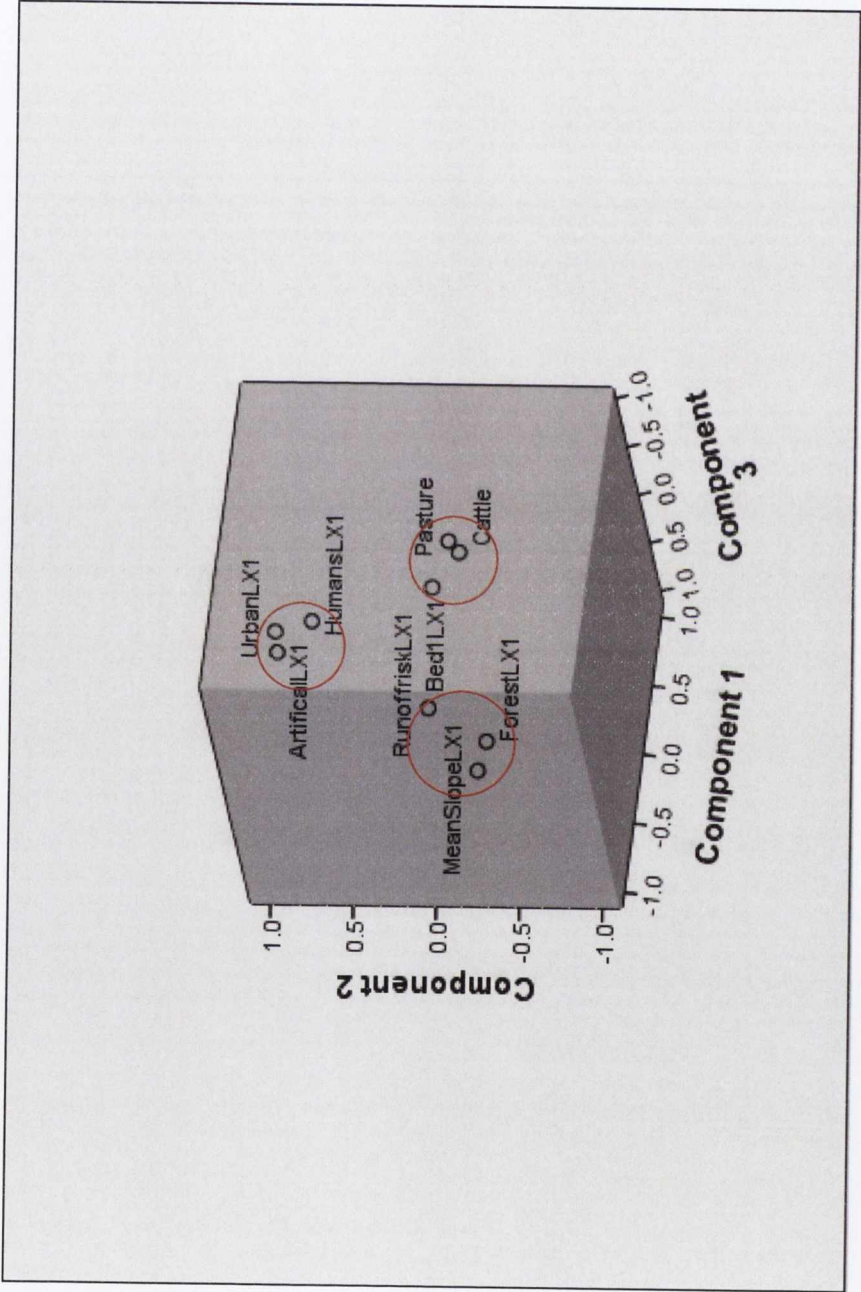


Figure 6.5b. Principal component analysis plot in rotated space (varimax rotation) of the significant predictors (environmental conditions) of concentrations of fwMRP in rivers. Data used are from the combined Rol-NI (EPA_NIEA) database (n = 72, 9 variables). Three Principal components were extracted (shown in the red circles)

Table 6.8a. Total variance explained by each Principal component from PCA performed on the significant predictors (environmental conditions in river catchments) of concentrations of fwMRP in rivers. Data used are from the Rol (EPA) database (n = 49, 11 variables)

Principal component	Initial eigenvalues		Extraction sums of squared loadings			Rotated sums of squared loadings	
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total
1	4.638	42.163	42.163	4.638	42.163	42.163	4.122
2	2.298	20.892	63.055	2.298	20.892	63.055	2.764
3	1.155	10.502	73.556	1.155	10.502	73.556	1.205
4	0.799	7.265	80.821				
5	0.642	5.832	86.653				
6	0.496	4.509	91.162				
7	0.401	3.645	94.807				
8	0.291	2.644	97.452				
9	0.16	1.45	98.902				
10	0.093	0.848	99.75				
11	0.028	0.25	100				

Table 6.8b. Total variance explained by each Principal component from PCA of the significant predictors (environmental conditions in river catchments) of concentrations of fwMRP in rivers using data from combined Rol-NI (EPA_NIEA) database (n = 72, 9 variables)

Principal component	Initial eigenvalues			Extraction sums of squared loadings			Rotated sums of squared loadings
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	
1	3.625	40.281	40.281	3.625	40.281	40.281	2.793
2	1.93	21.44	61.722	1.93	21.44	61.722	2.671
3	1.022	11.355	73.077	1.022	11.355	73.077	1.113
4	0.855	9.503	82.58				
5	0.541	6.01	88.59				
6	0.399	4.428	93.018				
7	0.326	3.624	96.642				
8	0.207	2.305	98.947				
9	0.095	1.053	100				

Table 6.9a. Principal component analysis scores of the variables representing environmental conditions in study river catchments of the Rol (EPA) database (n = 49, 11 variables). Bold font indicates the assignment of the particular environmental condition to the relevant Principal component

Predictor (environmental condition in river catchment)	Principal component		
	1	2	3
Cattle	-0.720	-0.295	0.400
Pasture	-0.837	-0.117	0.240
DrainageDensityLX1	0.797	-0.059	0.203
UrbanLX1	-0.131	0.925	-0.046
MeanSlopeLX1	0.866	-0.282	-0.057
RunoffRiskLX1	0.013	0.181	0.921
ArtificialLX1	-0.032	0.924	0.040
ForestLX1	0.631	-0.295	0.149
HumansLX1	-0.236	0.739	0.247
TWILX1	-0.830	0.248	-0.007
Bed3LX1	0.598	-0.378	-0.086

Extraction method: PCA
 Rotation Method: Varimax with Kaiser Normalisation
 Rotation Converged in 4 iterations

Table 6.9b. Principal component analysis scores of the variables representing environmental conditions in study river catchments in the combined Rol-NI (EPA_NIEA) database (n = 72, 9 variables). Bold font indicates the assignment of the particular environmental condition to the relevant Principal component

Predictor (environmental condition in river catchment)	Principal component		
	1	2	3
Cattle	0.822	-0.049	0.208
Pasture	0.886	0.020	0.184
UrbanLX1	0.076	0.948	-0.011
MeanSlopeLX1	-0.711	-0.321	0.289
RunoffRiskLX1	0.178	0.162	0.914
ArtificialLX1	-0.003	0.941	0.091
ForestLX1	-0.603	-0.382	0.140
HumansLX1	0.289	0.776	0.180
Bed1LX1	0.585	0.090	0.237

Extraction method: PCA
 Rotation Method: Varimax with Kaiser Normalisation
 Rotation Converged in 4 iterations

Table 6.10. Parameters of the multiple regression models (PCA-based) constructed to explain concentrations of fwMRP in the 72 study rivers using the environmental conditions of their respective catchments (encompassed as three Principal components). Diagnostic analysis for the winter and summer models based on both the Rol (EPA) and the combined Rol-NI (EPA_NIEA) databases are shown

Model/ Season	Unstandardised coefficients									
		B	Standard error	t value	Sig. level	Unique adj R ²	Model R ²	Model adj R ²	p-value	VIF
EPAdatabase Winter	Intercept	1.434	0.025	56	< 2E-16					
	PCA1	-0.167	0.026	-6.53	5.09E-08	0.29				1.0
	PCA2	0.119	0.026	4.65	2.93E-05	0.14				1.0
	PCA3	0.143	0.026	5.574	1.33E-06	0.21	0.6793	0.6579	3.49E-11	1.0
						Total 0.63				
EPAdatabase Summer	Intercept	1.499	0.027	54.603	< 2E-16					
	PCA1	-0.186	0.028	-6.69	2.95E-08	0.29				1.0
	PCA2	0.154	0.028	5.555	1.42E-06	0.19				1.0
	PCA3	0.145	0.028	5.226	4.32E-06	0.17	0.6958	0.6755	1.08E-11	1.0
						Total 0.65				
EPA_NIEAdatabase Winter	Intercept	1.476	0.028	51.834	< 2E-16					
	PCA1	0.182	0.029	6.338	1.60E-07	0.25				1.0
	PCA2	1.139	0.029	4.865	7.10E-06	0.14				1.0
	PCA3	0.142	0.029	4.961	4.95E-06	0.15	0.5654	0.5462	2.51E-12	1.0
						Total 0.53				
EPA_NIEAdatabase Summer	Intercept	1.549	0.031	49.718	< 2E-16					
	PCA1	0.190	0.031	6.042	1.90E-06	0.22				1.0
	PCA2	0.173	0.031	5.504	1.20E-06	0.18				1.0
	PCA3	0.156	0.031	4.964	4.90E-06	0.14	0.5735	0.5547	1.33E-12	1.0
						Total 0.54				

6.3.4. Results of variogram modelling

The experimental variograms detected spatial dependence in all four dependent variables (i.e. seasonal MRPLX1 values for both the Rol and Rol-NI databases) and the residuals of the multiple regression models that were based on principal components. The variogram structure and best-fitted models are shown in Figures 6.6 and 6.7. All models were tested for isotropic, Euclidian distance correlation, and were fitted with a spherical model. Table 6.11 summarises the degree of fit between model parameters and variogram structures. Overall, the nugget, sill and range parameters values were smaller (with one exception) than the values estimated by direct variogram analysis on the dependent variable (MRPLX1). The highest decreases of nugget values between dependent and residual models were associated with the combined Rol-NI database. Conversely, models based on the Rol (EPA) database showed a large decline of sill value from the dependent to residual model parameters when compared with the combined Rol-NI database. The distances at which SumMRPLX1 were no longer spatially correlated were 93 km and 71 km for, respectively, the Rol database and combined Rol-NI database. However, the residuals of both summer regression models had spatial dependence up to 102 km (Rol database) and 55 km (Rol-NI database).

