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**Modelling ecological pressures
and responses
in a west of Ireland lake**

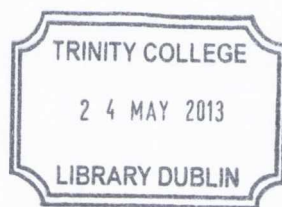
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*Thesis submitted to the University of Dublin, Trinity College, for the Degree of Doctor in
Philosophy.*

Discipline of Geography,
School of Natural Sciences

The University of Dublin,
Trinity College

2013



Thesis 9881

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Thesis Summary

Effective lake management requires an understanding of aquatic ecological pressure-response relationships. Deciphering the aquatic effects of multiple ecological pressures, such as climate variability and human activity, requires the analysis of long term monitoring data. However, monitoring data are rarely available, particularly for the period prior to human impact. Palaeolimnology can be used to investigate long term aquatic ecological pressures and responses, and the benefits of palaeolimnology for lake management have been well-established. Dynamic ecological modelling can also be used to reconstruct ecological pressures-responses relationships. However, although recognised as a potentially valuable tool for water quality management, ecological modelling is not widely applied in lake management.

A multidisciplinary approach, involving two coupled dynamic computer models, a catchment loading function (the Generalised Watershed Loading Functions, GWLF) and a coupled in-lake response model (Dynamic Reservoir Simulation Model - Computational Aquatic Ecosystem Dynamics Model, DYRESM-CAEDYM), palaeolimnology and a range of historical climate and catchment data, was used to elucidate long term ecological pressure-response relationships in a complex west of Ireland lake, Lough Mask, Co. Mayo. Palaeolimnological data, covering the last c. 6000 years, revealed that natural trophic variability was driven by complex interactions between climate, catchment conditions and in-lake processes. The complexity of these interactions and their effects, mediated through the characteristics of Lough Mask and its catchment, poses severe problems for the conventional analysis of palaeolimnological data and their use in dynamic simulations of future changes in aquatic ecological pressures and their impacts.

Analysis of the multidisciplinary (palaeolimnological, modelling and historical) datasets revealed major changes in climate and human drivers of trophic variability in Lough Mask during the 20th century. Prior to c. 1970 AD, variations in lake trophic conditions were associated primarily with variations in climate, in particular winter precipitation levels and the North Atlantic Oscillation (NAO), and human population. Post-c. 1970 AD, eutrophication was linked to elevated summer temperatures and enhanced thermal

stratification, and increased catchment P loading as a result of agricultural intensification. Analysis of the multidisciplinary datasets also indicated that climate variability, i.e. warming and associated enhanced thermal stratification, may be the main driver of eutrophication post-c. 1970 AD, followed by agricultural intensification. The combined effects of climate and agricultural intensification were also evident.

Reconstructed trophic conditions for Lough Mask for the 20th century using two independent techniques (palaeolimnology and modelling) also allowed the establishment of secondary baseline trophic conditions, representing conditions prior to significant human impact. Although results from both techniques indicated similar patterns of nutrient enrichment during the 20th century, sediment-based diatom-inferred total phosphorus (DI-TP) tended to overestimate available monitored Total Phosphorus (TP) data and were higher than hindcast modelled TP data for the lake. Secondary baseline trophic conditions were used to define water quality management targets for restoration. Scenario-based modelling allowed the effectiveness of a range of management options, for achieving water quality targets, to be assessed. Comparisons between the modelled and sediment-based reconstructions indicated that the reliability of the models could be improved with more widespread application of the approach and additional and higher resolution monitoring datasets. The findings of this study demonstrate the practical value of dynamic modelling for ensuring more successful lake management and, in particular, for providing more cost- and time-effective lake management plans than those currently in operation. Moreover, given the extent of projected future climate and environmental changes, dynamic modelling is likely to be an invaluable tool for the future management of aquatic resources.

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List of abbreviations and acronyms

>	greater than
<	less than
°	degrees
°C	degrees centigrade
'	minutes
%	percent
‰	per thousand
µg	microgram
µm	micrometre
µS	microsiemens
δ	delta (change in)
Δ	delta (change in)
σ	Standard deviation
¹³ C	stable isotope of Carbon
¹⁴ C	radioactive isotope of Carbon
¹⁵ N	stable isotope of Nitrogen isotope
¹³⁷ Cs	radioactive isotope of Caesium
²¹⁰ Pb	radioactive isotope of lead
²¹⁰ Po	radioactive isotope of Polonium
²²² Rn	radioactive isotope of Radon
²²⁶ Ra	radioactive isotope of Radium
²³⁸ U	radioactive isotope of Uranium
AD	Anno Domini
ADS	Arterial Drainage Schemes
Al	Aluminium
AMS	Accelerator Mass Spectrometry
Anon	Anonymous
AO	Arctic oscillation
ASS	Alternative Stable States
BASINS	Better Assessment Science Integrating point & Non-point Sources
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BP	before present (before 1950 AD)
BUFFER	Key nutrient transport mechanisms important for the prediction of nutrient and phytoplankton concentrations in European standing waters (EU FP5 project)
C	Carbon
c.	circa (about)
Ca	Calcium
CaCO ₃	Calcium carbonate
CAEDYM	Computational Aquatic Ecosystem Dynamics Model
cal	Calibrated
CCA	Canonical correspondence analysis
CFB	Central Fisheries Board, Ireland
CF-IRMS	Continuous Flow Isotope Ratio Mass Spectrometry
Chl	Chlorophyll
CLIME	Climate and Lake Impacts in Europe (EU FP5 project)
cm	Centimetre
CO ₂	Carbon dioxide
CONISS	Constrained Incremental Sums of Squares
CORINE	Coordination of Information on the Environment
CRS	Constant rate of supply
CSO	Central Statistics Office
DCA	Detrended Correspondence Analysis
DED	District Electoral Division
DIATCODE	A coded checklist of diatoms names
DI-pH	Diatom inferred pH (reconstructed epilimnic pH)
DI-TP	Diatom inferred TP (reconstructed epilimnic TP)
DM	dry matter
DOC	Dissolved organic carbon
DPM	disintegrations per minute
DYCD	DYRESM-CAEDYM
DYRESM	Dynamic Reservoir Simulation Model
EA-WR	east Atlantic - west Russia teleconnection

EDDI	European Diatom Database
EEA	European Economic Area
e.g.	for example
EPA	Environmental Protection Agency, Ireland
<i>et al.</i>	et alia (and others)
EU	European Union
F	diatom dissolution index
Fe	Iron
g	Gram
GIS	Geographical Information System
GWLF	Generalised Watershed Loading Functions
H ₂ O _{2aq}	Hydrogen peroxide
Ha	Hectare
HCl _{aq}	Hydrochloric acid
HF _{aq}	Hydrofluoric acid
HSPF	Hydrological Simulation Program - Fortran
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
i.e.	that is
IFI	Inland Fisheries Ireland
ILLUMINATE	Past, current and future interactions between pressures, chemical status and biological quality elements for lakes in contrasting catchments in Ireland (EPA project)
IPCC	Intergovernmental Panel on Climate Change
jack	jackknifing (statistical method of cross-validation)
K	Potassium
Kg	Kilogram
km	Kilometre
km ²	kilometre squared
l	Litre
ln	Natural logarithm
LOESS	locally weighted scatterplot smoothing

LOI	Loss-on-ignition
m	Metre
m ³	metres cubed
MAT	Modern Analogue Technique
mg	Milligram
ml	Millilitre
mm	Millimetre
Mn	Manganese
m s ⁻¹	Metres per second
N	Nitrogen
Na	Sodium
NAO	North-Atlantic Oscillation
No.	number
NO _x	Nitrogen oxides
NS	Nash-Sutcliffe coefficient
NTU	Nephelometric Turbidity Unit Organisation for Economic Co-operation and Development
OECD	Organisation for Economic Co-operation and Development
OPW	Office of Public Works
p	probability
P	Phosphorus
PAST	Palaeontological Statistics software
pers. comm.	Personal communication
PCA	Principle components analysis
pH	Potential of Hydrogen (a measure of acidity)
POMs	Programmes of Measures
PP	Particulate phosphorus
PtCo	Platinum-Cobalt Scale
Q	Max Cumulative Score
r ²	coefficient of determination
Ra	Radium
RBD	River Basin District

RBMP	River Basin Management Plan
RMSEP	root mean squared error of prediction
Rn	Radon
S	Second
SAR	sediment accumulation rate
SCP	spheroidal carbonaceous particles
SHETRAN	a physically-based, distributed hydrological model for water flow, solute and sediment transport in river catchments
Si	Silicon
S.I.	Statutory Instrument
SiO ₂	Silicate
SMT	sequential extraction method
SO ₂	Sulphur dioxide
SRP	Soluble reactive phosphorus
STP	Sewage treatment plant
SWAT	Soil and water assessment tool
TMDL	Total maximum daily load
TDP	Total dissolved Phosphorus
TN	Total Nitrogen
TON	Total organic Nitrogen
TP	Total Phosphorus
UK	United Kingdom
USA	United States of America
US EPA	United States of America Environmental Protection Agency
USLE	Universal Soil Loss Equation
v	degrees of freedom
Vensim	Ventana simulation computer software
W	Watt
WA	weighted averaging
WA-PLS	weighted averaging partial least squares
WFD	Water Framework Directive
WRBD	Western River Basin District

yr

year

Chapter 1

Introduction

1.1 Controls of variability in lake ecosystems

1.1.1 *Natural variability*

Ecological variability in lakes over long (geological) timescales is fundamentally controlled by climate and geomorphological setting (O'Sullivan & Reynolds, 2004; Smol, 2008). Climate affects the physical, chemical and biological structure and functioning of lake ecosystems (Wetzel, 2001; Moss, 2010; Shimoda *et al.*, 2011). Until the 1990s, long-term climate conditions were thought to exert a relatively constant influence on aquatic ecosystems, with little changes in the latter in temperate parts of the world since the end of the last ice age (i.e. during the Holocene). Over the last two decades or so, evidence for considerable natural climate variability during the Holocene has become more apparent (O'Brien *et al.*, 1995; Helama *et al.*, 2010) and the importance of climate in influencing variability in aquatic ecosystems during this time period is now well recognised (Mayewski *et al.*, 2004; Oldfield *et al.*, 2010). The human component of climate variability has also increased dramatically over the last c. 200 years (IPCC, 2007). However, the influence of climate on aquatic ecological conditions, and in particular interactions between climate and environmental variables impacting lake water quality, such as nutrient availability, is not fully understood (Battarbee, 2010).