6.3.5. Outputs of RK

Generation of geospatial models (by the application of RK on a combination of regression and variogram models developed using data from the Rol (EPA) database) generated R^2 values of 0.70 (summer) and 0.71 (winter) (Table 6.12). The equivalent R^2 values for geospatial models using the combined Rol-NI database were 0.56 (summer) and 0.58 (winter). All four geospatial models produced higher R^2 values than their corresponding regression model. Table 6.12 also summarises cross-validation diagnostics (RMSE) for each model. The lowest RMSE value relates to the winter geospatial model from the Rol database, and this model also showed the largest percentage increase in explained variability of MRP (8%). In general, the R^2 values of winter models increased by a greater percentage than summer models. Cross-validation analysis produced individual predicted values for each river monitoring point: the strength of the relationships between predicted and observed data (with 95% confidence intervals) are illustrated in Figures 6.8 and 6.9. The relationships are significant at $p < 0.05$.

The results of validation using data from river monitoring points and catchments external to the calibration databases show that the winter model based on the Rol database has much higher prediction accuracy than the summer model; the RMSE for winter prediction is $7 \mu\text{g l}^{-1}$ and $18 \mu\text{g l}^{-1}$ for summer (Table 6.13). Standardising the RMSE (RMSE divided by the standard deviation of

the observed values) provides a means to compare between different models: a standardised RMSE of 0.4 or less indicates good prediction accuracy (Hengl *et al.*, 2004). The winter model has a standardised RMSE of 0.3, within the limit of 0.4 recommended. The summer model, however, has poorer predictive ability (RMSE 18 $\mu\text{g l}^{-1}$) and a standardised RMSE of 1.9. Notably, the predictions from the summer model were predominately over-estimations, indicating that the model was simulating the transfer of greater amounts of MRP in the summer than observed in the rivers used for validation purposes.

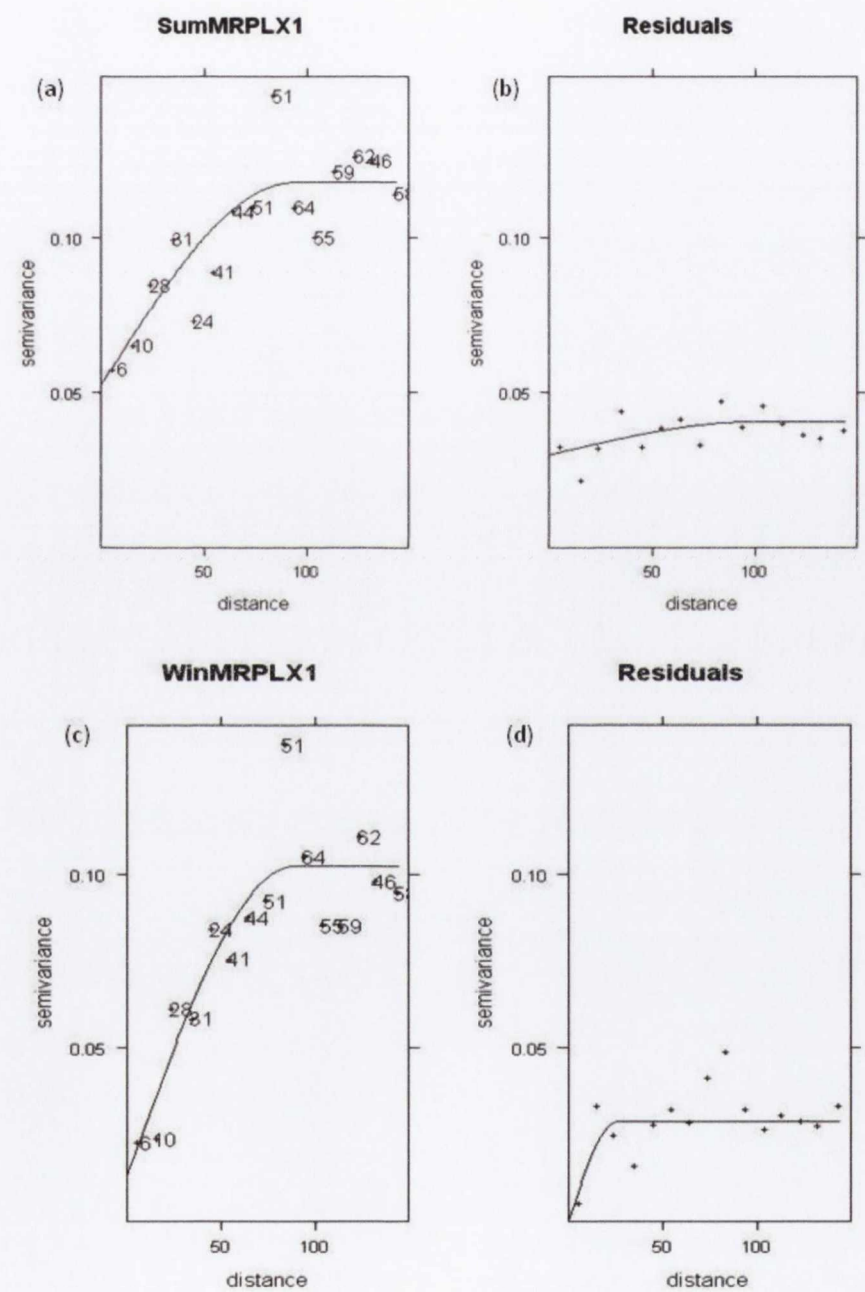


Figure 6.6. Variogram models for the RoI (EPA) database: (a) based on the dependent variable (MRPLX1) for summer (b) based on the residuals of the regression models (using Principal components) for summer (c) based on the dependent variable (MRPLX1) for winter (d) based on the residuals of the regression models (using Principal components) for winter

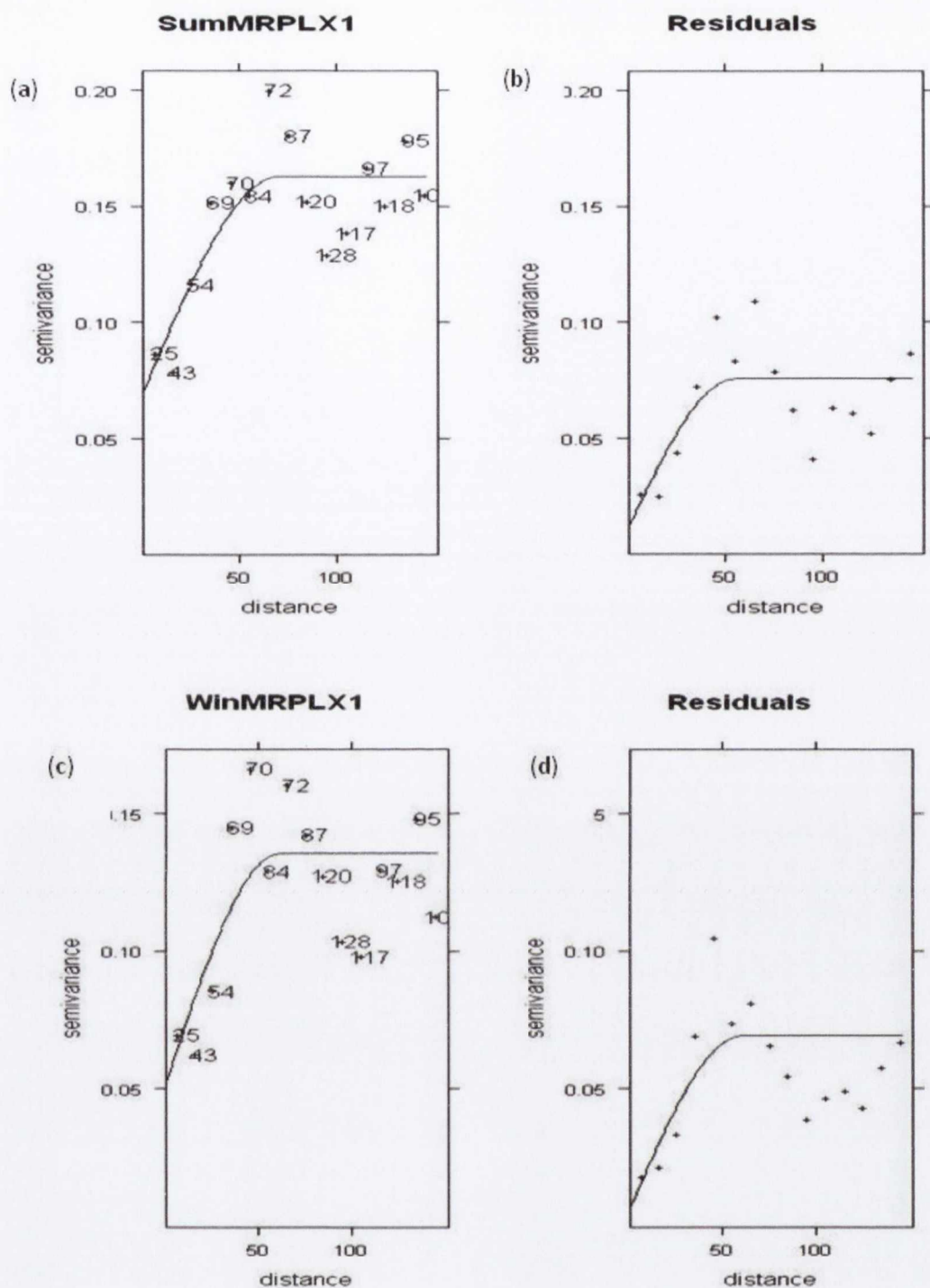


Figure 6.7. Variogram models for the combined RoI-NI (EPA_NIEA) database: (a) based on the dependent variable (MRPLX1) for summer (b) based on the residuals of the regression models (using Principal components) for summer (c) based on the dependent variable (MRPLX1) for winter (d) based on the residuals of the regression models (using Principal components) for winter

Table 6.11. Parameters of the variogram models (winter and summer) based on the dependent variables (SumMRPLX1 and WinMRPLX1) and residuals of the summer and winter regression models (based on Principal components) for both the Rol (EPA) database and the combined Rol-NI (EPA_NIEA) database. The nugget (C_0) variance corresponds to spatially uncorrelated variation (for example, measurement errors and variation that occurs over distances less than the shortest distance between river monitoring points). The sill variance ($C_0 + C$) is the maximum measure of semivariance at the autocorrelation range (a) that marks the limit of spatial dependence between two river monitoring points.