Geographical location and geomorphological setting (including topography, geology, pedology, hydrology and vegetation cover) are critical factors determining the nature of inputs from the catchment and influencing in-lake ecological variability (Allan & Johnson, 1997; Wetzel, 2001; O'Sullivan & Reynolds, 2004; Donohue *et al.*, 2005; Fritz, 2008). In general, where catchment characteristics are more heterogeneous, in-lake ecological variability is likely to be greater (Webster *et al.*, 2000). However, studies relating catchment characteristics to aquatic ecological dynamics remain relatively rare.

1.1.2 *Human impacts on lake ecosystems*

Lakes have been impacted by human activity over the last c. 200 years to the extent that the amplitude of natural variability in aquatic conditions may now have been exceeded (Moss, 2010). Moreover, human activity has tended to accelerate processes that are likely to have occurred naturally over much longer periods of time (Ahn *et al.*,

2006), e.g. accelerated sediment accumulation rates (SARs), eutrophication and acidification. Human-induced environmental impacts have been so extensive and profound that some have argued that a new geological epoch - the Anthropocene, representing the last 200 years - is warranted (Crutzen & Stoermer, 2000; Oldfield, 2005; Zalasiewicz *et al.*, 2008; Steffen *et al.*, 2011).

Eutrophication, the nutrient-driven increase of organic matter in freshwaters (Nixon, 1995), can occur naturally as part of the development of a lake over relatively long geological timescales (Rast & Holland, 1988; Smol, 2008; Miller, 2011). The occurrence of natural eutrophication depends on the morphology of the lake basin, and associated sediment accumulation patterns (Deevey, 1955) and the geological and pedological characteristics of the catchment (Murphy *et al.*, 1983; Rasanan *et al.*, 2006). Human-induced (or cultural) eutrophication, generally linked to increased inputs of phosphorus, P, and nitrogen, N, from human sources (Smith *et al.*, 1999; Jennings *et al.*, 2003), occurs over much shorter time periods and is widely regarded as one of the most common water quality problems in the world (Mason, 2002; Dokulil & Teubner, 2011). As P and N are the main limiting nutrients for phytoplankton growth in freshwater, the increased availability of these elements often leads to elevated primary productivity (Brönmark & Hansson, 2005; Khan & Ansari, 2005) and to major water quality problems, including oxygen depletion, pH variability, alterations of trophic structure and increases in toxic algal blooms (Reynolds & Petersen, 2000; Jennings *et al.*, 2003). As indicated previously, climate and weather variations (linked to changes in temperature and effective moisture) also influence aquatic conditions, although the extent to which these variables interact with - and may directly influence - changes in nutrient availability has received relatively little attention to date (Jennings *et al.*, 2009; George *et al.*, 2010)

Recent (i.e. post-c. 1800 AD) acidification of lakes has been linked primarily to human activity, in particular the increased industrial emissions of acidifying pollutants (e.g. sulphur dioxide, SO₂, and nitrogen oxides, NO_x) (Gorham, 1998; Battarbee *et al.*, 1990). The introduction of national and international policies during the 1980s and 1990s, aimed at reducing levels of atmospheric emissions of these pollutants, has resulted in reduced acidification pressures at some lake sites (e.g. Stoddard *et al.*, 1998; Skjelkvåle *et al.*, 2005). The success to date of international measures aimed at curbing and even reversing acidification pressures provides a clear example of what concerted

international action targeted at trans-boundary pollutants is able to achieve. Despite successes in reducing emissions, and in improving chemical water quality in some cases (Kernan *et al.*, 2010), evidence for large-scale ecological recovery from acidification remains scarce (Stendera & Johnson, 2008; Ormerod & Durance, 2009; Dunford *et al.*, 2012). Future recovery is likely to be increasingly influenced by anthropogenic climate change, although the role of climate variability in influencing lake acidification and recovery is complex and poorly understood (Whitehead *et al.*, 2009; Johnson & Angeler, 2010).

Anthropogenic climate change, linked to elevated greenhouse gas emissions from fossil fuel consumption (IPCC, 2007), presents one of the most severe threats to ecosystems globally (Rosenzweig *et al.*, 2007; Adrian *et al.*, 2009; Wassmann *et al.*, 2011). The role of recent climate change in driving trophic changes in lakes is not fully understood, and findings are to some extent contradictory (George, 2000; Monteith *et al.*, 2000; Weyhenmeyer, 2001; Straile, 2002; Battarbee, 2010; Nöges *et al.*, 2010). Moreover, deciphering the relative contributions from multiple stressors, acting individually and in combination on ecological conditions in lakes, is particularly difficult (Battarbee, 2010; George *et al.*, 2010; Smol, 2010; Desellas *et al.*, 2011). Linking aquatic ecological effects to particular causes or complexes of causes is essential if lake management aimed at improvements in water quality and the restoration of ecological functioning is to prove effective.

1.2 Deciphering aquatic trophic pressure-response relationships

Lakes are often impacted by combinations of pressures (Smol, 2008; Battarbee *et al.*, in press). Deciphering the roles of several drivers of aquatic ecological variability can be difficult because different pressures can have similar effects, and because of the potential for synergistic relationships between combinations of these (Vasseur & McCann, 2007). For example, the effects of climate change can differ depending on local-scale factors, such as catchment geomorphological conditions (Vasseur & McCann, 2007; Fritz, 2008; Battarbee, 2010), and have been found to exacerbate human-induced eutrophication (Douglas *et al.*, 2007; Steinberg *et al.*, 2011). Often these inter-relationships are not fully understood (Adrian *et al.*, 2009; Jeppesen *et al.*, 2010) and what supporting evidence there is often appears contradictory (George *et al.*, 2010; Battarbee *et al.*, in press).

Deciphering the effects of multiple stressors is further complicated by non-linearities in pressure-response relationships (Nickus *et al.*, 2010), whereby a small change in a particular pressure can lead to an abrupt in-lake response (Scheffer *et al.*, 1993). A well-documented example of a non-linear response is the occurrence of Alternative Stable States in shallow lakes, where a small change in nutrient loading can cause a rapid shift from oligotrophic and clear water conditions to eutrophic and turbid water conditions (Scheffer, 2004). Whether non-linearities occur appears to depend on the characteristics of the catchment, hydromorphological characteristics of the lake basin and stability of the water column (Scheffer & Van Nes, 2007). The phenomenon Alternative Stable States, commonly observed in shallow lakes, is generally not found in lakes that undergo thermal stratification (usually deep lakes), as these are generally regarded as more stable and have little interaction between the epilimnion and the sediments (Scheffer, 2004). Although non-linear ecological pressure-response patterns are easily observed, our understanding of these relationships and in particular the underlying mechanisms is incomplete and requires further research (Ibelings *et al.*, 2007; Scheffer & Van Nes, 2007; Hobbs *et al.*, 2012).

Changes in climate conditions can also induce non-linear responses, including prolonged shifts in ecological conditions in lakes (Scheffer *et al.*, 2001a). Climate warming has been shown to promote the stabilisation of eutrophic and turbid conditions in shallow lakes, and result in delayed or lagged responses to reductions in human pressures, e.g. nutrient loading (Jeppesen *et al.*, 2003). In contrast, other studies have indicated what could be regarded as the positive effects of warming, including the promotion of clear and oligotrophic conditions in shallow lakes (Scheffer *et al.*, 1992; Rooney & Kalff, 2000). A more complete understanding of the mechanisms underlying delayed or lagged responses to changes in aquatic pressures than is currently the case is vital for effective lake management and for predicting the impacts of future aquatic ecological changes. Computer-based, dynamic modelling and palaeolimnology are among the relatively few techniques available to investigate long-term and complex aquatic ecological pressure-response patterns (Irvine *et al.*, 2005).

Combining dynamic modelling and palaeolimnology provides a novel multidisciplinary approach that can help identify gaps in understanding and untangle the relative roles of multiple stressors on aquatic ecosystems (Scheffer & Carpenter, 2003). Furthermore, where the timescale of interest is greater than the length of time for which

instrumental data are available, palaeolimnology is often the only means for comparison of dynamic model output (Anderson *et al.*, 2006), and thus can potentially be a fundamental part of assessing the applicability of water quality models for use in water quality management (Pollard *et al.*, 2001; Anderson *et al.*, 2006; Dearing *et al.*, 2006). The applicability of dynamic modelling is, however, dependent on an in-depth understanding of the relative importance of key ecological processes and the availability of data available for model parameterisation and validation (Anderson *et al.*, 2006). Moreover palaeolimnological data are often based on models or inferences and, therefore, both palaeolimnological and dynamic modelling approaches need to be tested independently using high quality monitoring data.

1.3 Aquatic ecosystem management

The extent of deterioration of aquatic ecosystems as a result of human activities is now widely recognised as a major global environmental issue (Smol, 2008; Gal *et al.*, 2009; Naiman & Dudgeon, 2011). Human modification of ecosystems has led to the need for environmental management (Moss, 1999), and the development and implementation of legislation at national and international levels aimed at restoring and maintaining environmental quality (Bertahas *et al.*, 2006). One example of an international legislative response to the deterioration of aquatic resources is the EU Water Framework Directive (2000/60/EC) (WFD) (European Parliament and Council, 2000), which requires all freshwater bodies in EU member states to equate to at least to good water quality status, representing little or no human impact, by 2015 (Kirilova *et al.*, 2009).

Management of aquatic ecosystems is particularly difficult because of their inherent and complex interconnections with the terrestrial environment and the atmosphere (Irvine *et al.*, 2004; Linstead *et al.*, 2010). As indicated above, deciphering the relative effects of human and climate stressors on aquatic conditions is one of the most challenging issues currently facing water quality management. Sustainable management of any ecosystem requires the establishment of the relationships between ecological pressures and responses (Borja *et al.*, 2006). In order to understand these relationships, the analysis of long-term data is required. However, sufficiently long-term ecological monitoring data are only rarely available (Battarbee, 1999; Jennings *et al.*, 2008; Battarbee *et al.*, in press). Moreover, the range of variables monitored is often limited (Gal *et al.*, 2009). Mance *et al.* (2002) suggests that an integrated approach

utilising a range of information sources is required to elucidate the relationships between aquatic ecological pressures and responses. Dynamic ecological modelling potentially provides an important component of such an approach, providing an opportunity to reconstruct long-term aquatic ecological pressures and associated responses (Irvine *et al.*, 2005).

Models are effectively simplifications of reality (Irvine *et al.*, 2005) and for optimal use first require validation. Without validation, model output is conditional on the assumptions made in the model calculations (Beven, 2009). Validation ideally requires data that were not used in model construction (including model calibration). Such independent datasets are rarely available because of the paucity of long-term monitoring data, with whatever data are available having been used in model construction (Oreskes *et al.*, 1994). Palaeolimnology involves the reconstruction and interpretation of past environments from the physical, chemical and biological characteristics of lake sediments, based on models or inferences (Cohen, 2003). Palaeolimnology can be used to reconstruct long-term aquatic ecological pressure-response relationships (Battarbee, 2000; Smol, 2008). Such lake sediment-derived information provide additional long-term records: in some cases, monitoring data can be used to calibrate sediment-based environmental proxies (Dalton *et al.*, 2009). Although, palaeolimnology cannot be used for directly validating dynamic modelling output, a combined approach utilising both palaeolimnology and dynamic modelling can potentially provide a valuable comparison for improving the reliability of model simulations (Anderson *et al.*, 2006; Peng *et al.*, 2011).

1.4 Implementing water quality policy

Water quality management requires the establishment of reference conditions (i.e. natural ecological variability in the absence of significant human impact), determination of the extent of deviation of ecological conditions from reference conditions, identification of important drivers of aquatic ecological change and establishment of appropriate measures for restoring reference water conditions (Rekolainen *et al.*, 2003; Gal *et al.*, 2009). In Ireland, the Local Government (Water Pollution) Act, 1977 (Water Quality Standards for Phosphorus) Regulations, 1998, S.I. 258 (1998), more commonly known as the P Regulations, were introduced with the aim of reducing P inputs to water (Department of Environment, 1997). In Europe, national legislation relating to water

quality in EU member states, for example, the P Regulations in Ireland, has been subsumed within the WFD. The WFD requires water quality management to take place on a catchment-scale, via management units known as River Basin Districts (RBDs). A River Basin Management Plan (RBMP) must be developed for the water bodies within each RBD every six years (Irvine *et al.*, 2005). There are several knowledge gaps associated with the implementation of the WFD (Raadgever *et al.*, 2011), all of which require the analysis of long-term data. Both dynamic modelling and palaeolimnological techniques have been recommended as valuable tools for implementing the WFD and, in particular, for addressing associated knowledge gaps (Irvine *et al.*, 2005). The EU Directive (91/676/EEC), commonly known as the Nitrates Directive (Howarth, 2006) also plays a key role in the management of nutrient pollution in catchments and in the delivery of water quality improvements required by the WFD.

Palaeolimnology is a well-established tool in lake management (Battarbee, 1999; Luoto & Raunio, 2011). Dynamic modelling has a long history of application in environmental management for simulating environmental pressures and responses in the absence of long-term empirical data (Committee on Models in the Regulatory Decision Process, National Research Council, 2007). The use of dynamic models in the aquatic sciences has recently increased due to technological developments and the requirements of new legislation and policies, such as the WFD. Although improvements have been made, ecological modelling is still used in water quality management only relatively rarely, and models have not contributed significantly to the advancement of ecological understanding (Jennings *et al.*, 2003; Anderson *et al.*, 2006; Aumann, 2007).

1.5 Research rationale and thesis structure

1.5.1 Research rationale

Effective lake management requires understanding of aquatic ecological pressure-response relationships (Irvine *et al.*, 2005). However, up until the 1970s relatively little monitoring of lake trophic variability had taken place in Ireland (Jennings *et al.*, 2000). Although population levels in Ireland are currently relatively low compared with other parts of the developed world, population levels in rural areas were much higher prior to the famine of the mid 19th century (Leira *et al.*, 2006; Donohue *et al.*, 2010). Lakes in the west of Ireland in particular are also sensitive to climate variability and weather

anomalies associated with the Atlantic Ocean (Jennings *et al.*, 2000), and to atmospheric pollution loads from sources in North America (O'Dwyer & Taylor, 2010) in addition to locally. Lakes located in the west of Ireland have also been identified as highly sensitive to a range of human-induced water quality problems, including surface water acidification (Aherne & Farrell, 2002) and eutrophication (Dalton *et al.*, 2010; Donohue *et al.*, 2010).

Currently, in Ireland, water quality management is based primarily on recently established extensive monitoring programmes (Anon, 2006; Canney, 2009) carried out in RBDs. The Environmental Protection Agency (EPA) has produced a series of country-wide water quality reports based on these programmes, the most recent of which is for the period 2007-2009 (McGarrigle *et al.*, 2010), some of which now benefit from major investments in lake and whole catchment monitoring infrastructure.

Focusing on Lough Mask, a large complex lake in County Mayo, western Ireland and part of the Western River Basin District (WRBD), the main aim of the current study was to determine the extent to which a multidisciplinary approach, combining palaeolimnology, historical catchment and climate data and dynamic modelling, could contribute to improvements in both understanding of trophic pressure-response relationships and, ultimately, aquatic management. The aim of this study was addressed through four main research questions (described below) and a journal submission (Table 1.1), each of which forms the basis of a chapter in later parts of the thesis:

1. How have trophic conditions varied over the long term in a complex lake? (Chapter 4)
2. What are the relative roles of climate variability and human pressures in driving trophic changes in a west of Ireland lake during the 20th century? (Chapter 5)
3. Can a multidisciplinary approach, combining palaeolimnological and dynamic modelling methods, be used to elucidate long-term trophic dynamics? (Chapter 6)

Table 1.1 Details of thesis chapters and related publications. *last checked 12th September 2012

Chapter	Journal title	Status of submission*	Name	Contribution
1	n/a	n/a	Sarah Murnaghan Prof David Taylor	Writing Comments on chapter draft
2	n/a	n/a	Sarah Murnaghan Prof David Taylor	Writing Comments on chapter draft
3	n/a	n/a	Sarah Murnaghan Prof David Taylor	Writing Comments on chapter draft
4	Journal of Paleolimnology	Published (2012)	Prof David Taylor	Comments on chapter draft Secondary data collection Data analysis and interpretation Writing Fieldwork Comments on chapter drafts Fieldwork Comments on chapter drafts Fieldwork Comments on chapter drafts Comments on chapter drafts Comments on chapter drafts
5	Global Change Biology	-Submitted. Positively reviewed and rejected on the grounds of data from a single study site. Strongly advised to submit to another journal. -Submitted to the Journal of Quaternary Science	Prof David Taylor Dr Eleanor Jennings Dr Catherine Dalton Kim Olay-Bosch Barry O'Dwyer Sarah Murnaghan	Fieldwork Modelling Secondary data collection Statistical analysis and interpretation Writing Fieldwork Comments on chapter drafts Fieldwork Modelling advice and support Comments on chapter drafts

Table 1.1 continued

Chapter	Journal title	Status of submission *	Name	Contribution
6	Biology and Environment: Proceedings of the Royal Irish Academy	In press	Sarah Murnaghan	Modelling
				Secondary data collection
			Prof David Taylor Dr Eleanor Jennings	Statistical analysis and interpretation
				Writing
7	Journal of Applied Ecology	-Submitted and rejected on the grounds of unsuitability for the journal. Strongly advised to submit to another journal -Currently in preparation for submission to Water Research	Sarah Murnaghan	Comments on chapter drafts
				Modelling
			Dr Eleanor Jennings	Secondary data collection
				Statistical analysis and interpretation
8	n/a	n/a	Prof David Taylor	Writing
				Modelling advice and support
			Sarah Murnaghan	Comments on chapter drafts
				Comments on chapter drafts
9	n/a	n/a	Prof David Taylor	Writing
				Comments on chapter draft

1. Can dynamic modelling be used to design and test the effectiveness of water quality management plans? (Chapter 7)

1.5.2 Thesis structure

Chapter 2 provides a detailed description of the study site, including the available historical and contemporary data, for the research. Chapter 3 outlines the methodological framework of the project and details the techniques used in the research to provide a context for the results and interpretations presented in Chapters 4, 5, 6 and 7. Note that descriptions of the relevant techniques are not repeated in these results-based chapters, each of which focuses on a specific research question and forms the basis for work that has been published, accepted for publication or is in the process of being prepared for publication. Chapter 4, entitled ‘Middle to late Holocene environmental changes in western Ireland inferred from fluctuations in preservation of biological variables in sediment’ examines natural trophic variability and the possible controls of natural variability in a lake with spatially-heterogeneous catchment characteristics located in the west of Ireland, addressing Research Question 1. Chapter 5 addresses Research Question 2 by investigating the roles of climate and human drivers of trophic variability in the lake over the last c. 140 years. Chapter 6 uses two independent methods, dynamic modelling and palaeolimnology, to reconstruct long-term trophic variability in a west of Ireland lake during the 20th century, and compares reconstructions from both techniques, addressing Research Question 3. Chapter 7 investigates whether or not a scenario-based ecological pressure-response modelling approach can be used to test the effectiveness of measures for achieving WFD objectives in agriculturally-impacted catchments, addressing Research Question 4. Chapter 8 comprises a synthesis of the findings of the current research and discusses the key findings arising from Chapters 4, 5, 6 and 7, placing them in the wider context of the overall aim of the research. The findings presented in the research question-based Chapters 4, 5, 6 and 7 have also formed the basis for 4 papers that have been submitted to academic journals as part of the PhD research, one of which is now published (Murnaghan *et al.*, 2012). Details of these papers, the journals to which they were submitted and their publication status is provided in Table 1.1.