Dependent variable	Database	Variogram model	Nugget (C_0)	Sill ($C_0 + C$)	Range (a) km
SumMRPLX1	EPAdatabase	Spherical	0.053	0.065	93.360
Residuals (Sum)	EPAdatabase	Spherical	0.030	0.011	102.076
WinMRPLX1	EPAdatabase	Spherical	0.013	0.089	88.692
Residuals (Win)	EPAdatabase	Spherical	0.000	0.029	26.306
SumMRPLX1	EPA_NIEAdatabase	Spherical	0.070	0.093	71.058
Residuals (Sum)	EPA_NIEAdatabase	Spherical	0.012	0.063	54.977
WinMRPLX1	EPA_NIEAdatabase	Spherical	0.052	0.083	61.353
Residuals (Win)	EPA_NIEAdatabase	Spherical	0.007	0.062	60.880

Table 6.12. Parameters of the summer and winter geospatial model constructed from a merger of the multiple regression models (Principal component-based) and variogram models developed. Data for the models are from both the RoI (EPA) and combined RoI-NI (EPA_NIEA) databases. The geospatial models collectively explain the concentration of fwMRP in rivers as a function of environmental conditions (regression model component) in their respective catchments and the measure of spatial correlation between river monitoring points (variogram model component)

Geospatial model	Database	ME	MAE	RMSE	R ²	R ² (corresponding regression model)	% explained variance increase
SumMRPLX1	EPAdatabase	0.003	0.148	0.184	0.695	0.676	3
WinMRPLX1	EPAdatabase	0.004	0.124	0.161	0.714	0.658	8
SumMRPLX1	EPA_NIEAdatabase	4.520E-04	0.180	0.262	0.556	0.555	0.2
WinMRPLX1	EPA_NIEAdatabase	4.288E-06	0.148	0.231	0.579	0.546	6

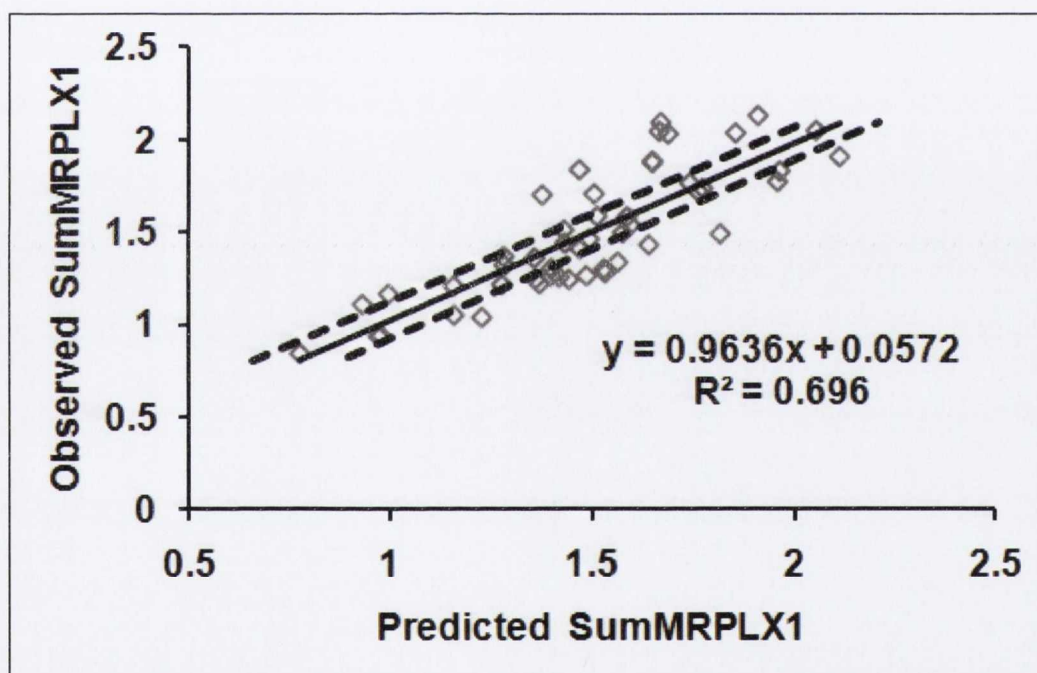
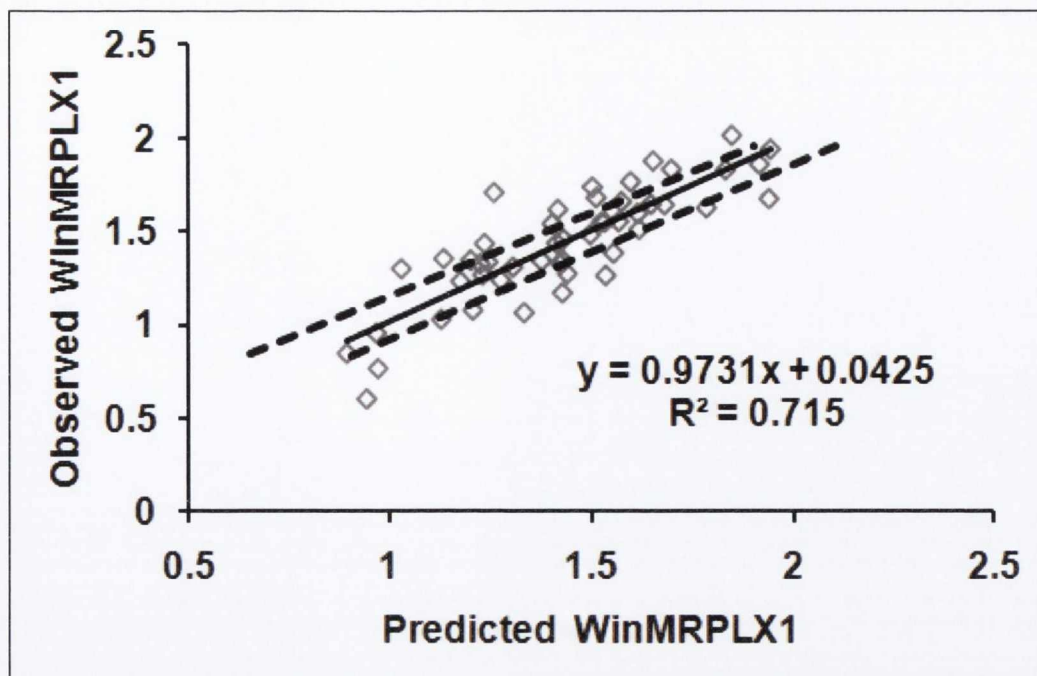


Figure 6.8. Simple linear regression plots (showing 95% confidence limits) between concentrations of observed MRPLX1 and MRPLX1 predicted from the geospatial models, $n = 49$, $p < 0.05$, Rol (EPA) database

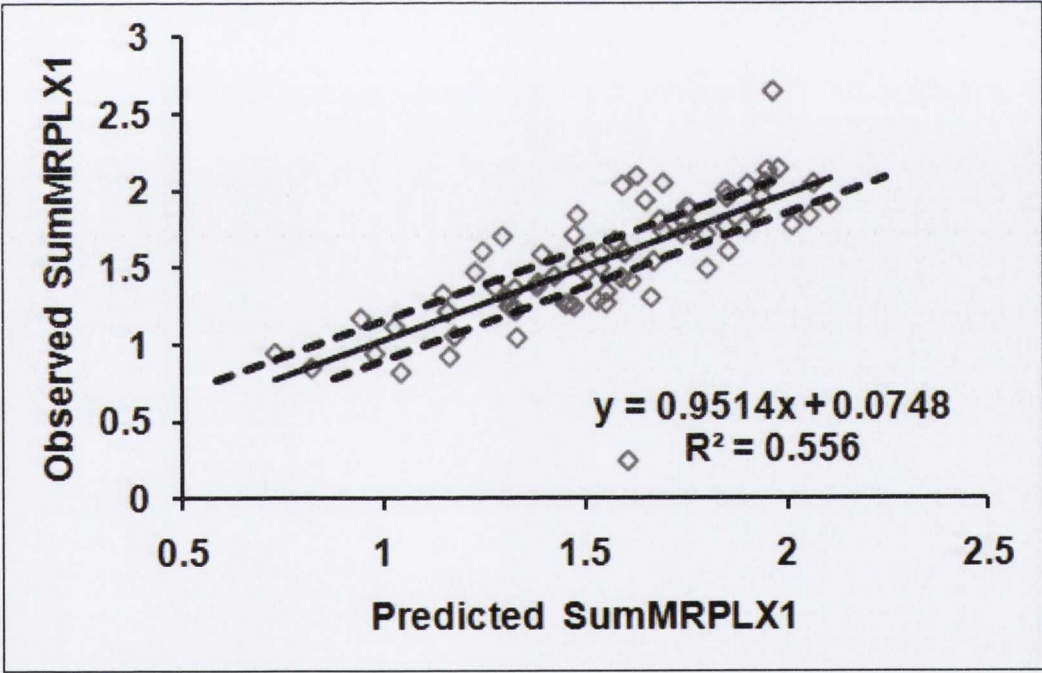
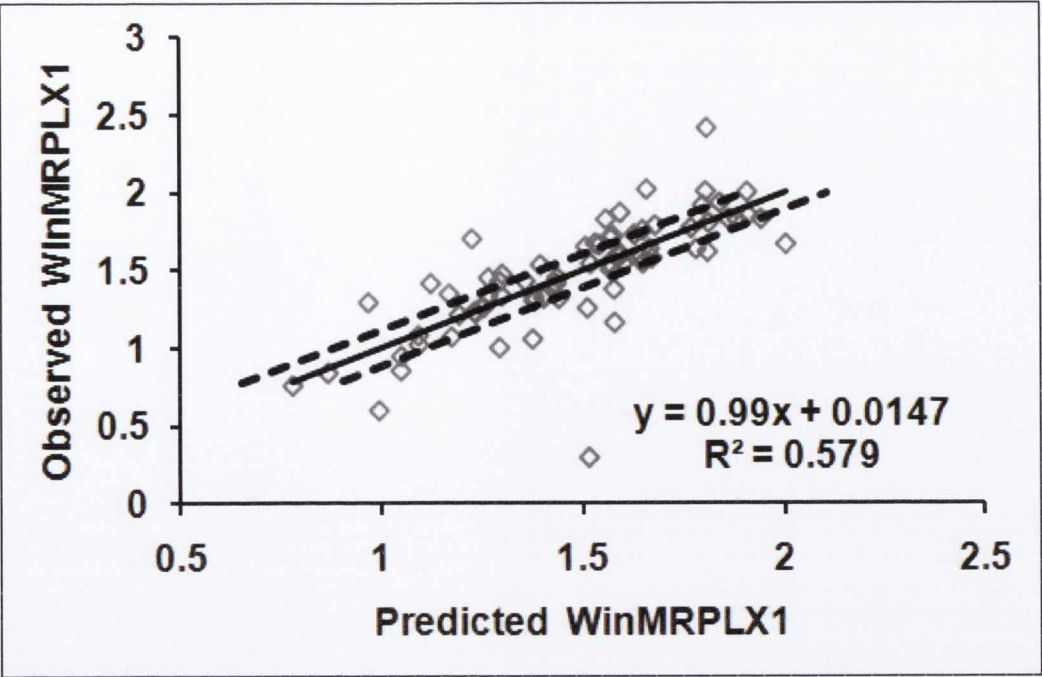


Figure 6.9. Simple linear regression plots (showing 95% confidence) limits between concentrations of observed MRPLX1 and MRPLX1 predicted from the geospatial models, n = 72: combined Rol-NI (EPA_NIEA) database

Table 6.13. Observed and predicted fwMRP concentrations ($\mu\text{g l}^{-1}$) for the five river catchments in the RoI used for validation of the summer and winter geospatial models developed from the RoI (EPA) database. CI = confidence interval

Validation catchment number	Observed fwMRP µg l ⁻¹	Predicted fwMRP (± 95% CI) µg l ⁻¹	RMSE µg l ⁻¹
Summer			
V1	13.10	12.72 ± 0.10	18.38
V2	10.78	40.19 ± 0.09	
V3	6.00	14.36 ± 0.10	
V4	15.00	32.57 ± 0.09	
V5	21.12	26.53 ± 0.10	
Winter			
V1	17.28	11.98 ± 0.01	7.08
V2	41.85	35.58 ± 0.02	
V3	6.00	17.06 ± 0.03	
V4	21.47	26.31 ± 0.02	
V5	13.72	19.84 ± 0.02	

6.4 Discussion

This component of the research set out to test the H_0 that there was no relationship between environmental variables at the landscape-scale and P values for river quality. In order to carry out the test, several georeferenced spatial datasets relating to agriculture, residential, urban and natural processes were used first to explore the possibility of relationships and second to quantify the form and extent of any deterministic relationships identified. Notwithstanding constraints imposed by limited availability of data, results obtained provided sufficient grounds to refute the H_0 . Moreover, the analysis presented here identifies the broad-scale level of influence particular environmental parameters apply on P concentrations in rivers. Elevated concentrations of P are associated with high values for topographic wetness saturation, runoff potential of gley soils, bedrock geology vulnerable to weathering, agricultural activities (land used for pasture and cattle density) and human residential parameters (population density and urban and artificial areas) in river catchments. However, high values for topographic variables such as mean slope, drainage capacity and the proportion of underlying bedrock resistant to weathering in catchments were associated with lower concentrations of P in rivers. Moreover, the results highlighted that, even after controlling for the environmental variables mentioned above, unexplained variation in P concentrations can be explained, in part, by a spatial correlation relationship between monitoring points in close proximity.

Statistically significant relationships were found to exist between fwMRP and several environmental parameters within the study catchments. These relationships collectively reflected the influence of environmental conditions on the loading and transportation of P from a terrestrial source in catchments to rivers. However, the causal relationships and prediction strengths underlying the associations between the individual predictor variables are complex, owing to considerable levels of multicollinearity. Two databases were constructed and utilised in the research – one comprised only sites in the RoI (EPA) database, the other comprised the RoI sites in combination with sites in NI (EPA_NIEA database). Differences in performance between models derived from the two databases were evident, with the combined database in general performing less well when compared with the performance of the RoI database. The DEM for NI was more coarsely resolved than the DEM for the RoI (50 m, compared with 20 m). As a result, variables derived from the DEM (drainage density, TWI and mean slope) were also more coarsely resolved, and this is likely to have influenced their predictive ability (Shiels, 2010).

6.4.1. Environmental determinants of P concentrations in rivers

The impact of urbanisation on concentrations of P in rivers was evident in both databases, owing to significant positive relationships between fwMRP and human population density in particular, but also the percentage of urban cover and artificial surfaces. The association between human population and negative water quality conditions has been widely reported (Johnes *et al.*, 1996; Bennett *et al.*, 2001; Donohue *et al.*, 2006; de Quevedo and Paganini, 2011; Mouri *et al.*, 2011). In this study, human population density was the strongest anthropogenic-sourced influence on P in the rivers, while proportions of urban and artificial surface land covers were also important, albeit less dominant.

Across the Irish Ecoregion, wastewaters from most rural dwellings are piped to and treated by septic tank systems. Given that some river catchments in this study did not contain WWTPs, the highly significant association between P concentration and human population levels suggest that septic tanks - particularly when they are poorly sited and not properly maintained - are an unsustainable form of wastewater treatment if measures aimed at reducing concentrations of P in rivers from rural sources are to succeed. The relationship between fwMRP and human population density was slightly stronger in winter than in summer, suggesting peak anthropogenic influence during what is often hydrologically the most variable period. However, retention of P in river sediments during the summer could have caused decreases in the concentrations of P observed in the water samples at this time, thus altering the relationships and causing the decreased explanation of variance (May *et al.*, 2001). Conversely, the variance of fwMRP explained by the percentage of urban and artificial surfaces was greater in summer than winter, indicating that these land covers pose a much higher risk of nutrient enrichment in rivers during the ecologically sensitive summer period when compared with winter. This finding most likely reflects the dominance of discharges from WWTPs, industry or runoff from artificial surfaces accounting for a significant proportion of P in riverflow during the summer months. Despite the continued control on discharges associated with sewage effluent together with improvements in treatment processes, this study highlights that urban areas/high densities of human population (usually contributing point sources of P) still have a major effect on the flow-weighted P concentrations of rivers in urban and rural catchments across the Irish Ecoregion.

Grassland based farm enterprises, specifically beef and dairy production, dominate the agricultural sector across the Irish Ecoregion, comprising, for instance, 90% of utilised agricultural area in the RoI (CSO, 2010). Of the agricultural-related variables investigated in this study, the percentage of pasture grasslands and the density of cattle population in catchments were drivers with positive impacts on concentrations of fwMRP in both the RoI and RoI-NI databases. The

percentage composition of pasture in a catchment explained 5% (Rol) and 3% (Rol-NI) more variance of fwMRP in summer than winter. The opposite was the case for cattle density, 6% (Rol) and 5% (Rol-NI) more variation in winter. These relationships reflect complex interactions in the agricultural landscape locally and are likely to be indicative of seasonally varying agricultural practices, including the spreading of fertilisers and housing over-winter of livestock. Positive relationships between pasture grasslands and P in waterbodies have been identified in other studies (Johnes and Heathwaite, 1997; Belsky *et al.*, 1999; Wood *et al.*, 2005; Withers *et al.*, 2007; Miller *et al.*, 2010) and Ireland's grass-based agricultural production system is known to contribute a significant proportion of soluble P to freshwaters (Kurz *et al.*, 2005). Over-fertilisation of pasture land and subsequent leaching from soils to freshwaters accounts for the relationship between pasture grassland and P concentrations (Cuttle and James, 1995; Withers *et al.*, 2007). However, historical additions of P that have subsequently accumulated in soils are also likely to be a factor through contributing to losses from leaching and runoff (Tunney, 2000; Jordan *et al.*, 2005b; Schulte *et al.*, 2010). Cattle stocking densities were also directly related to fwMRP concentrations in the study catchments. Moreover, pasture composition and cattle density were strongly related. Cattle are responsible for contributing both point and diffuse sources of P to rivers (McGechan *et al.*, 2005), either through direct addition of their faeces and urine or indirectly as a result of their physical destruction of river banks and re-suspension of river sediments (Jarvie *et al.*, 2010; Miller *et al.*, 2010).

Poorly drained (typically gley) soils are extensive across the Irish Ecoregion (Diamond and Sills, 2001), comprising impermeable soils on drumlins and slowly permeable soils on limestone, sandstone and shale formations. Gleys are characterised by waterlogging, which increases the risk of overland flow owing to saturation excess (Chesworth, 2008). A direct relationship was found between the potential for runoff and concentrations of fwMRP, with little seasonal variation in R^2 values evident, thus supporting the findings of Diamond and Shanley (1998). On the basis of results presented here, waterlogging of soils appears to have a greater influence over P concentrations in rivers in NI than in Rol: in the combined Rol-NI database, runoff risk was the first ($R^2 = 0.29$, $p < 0.05$) and second ($R^2 = 0.28$, $p < 0.05$) strongest predictor of fwMRP in summer and winter, respectively, whereas in the database comprising only catchments in the Rol, runoff risk was a slightly weaker predictor (summer and winter $R^2 = 0.25$, $p < 0.05$) and was not as influential as other catchment-linked variables. This finding may be a result the influence of a much larger proportion of gley soils in the NI catchments (44% of total catchment area) than the equivalent in the Rol catchments (28%). However, differences in the resolution of the DEM data used for the Rol and NI may have suppressed artificially the influence of catchment mean slope and TWI (the strongest predictors in the Rol database) for the NI catchments, because of their

more coarse resolution in the latter, thereby raising the relative hierarchal prominence of runoff potential as an explanatory variable.

A mean value for the slope of the land in catchments was inversely related to concentrations of fwMRP in rivers, with the lowest P values occurring with the steepest gradients, as has previously been reported for subcatchments in the Lough Mask catchment in the Rol by Donohue *et al.* (2005). Mean slope was the strongest predictor of fwMRP in the Rol database (summer $R^2 = 0.38$ and winter $R^2 = 0.4$) but was one of the weaker in the combined Rol-NI database (summer $R^2 = 0.15$ and winter $R^2 = 0.17$), again possibly owing to in the more coarse defined DEM data for NI. A combination of higher levels of precipitation, thinner soils, less vegetation, bedrock resistant to weathering, groundwater contribution and a decreased influence of anthropogenic and agricultural pressures explains the low P concentrations in upland and high relief parts of catchments (Soulsby *et al.*, 1998; Bowes *et al.*, 2003).

Of the environmental conditions in river catchments considered in this research, TWI was the second strongest driver of fwMRP, with an increase in TWI leading to higher fwMRP concentrations, (summer $R^2 = 0.32$ and winter $R^2 = 0.38$) in river catchments in the Rol. A proxy for overland flow owing to saturation-excess, TWI is a measure of an important mechanism involved in the transfer of large loads of P from land to freshwaters. Catchments can contain relatively small but well defined areas of saturation that can be responsible for a large proportion of overland flow (Gburek and Sharpley, 1998; Pionke *et al.*, 2000; Diamond and Sills, 2001). Where such areas overlap with high levels of soil P, substantial exports of P to freshwaters can arise (Gburek and Sharpley, 1998; Sharpley *et al.*, 2001; Gburek *et al.*, 2002).