Chapter 2

Study Site

This chapter presents a detailed description of the study catchment and lake used in the current research, including the criteria for selecting the study site and a summary of available relevant catchment and water quality monitoring data. The latter includes information collected during the research specifically to address data gaps. A summary of the potential drivers of change in these lakes is also presented, based on available meteorological and census data.

2.1 Selection of study site

Lakes are one of the best indicators of environmental change (Battarbee, 2000; Adrian *et al.*, 2009), as they are sensitive to climate variability (Smol, 2008) and changes in catchment conditions and human activity (Battarbee *et al.*, 2002). However, not all sites are equally sensitive to climate change or human activity. Lakes located in western Europe are likely to be sensitive to variations in climate, particularly precipitation, because of their proximity to the Atlantic Ocean (Jennings *et al.*, 2000). Furthermore, the west of Ireland is a region characterised by spatially-heterogeneous geology, soils and land use (Cross, 1998), and this heterogeneity in catchment conditions is likely to be a factor complicating lake ecological pressure-response relationships (Webster *et al.*, 2000). In addition, the west of Ireland has also undergone major changes in human pressures since the onset of the Anthropocene (Huang & O'Connell, 2000; Jennings *et al.*, 2008; Donohue *et al.*, 2010) and is an area where previous human impacts may have been greater than at present (Jennings *et al.*, 2008).

The choice of study site for the current research was based on the following criteria:

- the lake site should be located in an area known to be highly sensitive to variations in climate conditions
- the lake should have a history of human impacts
- there should be sufficient long-term and high-resolution secondary data (historical catchment and climate data) available for the lake catchment, for the purposes of driving a catchment model

-there should be a sufficient inflow and lake water quality monitoring dataset, including chemical and biological data, available for the site in order to run an in-lake aquatic ecological response model

Lough Mask, Co. Mayo, Ireland was selected as a suitable site for the current research as it met the criteria outlined above. The existence of particularly long and high-resolution historical secondary datasets, including human population, agricultural census and climate, available from c. 1900-2006 AD for the Lough Mask catchment, which are described in Section 2.2, was a pivotal factor in the choice of the lake as the focus of the current study.

2.2 Lough Mask

2.2.1 Location and bathymetry

Lough Mask (53° 36' N, 9° 22' W) is a large (c. 82 km²) partially calcareous lake located c. 30 km from the Atlantic coast of western Ireland (Figure 2.1). Locational and physical characteristics of the lake are summarised in Table 2.1. Lough Mask has a complex bathymetry (Figure 2.2) with the lake occupying several subbasins. The eastern part of the lake is a relatively shallow (c. 13 m depth) limestone shelf receiving inflows from the eastern and north-eastern parts of the catchment. The deepest point in the lake (c. 64 m depth) is located in an elongate, channel-like subbasin in the western part. The southwest part of the lake (c. 20 m depth) comprises isolated bays that drain the western part of the catchment.

2.2.2 Catchment conditions

The catchment for Lough Mask (c. 859 km²) is characterised by sharp geographical contrasts in geology, topography, hydrology, soil cover and land use between the eastern (Robe and Carra) and western (Finny, Srahnalong, Owenbrin, Glensaul, Srah, Cloon and Cartron Bower) subcatchments (Table 2.2; Figure 2.1 and 2.3). The River Robe in the east is the largest inflow to Lough Mask followed by the Keel canal, the only outflow from Lough Carra, a smaller marl lake in the north of the catchment (Figure 2.1). Several smaller inflows drain the siliceous uplands of the Partry mountains in the west, namely, Cloon, Finny, Glensaul, Owenbrin, Srah and Srahnalong (McGarrigle & Champ, 1999).

Table 2.1 Summary of locational and physical characteristics of Lough Mask, Co. Mayo

Location‡	Altitude* (ha)*	Lake area (ha)**	Catchment area (m)†	Max depth (m)‡	Volume (m ³)‡	Annual retention time (years)†
53° 36' 45 N 9 ° 22' 60 W	21	8,294	85,900	20	64	2.7 x 10 ⁹ 0.9

* indicates data from McGarrigle & Champ (1999); ** indicates data from BUFFER (EU Fifth Framework Programme) project (I. Donohue, Trinity College Dublin, pers. comm.). † indicates data from the Environmental Protection Agency (EPA); ‡ indicates data obtained from the current research

Table 2.2 Summary of physical characteristics of the main subcatchments of Lough Mask, Co. Mayo (based on data from Donohue & Irvine, 2003).

*West includes the Cloon, Srah, Glensaul, Cartron Bower, Owenbrin, Srahnalong and Finny subcatchments (see Figure 2.1 for locations)

Subcatchment	Area (km ²)	Slope range (mean) (°)	Max elevation (m)	Drainage density (km km ²)	Main bedrock geology
Robe	284.7	0.8-1.3 (1.1)	131.8	0.92	Upper Carboniferous limestone
Carra	113.9	1.4-1.8 (1.6)	61.6	0.80	
West*	343.2	4.1-17.2 (9.8)	684.2	1.90	Ordovician sandstone

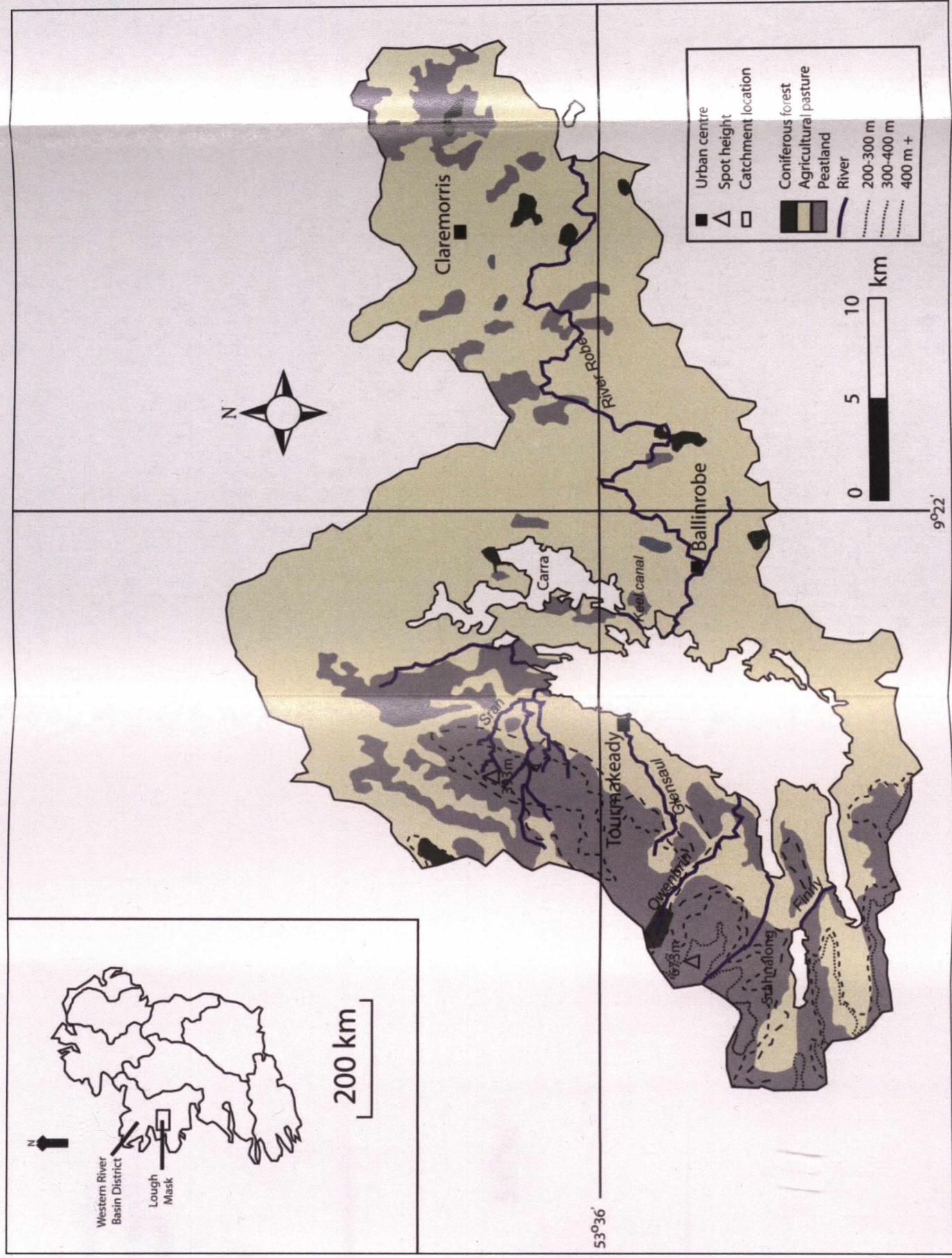


Figure 2.1 Map of the Lough Mask catchment showing topography, the main inflow rivers, two principle towns (Ballinrobe and Claremorris, the location of the synoptic meteorological station) and the predominant catchment land uses (see Table 2.3 for further details)