The extent of forestry cover was found to be inversely related to fwMRP. Relative to other environmental conditions, forestry showed intermediate prediction strength but was most influential in the river catchments in the Rol. The seasonal difference in explained variance of fwMRP was just 1%, implying that forestry-related processes that release/abstract P to or from the landscape vary little seasonally. Previous studies show that the presence of tree cover, buffer filter zones and associated natural processes leads to a decline in P export to freshwaters (Ballester *et al.*, 2003; Anbumozhi *et al.*, 2005; Mouri *et al.*, 2011). Forests utilise nutrients in a largely closed cycle (Abelho, 2001), resulting in relatively low losses to the drainage network. Moreover, forested areas typically have wider and more continuous riparian buffer zones (Booth, 1991) that protect aquatic systems by controlling runoff (Rodgers *et al.*, 2010). However, several studies have identified forest management practices, such as felling and the application of fertilizers, as diffuse sources of P (Ensign and Mallin, 2001; Nisbet, 2001; Cummins and Farrell,

2003; O'Driscoll *et al.*, 2011). These management operations alter nutrient cycling, hydrological conditions, P availability and export pathways, increasing the delivery of P to freshwaters (Piirainen *et al.*, 2007; Kreutzweiser *et al.*, 2008; Rodgers *et al.*, 2010). Nevertheless, the results of this study support the contention that, at the landscape scale at least, forestry has not caused major impairment of rivers by P in the Ecoregion of Ireland and can act as a filter to reduce loadings of P to rivers (Forest Service, 2000).

Geology was found to influence the concentrations of fwMRP in rivers. Two different categories of bedrock were the best predictor of fwMRP for each of the study databases. For the Rol rivers, bedrock type 3, the percentage composition of geological cover resistant to weathering, was found to be inversely related to fwMRP (summer $R^2 = 0.28$ and winter $R^2 = 0.21$). The percentage of bedrock type 1 (bedrock susceptible to weathering) was positively related to fwMRP in the combined Rol-NI database and explained a slightly higher percentage of fwMRP variance in winter (summer $R^2 = 0.11$ and winter $R^2 = 0.13$). The distribution of P concentrations in rivers has a strong dependence on the composition and type of bedrock geology underlying the catchment (Dillon and Kirchner, 1975a; Rothwell *et al.*, 2010). Interdependent relationships between bedrock types and additional predictor variables (drainage density, % urban, mean slope, % artificial area, % pasture, % forest, human density, runoff risk and TWI) were evident in the correlation matrices. Geology has a direct impact on overlying environmental conditions, such as hydrology, soils and relief, which are expected to influence P transfer (Skinner *et al.*, 2004). In England and Wales geological conditions are used in definition of geoclimatic regions that have largely similar ranges of nutrient export potential (and nutrient retention capacity) as a function of flow volume, timing and routing from land to river (Johnes and Butterfield, 2002). Geology can also indirectly affect P loading, for example, through its influence on human settlement and agriculture (Legg and Taylor, 2006; Jaroslaw and Hildebrandt-Radke, 2009).

6.4.2. Spatial dependence between river monitoring points

The regression models (based on Principal components) constructed in this research display relatively good predictive abilities (R^2 values from 0.55 to 0.68). However, results from variogram analysis also show that further variation in P can be explained by accounting for spatial correlation between river monitoring points in close proximity to each other (up to a maximum distance of 102 km in this study). Substantial evidence in the research literature supports the concept of correlation in nutrient data between monitoring points in rivers and lakes (Peterson and Urquhart, 2006; Kočić *et al.*, 2008; Gardner and McGlynn, 2009; Yang and Jin, 2010). Nevertheless, few water quality studies have examined the spatial structure of errors left over

after regression analysis, and even fewer examine P values, giving limited scope for direct comparison with the results of this study.

The proportion of variance that was not spatially structured (nugget variance) was low in the variogram models, suggesting that very little measurement error or spatial dependence at scales smaller than those measured affects the data (Isaaks and Srivastava, 1989). The distance up to which concentrations of fwMRP are spatially correlated ranged from 26 km in the winter to 102 km in the summer. These relatively long distances imply that P concentrations are correlated between monitoring sites that are far apart. The maximum range between the river monitoring points feasible in this study is approximately 450 km (catchment numbers 1 and 45), making the finding here possible.

A correlation range up to a distance of 102 km may be attributed to the significant regional variation in the sources and environmental stressors of P across the Irish Ecoregion. The RoI and NI census data show evidence of significant regional variation in farm structures and activities, livestock densities, landuse, human population and municipal and industrial discharges across the Irish Ecoregion. The north-west and western parts of the RoI, for example, have relatively high concentration of small, intensively operated beef farms, and a lower proportion of inhabitants and WWTPs. By comparison, the eastern region comprises larger, more intensive dairy and tillage farms, together with a greater number of inhabitants and WWTPs. The river basins based in these areas would, therefore, have similar pressures contributing P, creating a regional pattern of concentrations of P in rivers. In support of this finding, the EPA in the RoI have acknowledged that the river basins within the east and southeast have a much higher risk of failing to achieve the water quality goals prescribed by the WFD on account of the higher concentrations of nutrients observed in rivers in these areas (EPA, 2008, 2009). Owing to the limited number of catchments used in this study, however, anisotropic correlation to detect if spatial patterns were dependent upon specific directions (Webster and Oliver, 2007) was not possible.

6.4.3. Geospatial models

The geospatial models constructed in this research improved the predictive capability of fwMRP in rivers, when compared with the strength of the regression models produced initially. This was particularly the case for rivers/catchments in the RoI database. The R^2 value in the summer geospatial models was 3% (RoI database) and 0.2% (RoI-NI database) greater than in the regression models. However, slightly larger increases occurred in the winter models (8% RoI database, 6% RoI-NI database), which may reflect a greater spatial correlation between river

monitoring points during the hydrologically more variable months, influenced by ecological and hydrological processes acting at different spatial and temporal scales. The final geospatial models based on the RoI database explained 70% (summer) and 71% (winter) of fwMRP variance, while 56% (summer) and 58% (winter) of fwMRP variance was explained by the models derived from the combined RoI-NI database. Cross-validation of all geospatial models showed that those based on the RoI database had the lower RMSE values (0.18 in summer and 0.16 in winter), and can therefore be regarded as the more accurate model when compared with their corresponding regression models and all of the models (geospatial and regression) derived from the combined RoI-NI database. Inaccuracies in the data used to calibrate the NI-RoI models are likely to have influenced the low prediction ability of these cross-border models. The validation of the RoI geospatial models, based on data from a set of five river catchments in the RoI not used previously, revealed that the winter geospatial model for the RoI had a greater predictive skill than the summer model, with the latter tending to over-estimate fwMRP concentrations. Further refinement of the RoI geospatial models, and their extension to the entire Irish Ecoregion, should be possible as greater amounts of high quality (including high spatial and temporal resolution), Irish Ecoregion-wide data become available following WFD monitoring.

Chapter 7

Discussion and Conclusion

7.1. Introduction

The importance of understanding, preventing and reversing the effects of P enrichment in rivers and lakes has never been greater. Under the WFD, POMs in catchments containing freshwaters classified as below good status or at risk of not reaching good status by 2015 must be fully implemented by the end of 2012 (Kavanagh and Bree, 2009; McNally, 2009). However, meeting good status poses a major challenge for the Irish Ecoregion. Although POMs targeted at preventing P loss from catchments have been implemented, there is inadequate information available on the most appropriate POMs in different environmental settings. The effective management of P requires unequivocal evidence of the environmental processes in a catchment that control P in freshwaters. Given the paucity of sufficient field-based resources to provide this information, the most economical and practical way of testing hypotheses, and augmenting current understanding, is through the utility of catchment-scale modelling of available data.

Chapter 2 contextualized the background of the research, providing an overview of the P transfer continuum and an inventory of widely used approaches to model the dynamics of P transfer. Building on this knowledge, a three-part methodological framework based on mathematical modelling provided a means of addressing the research questions stated at the onset of the research. Three discrete assessments were pursued, comprising:

- (i) An evaluation of the impact of sources of P and environmental conditions on the effectiveness of measures aimed at reducing the loading of P to seven rivers located in the drumlin area of the Irish Ecoregion (Chapter 4)
- (ii) An assessment of the influence of internal loading of P on the recovery of a eutrophic shallow lake draining the rivers studied in part (i) (Chapter 5)
- (iii) A landscape-scale analysis to quantify the hierarchy of environmental conditions that significantly control variation in concentrations of MRP in rivers across the Irish Ecoregion (Chapter 6)

The objective of this final chapter is to highlight the main findings and consider the supporting evidence in the context of the current literature. The practical applicability of the research models developed for use as decision-support tools in the Irish Ecoregion is discussed. Limitations of the research methods and materials employed are acknowledged and the directions for further research are highlighted. Finally, an overall conclusion to the research is provided.

7.2. Synthesis of key research findings

7.2.1. Modelling hydrological pathways of P for source apportionment at the subcatchment scale

The catchment for Lough Sheelin proved to be a suitable study area to explore spatiotemporal controls on P dynamics in response to mitigation measures at the subcatchment-scale (Chapter 4). Utility of the most appropriate and accurate means of isolating loads of P (MRP and TP) from point or diffuse origins for the time before, during and after P-related POM implementation was imperative to adequately address the guiding research question. Although Chapter 2 identified many methods for P load estimation at the catchment-scale, most of these were not suitable for the nature of the current study. For instance, process-based models were too demanding of data. Other approaches were highlighted in the literature as having large uncertainties in identifying preferential pathways of P (e.g. export coefficient model by Johnes (1996)), which are essential for load apportionment (Jordan *et al.*, 2007). Therefore, distinct relationships between loads of P delivered from point or diffuse sources and river flow were encapsulated in a LAM. This yielded the first attempt of using LAMs in this context in the Irish Ecoregion.

Modelled estimates from LAMs suggested that statistically significant temporal changes in the magnitude of the segregated P loads were coincident with the implementation of POMs in subcatchments. Lower P export rates followed specific mitigation measures of P. For example, the LAM estimated up to 80% decreases in point MRP load after enhanced P removal at WWTPs in urban subcatchments and the implementation of septic tank and agricultural bye-laws in rural subcatchments. The accuracy of the LAM estimates at indicating these reductions gave confidence in the reliability of the LAM approach to separate P load. Hence, an effective means was provided to identify variations in the effectiveness of POMs between subcatchments according to differences in P loading and environmental setting.

Previous catchment-scale studies using empirical loading estimation to examine the impact of P mitigation on water quality have produced uncertainty as to the main controls on P. The results

of such studies have most likely been limited by factors such as the complexity in approximating fluxes of P from a wide range of environmental conditions (e.g. Foy *et al.*, 1995; Johnes *et al.*, 2007). As responses to mitigation are typically site specific and depend on the interrelationship between P pressures and the inherent environmental sensitivity of the landscape, unique model coefficients were fitted for each subcatchment and time step in this study. Estimates of P load from LAMs are based directly on measured river data, therefore the loads estimated in this study are more robust compared to models based on published export coefficients that often show discrepancies for certain sources of nutrients (Johnes, 1996; Carvalho *et al.*, 2003; Frost, 1996; Foy and Lennox, 2000).

Relatively poor correlation between point-sourced loads of P estimated from the LAMs and export coefficients in this study appear to confirm the limitations of the export coefficient method for the purposes of this study. An accurate measure of P load against which outputs from LAMs can be compared (flow-weighting) was used as a second approximation in the current study. Flow-weighting is a standard and acceptable method of nutrient load estimation using empirical data (Salles *et al.*, 2008). Strong relationships were observed for both MRP and TP loads; however, the LAM method improves on the flow-weighted method by separating the P load into sources.

Identifying the effects of different mitigation measures based on annual loads of P also provides substantial uncertainty pertaining to the main controls driving high loading of P at various times during the year (Radcliffe *et al.*, 2009). Here, this problem was resolved by segregating data into seasonal components (summer and winter) and applying the LAMs to these separated data. Results of GLM showed a strong seasonal dependence of total exports of P, with distinct differences occurring in the characteristics of model parameters between summer and winter. Such as, significantly higher loads of P were delivered from point sources in summer compared to winter. In comparison, the magnitude of P from diffuse sources (linear and exponential pathways) was greater in winter periods. The LAM worked more efficiently within this seasonal framework; increased explanation of variation of P with runoff was obtained by calibrating models with data separated by seasons, rather than annual models.

Estimated sources of P in subcatchments typically reflected seasonal nutrient inputs and rainfall patterns (May *et al.*, 2001), however some LAMs based on summer data included high concentrations of P sampled at high runoff values. Observation of the timing of these diffuse-sourced loads indicates that summer storms or the first major rainfall event after the summer dry period are most likely responsible. Bowes *et al.* (2005) suggested these types of events are characteristic of the impact of the rapid entrainment and transport of P that had previously

sequestered to sediment during the low dilution of point sources of P in the dry weather conditions of the preceding months. However, beyond this hypothesis, water flow over soil after periods of hydrological inactivity is known to mobilise a flush of solutes released by biogeochemical processes during summer (Stutter *et al.*, 2008).

A novel aspect of the LAM developed here, compared with the version developed in the UK by Bowes *et al.* (2008), is the unconstrained nature of parameter coefficients. This modification allows for adjustment of the model to account for hysteresis in the P concentration-discharge relationship (House and Warwick, 1998). Data from subcatchments containing impermeable soils highlighted the importance of capturing hysteresis trajectories; a rapid increase in the export of P from diffuse sources occurred during a rising hydrograph, followed by lower values owing to source exhaustion in the declining phase. The hysteresis aspect of the model is particularly important to adequately represent these storm-induced loads of P, which typically contributed a large proportion of annual diffuse P load over a number of ephemeral events, and in some cases negated a trend of declining P concentrations in rivers.

Modelled outputs indicated that temporal and spatial heterogeneity of sources of P existed within and between subcatchments. However, a high proportion of poorly drained soils in subcatchments exerted the strongest pressure on P from diffuse sources (attributed to human population in rural areas, cattle density and the application of fertiliser to agricultural lands) entering rivers. The effectiveness of some POMs appears to have also been reduced by factors such as high rainfall and accidental pollution events, suggesting that relatively short-duration events outside the control of mitigation management may have attenuated a signal of improving water quality. Markedly, significant evidence of P from point sources was apparent in rivers draining rural subcatchments. This observation is likely due to septic tanks, farmyard runoff, cattle access points and artificial land drains (e.g. Jarvie *et al.*, 2010).

Notably, results here show that the human population in rural areas, rather than cattle stocking densities or fertiliser application, was the strongest predictor of P loads from point sources. The efficacy of POMs targeted at particular diffuse sources of P (e.g. restrictions on agricultural contributions of P) appears to have been diminished by contributions of P from septic tanks. These are small but widely distributed point sources of P. A high and dispersed human population in rural areas of the Irish Ecoregion, combined with areas of soils displaying low permeability, predisposes landscapes to the effects of poorly sited or malfunctioning septic tank systems (Douglas *et al.*, 2007). Macintosh *et al.* (2011) recently employed high-resolution technology to monitor improvements owing to the strategic replacement of defective septic tank systems with

modern systems in rural drumlin catchments (3 - 5 km²). Results showed that the concentration of P at low flows in the stream of one catchment decreased by 32 µg l⁻¹ over a four year period. However, mitigation efforts in the other catchments were offset by the construction of new houses that increased the density of septic systems, inducing greater P concentrations at low flows. Notwithstanding these clear links to septic tank pollution of waterbodies at low flow, the results of the current research also highlight that loads of P delivered to rivers from septic tanks may show diffuse-source characteristics, possibility owing to extreme runoff events flowing into and through tanks.

Rivers were found to be sensitive to flow regime, which can result in eutrophication in rivers during summer and lake enrichment in the event of storm events. In addition to estimating the magnitude of loads of P from point and diffuse supplies in the catchment, the frequency of occurrence of both sources during the year (i.e. temporal dominance) is an important factor. The R_e parameter of LAMs estimates the runoff depth at which point sources of P (runoff < R_e) or diffuse sources of P (runoff > R_e) have the predominant influence on rivers over a hydrological year. For one sewage impacted river, the LAM estimated that point sourced P contributed up to 90% of annual MRP load delivered during a hydrological year and dominated flows up to 83% of days. In the other rivers, despite diffuse P forming a majority of the annual load of P exported, point sources of P dominated flows for up to 81% during summer months. Therefore, the effectiveness of POMs focused on the amelioration of diffuse sources of P, the perceived problem as regards load magnitude, may not have been reflected in concentrations of P measured owing to the underestimation of the importance of P from point sources. This finding indicates that rivers were at a much higher risk of eutrophication in the more biologically active summer period than indicated by the load of P delivered from point sources alone.

Contributions from dispersed point sources maintain high P concentrations that are likely to sustain an enhanced trophic state in rivers, thereby threatening aquatic ecological health, particularly if high concentrations of P are in soluble, biologically-available forms and coincide with the growing season (Withers *et al.*, 2011). The extent of overlap between periods of oversupply of P and biological demand is therefore critical in determining the relative importance of different sources and their aquatic ecological impacts (Edwards and Withers, 2007). These findings have important significance as regards possible reasons for poor performances of POMs at preventing high P concentrations in rivers.

7.2.2. Identifying the changes in lake TP sedimentation rates

Although assessment of the efficiency of P mitigation is typically focused towards changes in the external loadings of P from catchments, internal loading of P must also be considered (Chapter 5). Empirical data on the release of P from lake sediments in the Irish Ecoregion are limited (but see examples of Foy (1986), Jordan *et al.* (2002), Jordan and Rippey (2003) and Hobbs *et al.* (2005)). Rather, most studies have used water quality data applied to models to generate estimates of TP sedimentation (e.g. Gibson *et al.*, 2001). In the current research, using an exclusive and high-resolution dataset on TP water quality, a recent TP budget for Lough Sheelin was reconstructed for the time before, during and after POM implementation of the P Regs. The key components driving the concentration of TP in the lake, including sedimentation rates for TP, were inferred from the data. Findings suggest that, although the lake was relatively well flushed, overall retention of TP in the sediments exceeded release. On average, 73% of TP delivered was stored in the lake sediment over the duration of the time studied. This extent of sedimentation is consistent with the sediment trapping efficiencies of similar lake types found in Ireland. However, when compared with the TP retention rates of lakes globally, 73% is at the high end of the scale (Koiv *et al.*, 2011). Brett and Benjamin (2008) suggest that lakes with short hydraulic retention times may receive relatively greater contributions of allochthonous, mineral-bound PP than lakes with longer hydraulic retention times. Considering PP is more inclined to settle (Braskerud, 2002), lakes with shorter hydraulic retention times may then display greater sedimentation of TP.

The estimated sedimentation rate for TP in Lough Sheelin showed significant evidence of decline during the latter stages of the study period, accompanied by a trend of increasing concentrations of TP in the lake. These increases occurred despite an overall reduction in the loadings of TP from the drainage basin. Internal loading of P is frequently reported as a main cause hindering the recovery of shallow lakes following reductions in the external load of P entering the lake (e.g. Jeppesen *et al.*, 2005; Phillips *et al.*, 2005; Søndergaard *et al.*, 2003, 2005, 2007). For instance, while inputs of TP entering Loch Leven, a shallow lake in Scotland, were reduced by more than 60% between the 1970s and 1990s, recovery was delayed (May *et al.*, 2011). The lake only showed significant improvements in water quality 20 years after intervention measures were introduced (D'Arcy *et al.*, 2006). Estimations of TP released from sediments were positively correlated with annual average concentrations of TP in Lough Leven, highlighting the role of internal loading in maintaining poor water quality conditions (Spears *et al.*, 2012). In the case of Lough Leven, variation in the magnitude of internal P loading in the lake is naturally influenced by climate conditions (wave mixing depth in spring, summer water temperature and spring secchi depth). By comparison, the internal loading of P in Lough Sheelin is likely due to the action of

zebra mussels, which appear to have hindered any positive impact in response to P mitigation in the catchment (Millane *et al.*, 2008).

Contrasting impacts of zebra mussels on P concentrations in lakes are apparent from the literature (Fahnenstiel *et al.*, 1995a; Maguire *et al.*, 2003; Qualls *et al.*, 2007; Higgins *et al.*, 2008). These observations are known to be due to differences in the trophic status of lakes when invasion commenced (Qualls *et al.*, 2007). Initially, the availability of soluble P tends to increase in an infested P-abundant lake, owing to P homeostatic excretion by the mussels. In P-deficient systems, mussels excrete less P to sustain a constant P concentration in their tissues (Vanderploeg *et al.*, 2002). However, post-establishment, the magnitude and extent of influences of resident zebra mussels on water quality are primarily related to the abundance and biomass of the population (Vanderploeg *et al.*, 2002; Burlakova *et al.*, 2006). Biomass is most prominent as it corresponds directly to filter-feeding capacity. A survey of the zebra mussel population in Lough Sheelin for 2005 and 2006 revealed that the population was still expanding during that time (Millane *et al.*, 2008). The total biomass of the population almost increased twofold from 2005 to 2006. This is common in the years after colonisation and mussel populations usually reach maximum density from 7 to 12 years (Burlakova *et al.*, 2006). As zebra mussel biomass increases, the time taken for the collective filtration of total lake volume decreases, for example, filtration rates changed from 22.4 days to 13.1 days from spring 2005 to 2006 respectively for Lough Sheelin (Millane *et al.*, 2008). Enhanced filtering activity results in increased transfer of energy from the plankton to the benthos (Gergs *et al.*, 2009). The deposition of faeces and pseudofaeces on the sediment decreases oxygen penetration into the sediments, releasing Fe-bound P (Søndergaard *et al.*, 2003; Brönmark and Hansson, 2005; Bykova *et al.*, 2006). This effect has the potential to release large stores of TP held in lake sediments, such as those estimated for Lough Sheelin in this study.