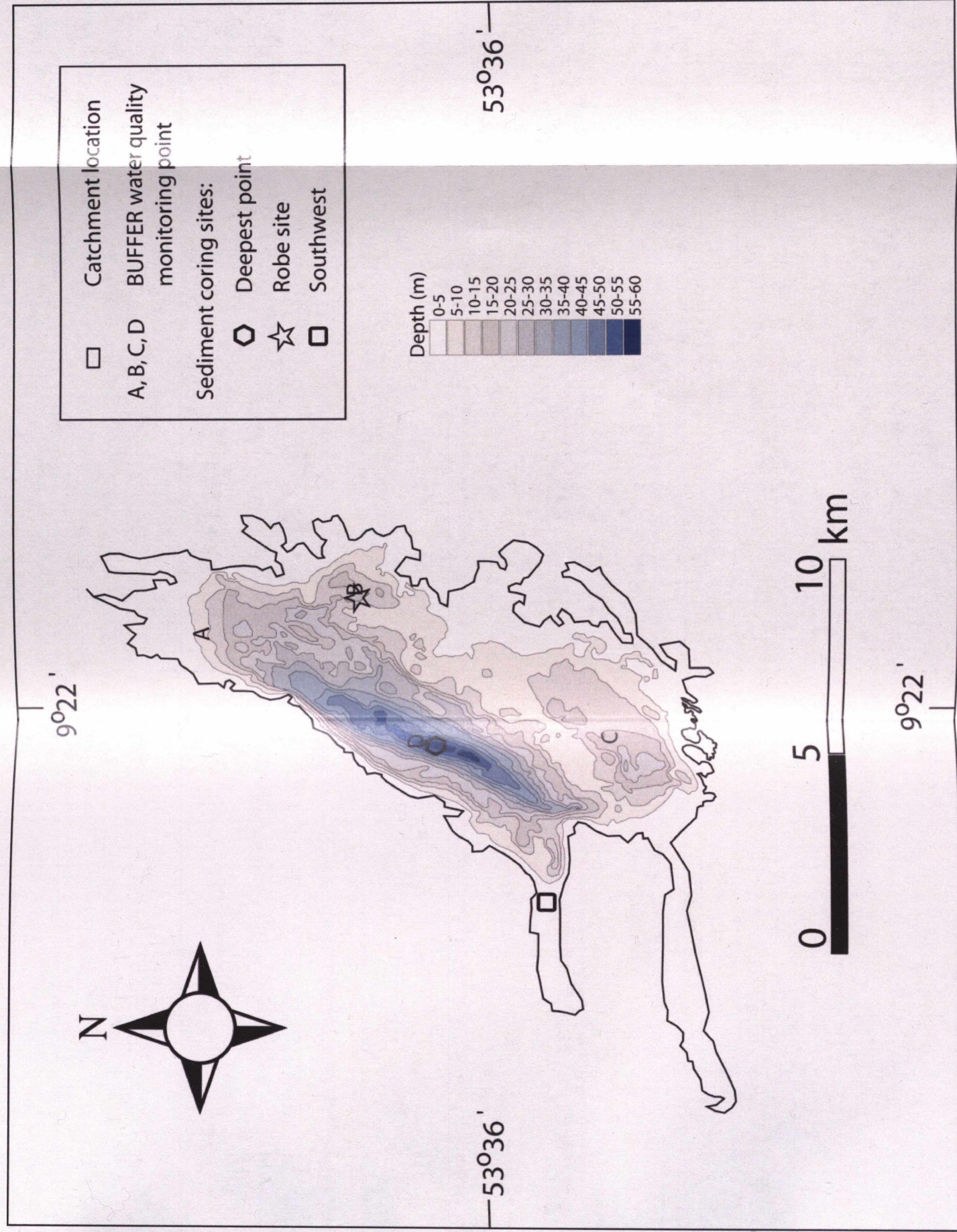


Figure 2.2 Lough Mask bathymetry (supplied by the Mr Kevin Rogers, Western Regional Fisheries Board), sediment coring site locations (symbols) and the locations of water quality sampling points (letters) for the BUFFER project datasets (I. Donohue, Trinity College Dublin, pers. comm.)

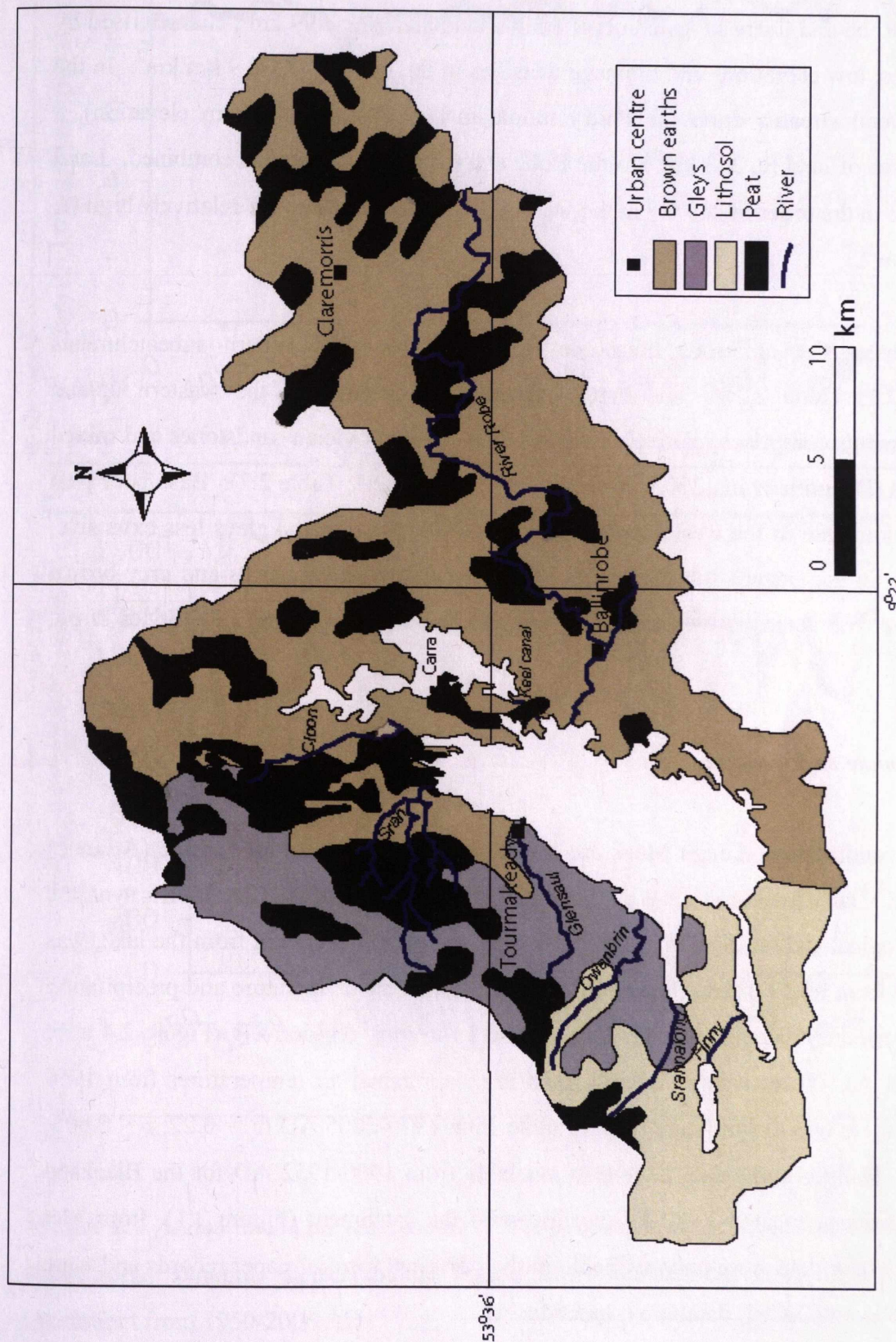


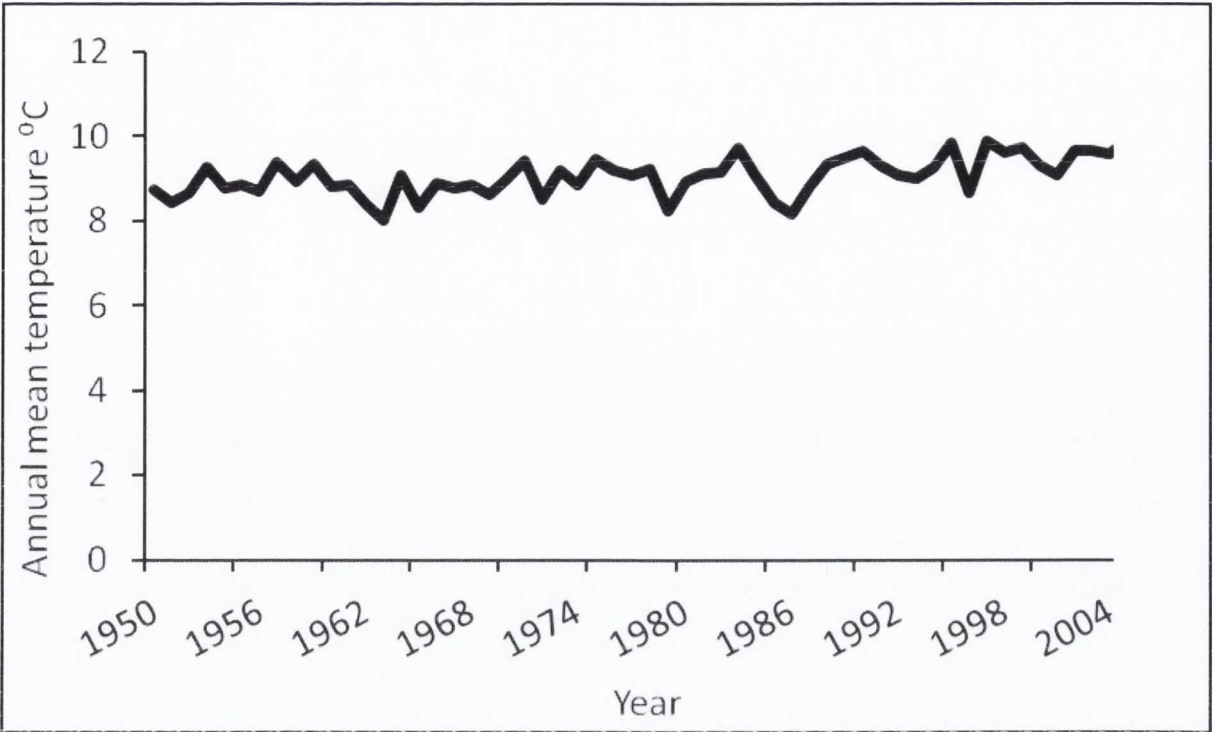
Figure 2.3 Map of the main soil types in the Lough Mask catchment (adopted from Styles *et al.*, 2006)

Lough Mask discharges primarily via underground seepage through karst limestone into Lough Corrib, Co. Galway (Delany, 1988). The east and west parts of the catchment differ in their hydrological characteristics (Table 2.2; Donohue & Irvine, 2003). In the east, the Robe and Carra subcatchments drain a land area of c. 399 km², characterised by low slopes, low elevations and drainage densities in the range c. 0.8-0.9 km km². In the west, several streams drain the Partry mountains (c. 684 m maximum elevation), a similar area of land (c. 343 km²) to the Robe and Carra subcatchments combined. Land slopes are in the order of c. 9.8 ° in the west and drainage densities are relatively high (c. 1.9 km km²).