Application of published TP loading-response models to empirical data indicated an increase in internal loading of TP subsequent to the establishment of a zebra mussel population. The retention model, Ostrofsky (1978b), which used the highest value for R (i.e. the highest rate of TP retention in sediments) of the models studied, provided the most accurate estimate of TP retention before a zebra mussel population was established. In the latter stages of the study (post-zebra mussel), a decrease in the net rate of TP sedimentation was supported by the fact that the most accurate prediction models used a lower value for R (Kirchner and Dillon, 1975; Nürnberg, 1984). Greater accuracies of the R-based models compared with models that use scaling functions for the flux of TP in the lake into sediments (i.e. OECD, 1982 and Foy (1992)) suggest that net sedimentation of TP in Lough Sheelin was more strongly related to TP load rather

than the mass of TP in the lake or the effect of hydraulic flushing. These findings, although they do not justify the adoption of any one TP loading-response model to manage similar shallow lakes in the Irish Ecoregion, underscore the major factors to target for the monitoring and assessment of P mitigation in lakes.

A dense population of zebra mussels can modify food web structure and alter ecosystem function (Mills *et al.*, 2003; Wikstrom and Hillebrand, 2012) by selective consumption of phytoplankton through filtration (Bastviken *et al.*, 1998; Hwang *et al.*, 2011). This filtration behaviour results in large reductions in the biomass of phytoplankton (MacIsaac, 1996), increases in water clarity (Zhu *et al.*, 2006), and alterations in the habitat complexity of benthic communities (Burlakova *et al.*, 2012), providing additional habitat for zebra mussels to colonise (Higgins and Vander Zanden, 2010). In a meta-analysis, Higgins and Vander Zanden (2010) showed that zebra mussels reduced phytoplankton biomass by 35% up to 78% in infested lakes and rivers. A similar decrease was observed in data for chlorophyll a sampled in Lough Sheelin from 2004. Owing to these changes in chlorophyll a concentrations, the lake was assigned a mesotrophic status despite the TP concentration indicating a eutrophic condition (Chapter 5). In cases such as this, a sudden decline in the zebra mussel population, possibly from the presence of predators, parasites and ecological competitors (Molloy *et al.*, 2001), may result in the reoccurrence of significant eutrophication problems. Primary production will no longer be suppressed resulting in extensive ecological alterations.

Challenges are highlighted here for the use of both types of models (TP loading - response and chlorophyll a - TP) studied to control P and ecological status in lakes in which the P cycle is not fully understood or has recently been altered. Not only will the OECD classification system for assessing trophic status of lakes be insufficient in these circumstances but the WFD methodology of using the chlorophyll a-TP relationship to define a biological standard for phytoplankton levels will be redundant. To guide and evaluate the success of POMs in all lakes across the Irish Ecoregion, and further afield, separate standards and models need to be developed for invaded and non-invaded water bodies.

7.2.3. Quantifying a hierarchy of the influential environmental conditions of P concentrations in rivers at the landscape scale

The outputs generated from statistical analysis of data from multiple river catchments dispersed across the Irish Ecoregion has provided new information on the hierarchy of environmental conditions that influence seasonal P loss at the landscape scale (Chapter 6). These key findings are summarised in Table 7.1. In particular, the results from the RoI stress the importance of environmental conditions relating to hydrological transportation and connectivity (i.e. slope, TWI) as the fundamental control of concentrations of P in rivers. According to the data, these environmental conditions exert a greater dominance on P in rivers in comparison with conditions associated with sources of P (e.g. human population or pasture land).

There is great uncertainty related to identifying high risk sources of P at the catchment scale, particularly owing to variations of soil moisture and rainfall levels (Doody *et al.*, 2012). Isolating these high risk areas is difficult because diffuse sources of P do not originate from all parts of a catchment, or even where P is available in excess. Rather, P is transported to waterbodies when high P source areas (CSAs) coincide with hydrologically active areas (VSAs) that are directly linked to a waterbody by hydrological pathways (Frey *et al.*, 2009; Reaney *et al.*, 2011). The VSAs occur as a function of high rainfall intensity, coupled with catchment slope, soil type and soil water content and degree of surface saturation. These parameters were encapsulated in both hydrologically-related environmental conditions that were highlighted in the current research as most dominant in terms of predicting P in rivers. Empirical-based studies of controls of P in rivers at the landscape scale in the past have generally neglected the role of hydrological transport, focusing primarily on sources of P. However, this study suggests that a greater explanation of the variability of P can be achieved by using simple measures of hydrological connectivity based on high resolution DEM data. Although the CSA concept works most optimally at the field or hillslope perspective (e.g. Reaney *et al.*, 2011; Wall *et al.*, 2011), catchment scale assessment provides an efficient means of identifying high risk areas for P loss in the absence of detailed field data.

Critical source areas for P are likely to be dynamic, as the initiation and location of hydrological transport pathways creating VSAs change spatially and temporally (Gburek and Sharpley, 1998; Pionke *et al.*, 2000; Srinivasan and McDowell, 2009). The area of a catchment in which surface runoff is initially generated expands upslope in response to increased wetting of the soil by rainfall in the wetter months, and contracts later when the supply of water is reduced (Srinivasan *et al.*, 2002). Connectivity with surface runoff will therefore determine whether source areas of P become CSAs and create problems in the receiving waters. In the current research, both the

mean slope and TWI of catchments were significantly related to sources of P in catchments (e.g. pasture land, cattle densities), thus reflecting the basis of the hydrologically-connected CSA concept. Furthermore, the strength of relationships between mean slope and TWI with fwMRP decreased during the summer months. This reflects the reduced connectivity that occurs in drier conditions when surface runoff-producing areas are less extensive and may not fully connect with the entire critical source areas of P.

Overall, rivers studied from NI ($n = 23$) displayed higher concentrations of P than those in the RoI ($n = 49$); median values were $50 \mu\text{g l}^{-1}$ (NI) and $26 \mu\text{g l}^{-1}$ (RoI). This reflects the general consensus that waterbodies in NI are subjected to greater levels of pollutants from anthropogenic sources compared to the RoI. Accordingly, the most recent reports on water quality for both the RoI (McGarrigle *et al.*, 2010) and NI (NIEA, 2011) give support these comparative findings; 52% of rivers in the RoI have achieved a good status in comparison with 25% of rivers in NI.

Further findings detailed in Chapter 6 indicate the precedence (in winter) of human population over conditions associated with agricultural practices to explain greater variation in concentrations of P in rivers in both the RoI and NI. This output strongly suggests that nutrient pollution by sewage discharges across the Irish Ecoregion remains highly significant. In the RoI, Toner *et al.* (2005) reported that P from point sources, usually sewage or industrial discharges, were the major cause of serious pollution in rivers during 2001 to 2003. However, at the start of 2008 sewage continued to be discharged with either no treatment or basic treatment for P removal at 112 river sites (Monaghan *et al.*, 2009). More recently, Monaghan *et al.* (2012) revealed that almost half of WWTPs in the RoI have not reached national or EU standards. No national performance standards or monitoring arrangements currently exist for septic tank systems in the Irish Ecoregion. Given the widely dispersed nature of these systems throughout the Irish Ecoregion, little data is available on their combined contribution to water quality. However, the findings of this study strongly suggest that the operation of a large number of these in rural areas, many of which are poorly maintained, are unsustainable if goals in relation to water quality are to be realised for the WFD.

Table 7.1a. Summary of major findings from the small scale component of the research (Chapter 6): R^2 value ($p < 0.05$) and rank number indicate the hierarchical position of each environmental condition in decreasing order of strength to predict MRP in rivers from the Rol ($n = 49$). (+) indicates a positive influence on MRP and (-) signifies a negative influence on MRP

Predictor (environmental condition in river catchment)	Winter		Summer	
	R^2	Rank	R^2	Rank
Mean slope	0.401 (-)	1	0.383 (-)	1
TWI	0.384 (+)	2	0.315 (+)	2
Human population density	0.328 (+)	3	0.269 (+)	5
Runoff risk of gley soils	0.248 (+)	4	0.252 (+)	6
% pasture land	0.234 (+)	5	0.270 (+)	4
% forestry land	0.232 (-)	6	0.222 (-)	8
Cattle stocking density	0.225 (+)	7	0.174 (+)	10
% bedrock resistant to weathering	0.213 (-)	8	0.279 (-)	3
% urban area	0.154 (+)	9	0.251 (+)	7
% artificial surfaces	0.133 (+)	10	0.208 (+)	9
Drainage density	0.082 (-)	11	0.143 (-)	11

Table 7.1b. Summary of major findings from the small scale component of the research (Chapter 6): R^2 value ($p < 0.05$) and rank number indicate the hierarchical position of each environmental condition at predicting the concentration of MRP in rivers from the Rol and NI ($n = 72$). (+) indicates a positive influence on MRP and (-) signifies a negative influence on MRP

Predictor (environmental condition in river catchment)	Winter		Summer	
	R^2	Rank	R^2	Rank
Human population density	0.314 (+)	1	0.273 (+)	3
Runoff risk of gley soils	0.282 (+)	2	0.287 (+)	1
Cattle stocking density	0.274 (+)	3	0.233 (+)	4
% pasture land	0.253 (+)	4	0.278 (+)	2
Mean slope	0.170 (-)	5	0.152 (-)	7
% urban area	0.156 (+)	6	0.222 (+)	5
% artificial surfaces	0.144 (+)	7	0.196 (+)	6
% forestry land	0.136 (-)	8	0.146 (-)	8
% bedrock vulnerable to weathering	0.130 (+)	9	0.109 (+)	9

7.3. Practical applicability of research models in the Irish Ecoregion

This is the first study in the Irish Ecoregion to adopt the LAM approach at the subcatchment scale and also to demonstrate the benefit of a geospatial framework for water quality risk analysis at the landscape scale. Both types of models developed using these approaches show relatively strong accuracy; up to 78% validation efficiency for LAMs and predictions of the seasonal geospatial models produced R^2 values of 0.70 (summer) and 0.72 (winter).