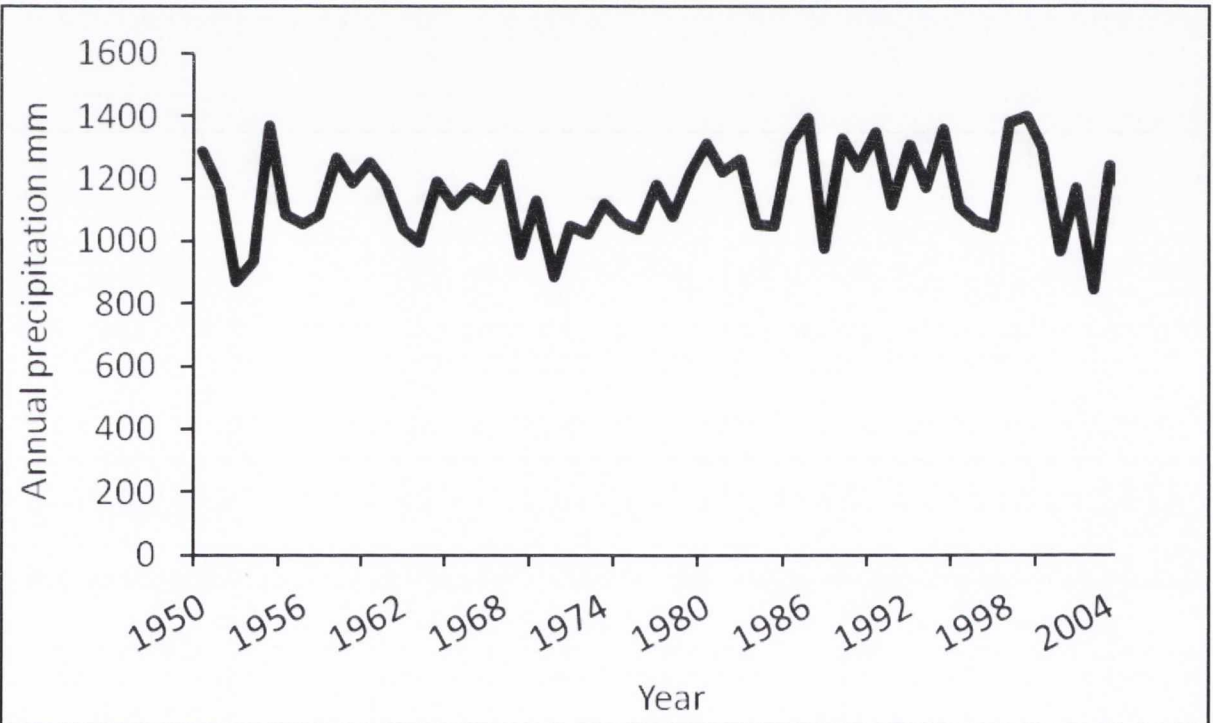
Upper Carboniferous limestone forms the low-lying eastern subcatchments (Figure 2.1; Table 2.2). The Partry mountains characterising the western upland subcatchments comprises relatively resistant siliceous Ordovician sandstones and mixed volcanics (Donohue *et al.*, 2005; Holland, 2009) (Figure 2.1; Table 2.2). Base-poor peat soils predominate in the western subcatchments, with podzols and gleys less extensive; soil cover in the eastern subcatchments is predominately brown earths and grey-brown podzolics, with some smaller areas of gleys and basin peats (Figure 2.3) (Styles *et al.*, 2006).

2.2.3 Climate and weather

Climate conditions at Lough Mask are cool-temperate with a strong oceanic (Atlantic) influence. Daily meteorological data from 1950 AD to present for Claremorris synoptic meteorological station located in the Robe subcatchment, c. 17.5 km from the lake, was available from Met Éireann (Figure 2.1). Mean annual air temperature and precipitation for the period 1950-2005 AD were 9.1 °C and 1146 mm, respectively (Figure 2.4 a, b; Appendix A). There was no overall trend in mean annual air temperatures from 1950 AD, but there was a significant upward trend from 1970-2005 AD ($r^2 = 0.22$; $p < 0.005$; $v = 34$). Daily climate data were also available from 1900-1952 AD for the Blacksod weather station, located c. 40 km northwest of the catchment (Figure 2.1), from Met Éireann. These data were only available in their original form of paper records and were compiled in an EXCEL database (Appendix A).



(a)



(b)

Figure 2.4 Annual mean air temperature ($^{\circ}$ C) (a) and annual precipitation (mm) (b) at Claremorris synoptic meteorological station (see Figure 2.1) in the Lough Mask catchment from 1950-2006 AD

2.2.4 Human pressures

Census data were available from the Central Statistics Office (CSO) on the basis of District Electoral Divisions (DEDs) (Appendix B) or Rural Districts (Appendix B and C) for all census years between 1880-2006 AD. Census data from 1880-1980 AD were available in paper records and were transcribed as part of the research; data from 1980-2006 AD were available in digitised form. DEDs were described using Arc GIS shapefiles of the Lough Mask catchment and DED boundaries from the BUFFER (EU Fifth Framework Programme) project (I. Donohue, TCD, pers. comm.) (Figure 2.1; Appendix D). A map of Rural Districts for the catchment was obtained from Simon Fernandez (Glucksman Map Library, Trinity College Dublin). The Lough Mask catchment comprises 48 DEDs (Appendix D): ten are situated in the catchment in their entirety. In the 38 DEDs that are only partially located in the catchment, the population levels within the part of the DED or Rural District contained in the catchment were determined on a proportional area basis that also accounted for the locations of any urban centres of population.

2.2.4.1 Human population

Human population data were available for all census years from 1880-2006 AD from the CSO. Human population levels were at their highest at 35,509 in 1880 AD and decreased consistently to 18,220 in 1970 AD (Figure 2.5 a, d; Appendix E). From c. 1970 AD, population levels in the catchment continued to fall, reaching a low of 15,203 in the 1996 AD census. Population levels increased slightly between 1996-2006 AD. The Robe subcatchment in the east comprised, on average, 66% of the total catchment population, while the western and Carra subcatchments comprised c. 25 % and c. 14 %, respectively, between 1880-2006 AD. The Robe subcatchment also contains two urban centres (Ballinrobe and Claremorris). Both are located in the Robe subcatchment, and each had populations of about 2,500 in 2006 AD. Development of rural housing, particularly during the late 20th century, has been highlighted as a potentially important contributor to nutrient loading in the catchment (Hobbs *et al.*, 2005) as found elsewhere in rural Ireland (Jordan *et al.*, 2012).

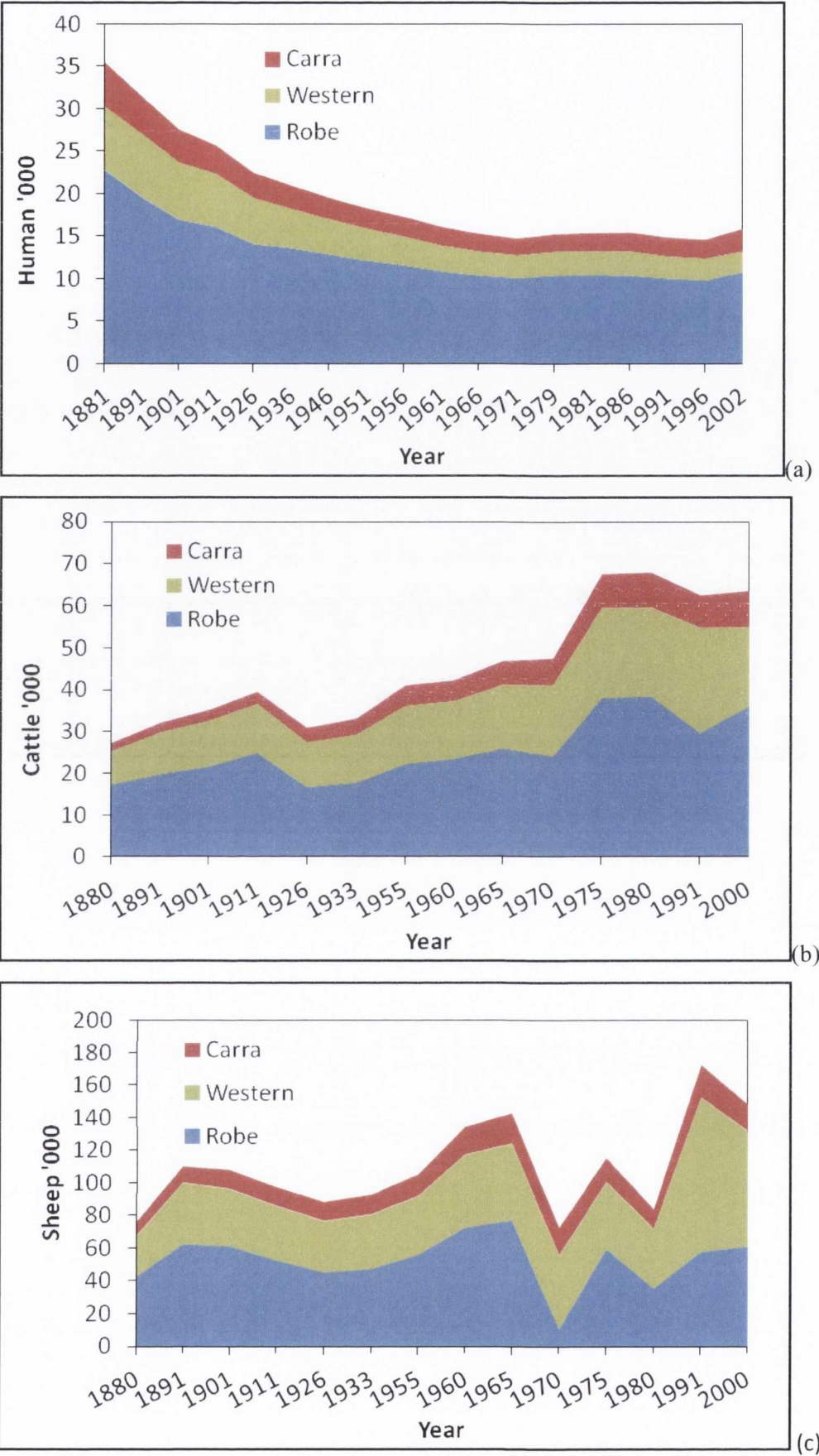
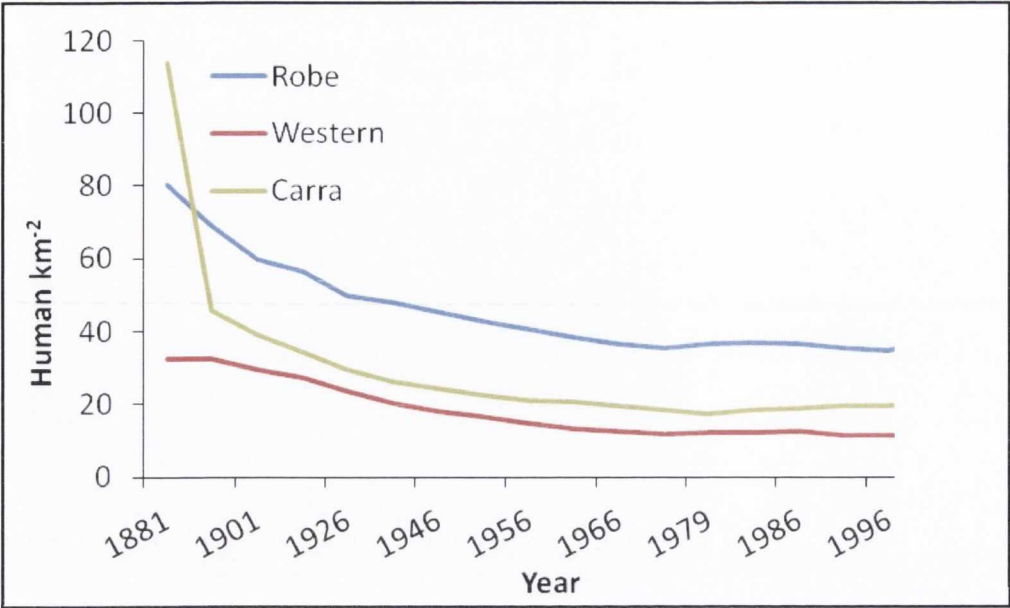
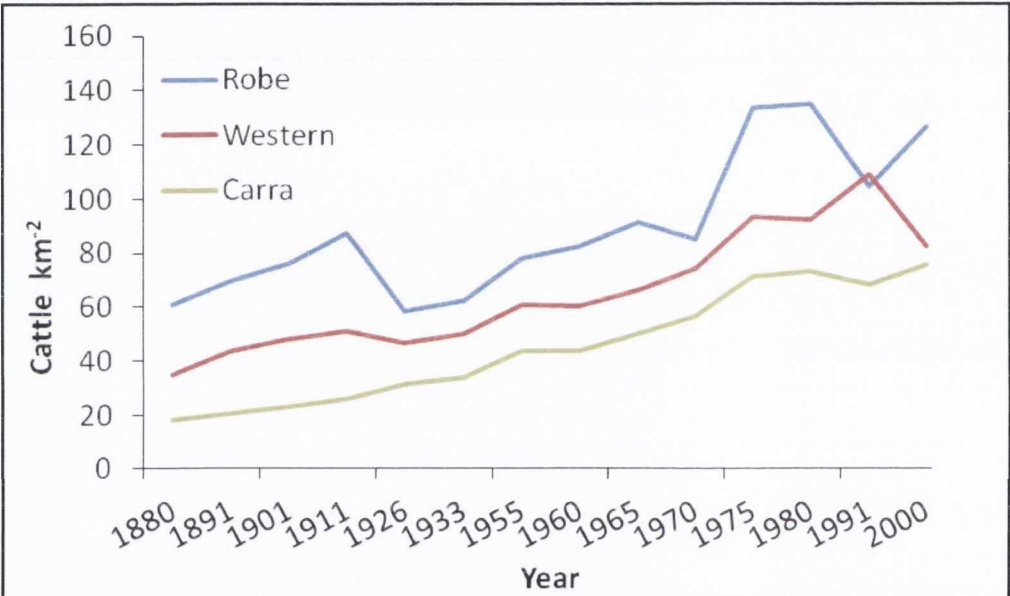


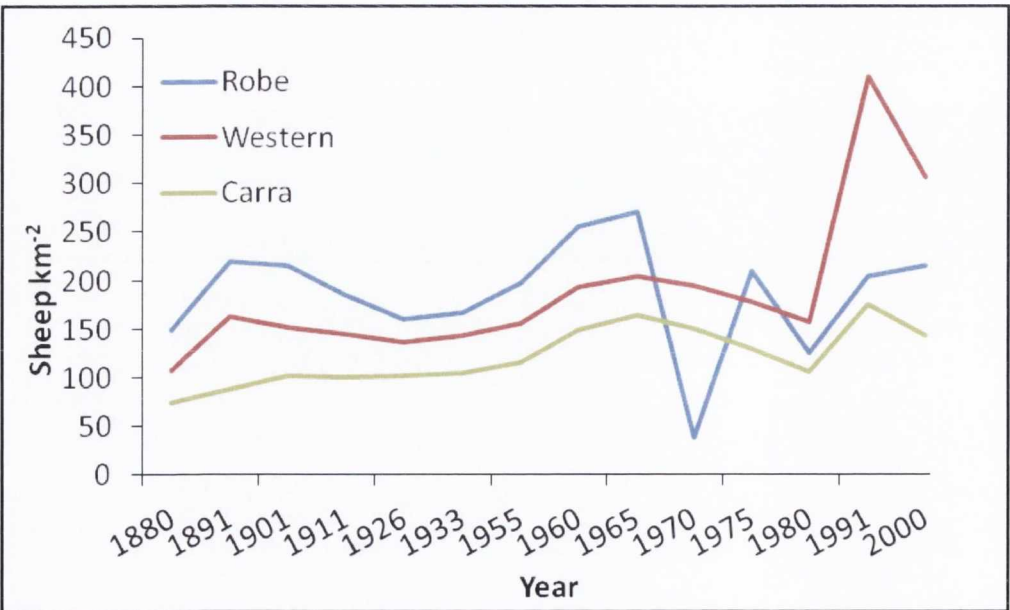
Figure 2.5 Historical census data (absolute numbers, a-c, and densities, d-f) for the main Lough Mask subcatchments, 1880-2006 AD: human population (a, d), cattle (b, e) and sheep numbers (c, f)



(d)



(e)



(f)

Figure 2.5 (continued)

2.2.4.2 Land use

The availability of historical land use data for the Lough Mask catchment was inconsistent; land use records were available from the CSO for census years between 1841-1911 AD and between 1981-2006 AD, on the basis of Rural Districts (Appendix F). The land use classification system used during the earlier period for which the historical data are available differed from that used in the more recent dataset. The process through which the data were harmonised is outlined in Appendix G.

Land use in the Robe subcatchment is dominated by pasture (c. 64 % of the subcatchment area) (Table 2.3), used mainly for cattle grazing. The remaining land area comprises crops (c. 20 %), peat bogs (c. 14 %) and forestry (c. 2 %). Land use in the Carra subcatchment is similar to that of the Robe, with c. 63 % of its area taken up by agricultural pasture, and the remaining land area used for crops (c. 20 %) and peat bogs (c. 15 %). In contrast, land use in the western subcatchments is primarily upland blanket peat bogs (c. 70 % of the area), which are grazed mainly by sheep, followed by pasture (c. 30 %) and forestry (c. 5 %). Historical data indicate that there were no major changes in land use in the Lough Mask catchment over the 1880-2006 AD period (Figure 2.6 a-c; Appendix F). However, the area of land classified as crops decreased between c. 1901-1926 AD, in the Robe and Carra subcatchments, and was coincident with an increase in that classified as pasture. Furthermore, the area of land classified as crops increased in the latter part of the 20th century, while that of pasture decreased slightly (Figure 2.6 b).