Source apportionment of nutrient loads has risen in importance because the implementation of measures needs to accurately target P pressures and pathways specific to the environmental setting of a catchment. In this context, the LAM developed here provides a solution to two important problems concerning the mitigation of P-induced aquatic impacts: the need to quantify the delivery of loads of P from various sources in terms of magnitude and duration, and the need for a feasible, cost-effective monitoring programme that provides information on actual the effects of environmental processes with acceptable levels of statistical certainty. In particular, the LAM, with the potential to estimate point and diffuse source loads and provide an insight into P dynamics in catchments lacking detailed field-based data, offers a means of supporting decision-making relating to current WFD POMs. If applied, the outcome of the LAMs can also provide a basis for any modifications of current measures that might be required in order to achieve water quality objectives by 2015.

The most accurate geospatial model developed (RoI) may be used as a tool to guide decision-making to target limited resources to areas where mitigation would be the most beneficial. The model is particularly valuable for data-poor areas, such as unmonitored rivers. Monitoring of freshwater quality by the EPA in the RoI currently targets a sample of sites that are regarded as representative, leaving many rivers and lakes unmonitored (EPA, 2006). However, under the WFD, the EPA is obliged to submit an up-to-date report of the chemical and ecological status of both monitored and unmonitored waterbodies in 2015. The geospatial model can be used to identify waterbodies that are vulnerable to external loadings of P, and this information can be used as a guide to their relative chemical and ecological status.

Models are employed in environmental policy and management because they provide practically useful outputs (van Daalen *et al.*, 2002). However, Oxley *et al.* (2004) highlights the differences between models used for research purposes (research models) and the practical application of such models as decision-making tools to guide policy or management (policy models). This distinction is particularly relevant regarding the practical applicability of the models developed here for water quality management in the Irish Ecoregion. Model transparency, simplicity, user-

friendliness and data availability are crucial factors for their successful use in policy and management. Proven accuracy of predictions is also vital. For the LAM, these issues are easily addressed; the model is simple in mathematical terms, requires just two commonly measured parameters for calibration and validation and can be run using any computer software with non-linear regression capabilities. Moreover, to increase user-friendliness, the model can be made available as a computer software package in the R environment, linked to databases comprising concentrations of P and flow values maintained by organisations such as the EPA in the RoI. In comparison, practical application of the geospatial model is more complex owing to the use of multiple spatial datasets and statistical procedures. However, feasibility remains for the application of this model as an automated model in R, provided access to the data is available. Furthermore, the concept of the EVO (Emmett *et al.*, 2011), currently linking environmental data and model structures in a cloud-based resource for the UK, is highly appropriate for the effective use of both models by a wider and more diverse audience.

7.4. Limitations

Modelling environmental data has been shown to be a powerful and cost-effective method for describing, understanding and predicting the risk of pollution by P in freshwaters, together with assessing the effectiveness of P mitigation. However, there is a consensus that scientific data and models are associated with uncertainty (Krueger *et al.*, 2009). Hence, the modelled outputs in this thesis may be limited by a number of factors that have an impact upon the data used, guiding assumptions and modelling framework. Nonetheless, with caveats considered, these uncertainties should not detract from the contributions of this study.

The integration of data from RoI and NI was particularly challenging because of differences in the level of availability of relevant data of sufficient quality. Estimates of P loading into rivers or lakes are highly dependent on the chemical behavior of P in solution, and in particular of their high affinity for suspended particulate matter (Heathwaite and Dills, 2000; Stutter *et al.*, 2008). Therefore, concentrations of soluble P in any aquatic system are controlled by heterogeneous reactions which may explain most of the main seasonal variability observed in data. Nevertheless, modelled estimates from LAMs pertaining to sources of TP loads follow a similar trend to MRP, which confirms that the same relationships existed and sorption of MRP does not have a significant influence on the results.

Phosphorus in groundwater has been reported to contribute to the eutrophication of rivers and lakes in some areas of the Irish Ecoregion (Toner *et al.*, 2005). This is particularly the case if

groundwater stores supply significant amounts of base-flow during the summer months. Therefore, all models used in this thesis may be limited by the potential impact of groundwater contributions of P and their transmissivity on the P loading regime. Moreover, the LAM concept of point sources providing the only significant low-flow contributions of P may be countered in catchments with eutrophic groundwater-dominated river flow. Therefore application of the LAM is restricted to surface pathway dominated river catchments, typically containing large areas of soils with restricted drainage and/or impermeable geology. As a consequence, evidence pertaining to the factors that appear to influence the efficacy of POMs, may not be representative for the entire Ecoregion. However, freshwater pollution problems tend to be most acute in these areas of the Irish Ecoregion, especially where intensive crop and livestock production occur (Jennings *et al.*, 2003; Kurz *et al.*, 2003).

7.5. Directions for further research

Advances in determining the most appropriate POMs to target pollutant pressures in a catchment are partly dependent on the availability of high resolution datasets, one of the major limitations to the current understanding of P transfer. Research on POM effectiveness presented in this thesis used a long-term dataset covering a range of subcatchments collectively discharging into Lough Sheelin. With regards to the time period studied, and the frequency of sampling, a dataset of this extent is a rare occurrence in the Irish Ecoregion. However, advances in high-resolution technologies to monitor P dynamics at the bank-side have emerged in recent years and these offer potential for advancing the LAM approach. Relationships between P and discharge can be further explored in different catchment types using data describing various fractions of P. In the Irish Ecoregion, such data are being collated by the ACP. The ACP operates to evaluate the Nitrates Directive regulatory framework, specifically looking at the effect of agricultural management changes on water quality with regard to P and N use (Fealy *et al.*, 2010; Wall *et al.*, 2011). Working in six rural catchments (3-30km²) that cover a range of grassland and arable settings, water quality and flow has been sampled on a 20 min time-step since 2010. In particular, there is potential to further develop the hysteresis component of the LAM which will help to advance the understanding of spatial and temporal controls of P transfer during low and high river flows, together with further assessing controls of environmental conditions. Moreover, once a LAM is calibrated for a particular catchment, it should be possible to determine the effect of introducing various remediation strategies on the P concentration in the river. This could then be used to establish the extent of remediation that would be required to reach WFD water quality targets. The assessment of the effects of spatial scale on mitigation effectiveness would also

provide new knowledge on how best to manage catchments for P abatement and good water quality.

The results of the application of TP loading-response models in Chapter 5 highlight the need for improvements in the knowledge governing the assumptions of such models. This is especially important for eutrophic lakes as they require the most attention in terms of management.

Alteration of the overall behavior of lakes as a result of the invasion of exotic ecology and climate change may also limit the accuracy of these models, most of which were developed at least two decades ago. Such as, Lough Sheelin comprises the correct environmental conditions to further understand changes in internal loading of P as a result of zebra mussels. Through the use of (i) the extensive database on P water quality continuously added to by the IFI, (ii) a greater understanding of the processes occurring in the sediment by sediment core analysis and (iii) a revised survey of the zebra mussel population in the lake, a model that considers the effect of zebra mussels can be developed.

The inclusion of estimates of point and diffuse loads from LAMs into the geospatial model has the potential to provide more specific information on the main controls of P. Alternatively, a grid-based modeling approach could be adopted, predicting the risk of high P runoff at a grid resolution (e.g. 2km², 50m, and 20m) across the Irish Ecoregion. This approach would require regeneration of the explanatory variables for P at a 5km² grid basis. However, variables that emerged as the dominant predictors of P (e.g. TWI, slope) could then be represented in more detail (actual value for TWI or slope at each 5km² grid), providing increased information, at the landscape scale, on those areas of a catchment that have potential to act as CSAs.

7.6. Conclusion

Evidence from both scales of study provides a sound basis for rejecting the collective H_0 that underpin the research questions guiding this thesis, thereby suggesting that sources of P, coupled with environmental conditions in catchments, have strong influences over P concentrations in water bodies in the Irish Ecoregion, and thus on the effectiveness of POMs at reducing high levels of P in freshwaters. Although there may be a wide range of recommended practices for controlling P fluxes to rivers and lakes, the results of this research show that the relative importance of each source and delivery pathway of P will vary with environmental circumstance. Lakes and rivers are highly susceptible to the adverse effects of P because they integrate various sources of P transferred from activities in the surrounding catchment, including intensive

agriculture and urbanisation, but also owing to processes within the waterbody (e.g. internal loading of P). All sources of P require attention under the WFD, however, with limited resources for inspecting the success of mitigation measures, identifying and targeting the critical sources of P that are hydrologically connected to waterbodies assumes great importance for reaching good water quality status by 2015.

The scale and diversity of P transfer mean that separating individual sources of P, their delivery pathways and their specific impact on water quality tend to be extremely challenging. However, LAMs have been used here to apportion both point and diffuse sources of P from total loadings delivered to seven rivers in the Lough Sheelin catchment. This approach allowed the identification of subcatchments constituting a higher P export risk and sensitive transport pathways, the major challenges facing P mitigation attempts. The frequency of occurrence of P source during the year, an important factor in terms of controlling point and diffuse transfers of P and their relative impacts in flowing or standing water bodies, was also quantified by the LAMs. Construction of a long-term P budget coupled with P loading-response models for Lough Sheelin demonstrated the relative importance of internal loading of P from lake sediments in negating the positive impacts of reduced P loading from the catchment. At the landscape scale, quantification of a wide variety of catchment-related environmental drivers (with both positive and negative impacts) of P concentration in rivers enabled the development of a hierarchy of the dominant influences on P. A geospatial model was also developed from these relationships, highlighting the benefits of using this approach to identify rivers with a high likelihood of vulnerability to impairment by P.

The results presented in this thesis have improved understanding of the sources and stressors of concentrations of P in freshwaters. This understanding is particularly important in light of climate change and human population growth that may drive modifications in landuse management, increase pressures on sewage treatment facilities and heighten demands on potable freshwater resources. Predicted wetter winters and drier summers owing to climate change are also likely to amplify P concentrations in rivers both during high runoff events and during low flows, particularly in catchments with similar characteristics to the catchment studied in detail here. Without understanding how environmental processes operate and interact currently, the impacts of future demands on resources and changes to P cycles will be more difficult to anticipate and control. Effective management of inputs of P to freshwaters can only realistically be possible when the processes that control the effects of point/diffuse loads of P in rivers and external/internal loads of P in lakes are well understood; the research presented here can be considered to have advanced the level of understanding towards that goal.

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