Table 2.3 Corine (2006) land cover data for Lough Mask subcatchments, expressed as a % of the subcatchment area. *West includes the Cloon, Srah, Glensaul, Cartron Bower, Owenbrin, Srahnalong and Finny subcatchments

Subcatchment	Pasture	Peat bogs	Forestry	Urban	Cereals	Other
Robe	64.0	14.3	1.6	0.3	19.6	0.2
Carra	62.5	14.9	3.1	0.0	19.5	0.0
West*	26.9	66.9	4.7	0.0	1.5	0.0

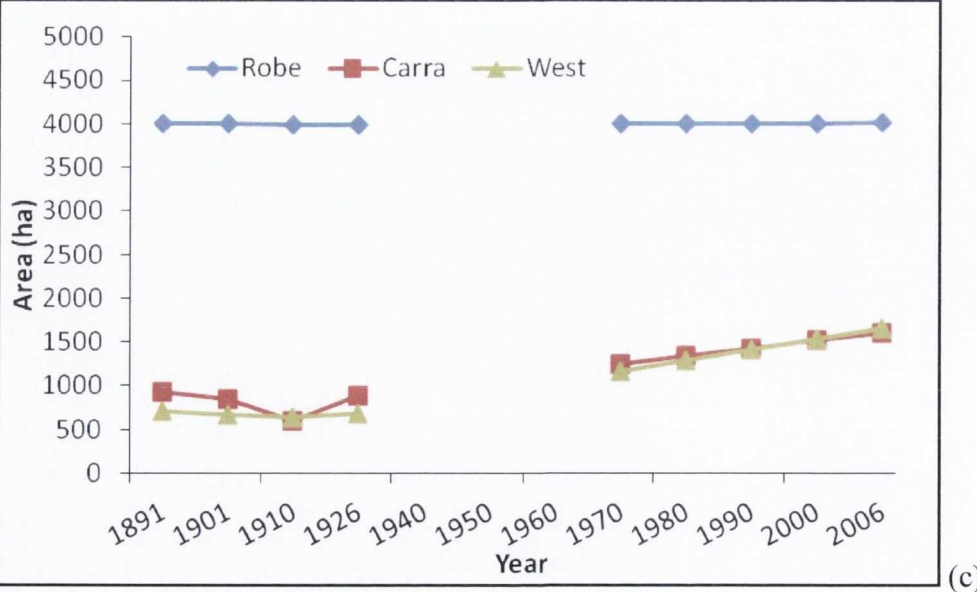
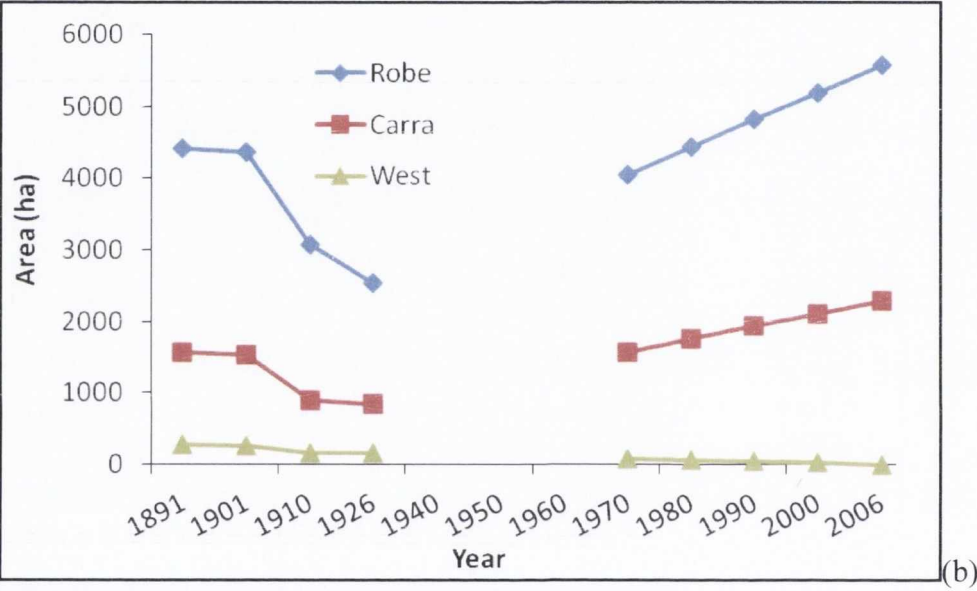
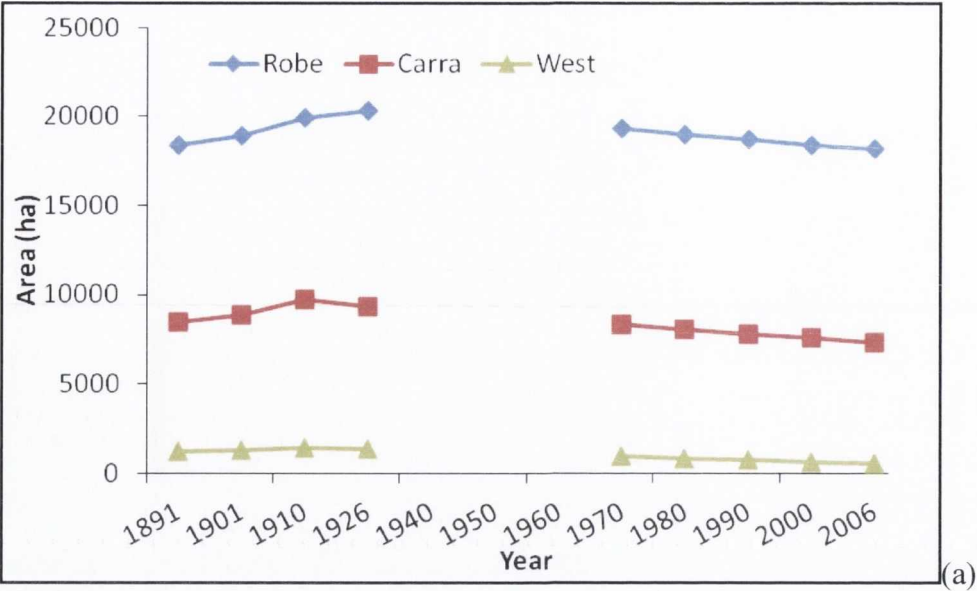


Figure 2.6 Historical data for the predominant land uses in the main Lough Mask subcatchments: pasture (a), crops (b) and peat (c)

2.2.4.3 Agricultural activity

Cattle numbers in all of the Lough Mask subcatchments increased during the 1880-1980 AD period, from c. 27,400 (c. 38 head km⁻²) in 1880 AD to c. 68,000 (c. 100 head km⁻²) in 1980 AD, with the exception of a decrease between c. 1911-1926 AD (Figure 2.5 b, e; Appendix E). Cattle numbers decreased between 1980-1991 AD, but increased slightly between 1991-2006 AD. The sheep population in the catchment was relatively high in the early part of the 20th century; census data indicate that there were c. 75,707 sheep (c. 110 head km⁻²) in 1880 AD (Figure 2.5 c, f; Appendix E). Stocking levels increased to 110,162 (c. 157 head km⁻²) in 1891 AD and declined thereafter until 1926 AD, and then increased again until 1965 AD to peak at 144,775 (c. 213 head km⁻²). The sheep population in the catchment was highly variable between 1965-2006 AD. An increase in numbers of cattle and sheep during the 20th century was not associated with a commensurate increase in area of land classified as pasture (Figure 2.6 a). Instead, the increased numbers raised stocking densities on the existing area of grazed land.

Previous studies have concluded that diffuse P loadings arising from agricultural sources in the Robe, where they contribute up to c. 85 % of the total P load to Lough Mask (McGarrigle & Champ, 1999), and Carra subcatchments have increased during the late 20th century, particularly during the winter months (McGarrigle & Champ, 1999; Irvine *et al.*, 2003). Agriculture in the catchment is therefore regarded as the most likely source of increased eutrophication pressures. In the west, the Owenbrin subcatchment has been negatively impacted by overgrazing by sheep (McGarrigle & Champ, 1999).

2.2.4.4 Hydromorphological modifications

The Lough Mask catchment underwent substantial hydromorphological modification as a result of Arterial Drainage Schemes (ADS) during the 19th century. ADS took place in all of the Lough Mask subcatchments between c. 1845-1860 AD, for the purpose of economic development: increasing mill-power and extending the area of land available for agriculture (Harding, 1846). Intensive ADS significantly altered the hydrodynamics of the catchment. In particular, ADS resulted in dekarstification of much of the eastern part of the catchment by draining flooded land (>7 % of the total catchment area), creating entirely new river systems, modifying existing rivers and linking lakes and turloughs (Harding, 1846; Coxon & Drew, 1986). The hydrological effects of ADS in

the catchment include more rapid surface water flow (Coxon & Drew, 2000) and increased sediment and nutrient load capacities of inflows (Bhattarai & O'Connor, 2004). Prior to ADS, drainage of the eastern part of the catchment would have been primarily via groundwater. Smaller-scale ADS also took place in the Robe subcatchment between c. 1920-1940 AD, for the purpose of extending and improving land for grazing livestock (Walsh, 1974; Coxon & Drew, 1986). There is no evidence for ADS in the western part of the catchment during this period. Further phases of ADS continued in the Robe subcatchments during the late-1940s and between 1979-1980 AD.

2.2.4.5 Point sources of pollution

There are two main sewage treatment plants (STPs) located in the Robe subcatchment (at Ballinrobe and Claremorris) (Figure 2.1), which contribute relatively minor amounts of nutrients to the River Robe, <5% of total annual loading of P and N (Donohue *et al.*, 2005), and have mean effluent discharges of <1 mg l⁻¹ (Irvine *et al.*, 2003). Primary treatment of waste commenced at both STPs in the late 1940s, while secondary treatment (with P removal) was installed in Ballinrobe STP in 1996 AD (McGarrigle & Champ, 1999), and in 2000 AD in Claremorris (K. Shally, Mayo County Council, pers. comm.).

2.2.5 Lake monitoring data

2.2.5.1 Lake physico-chemical conditions

Because of the insular and oceanic location, water temperatures in Lough Mask normally fluctuate between 4-21 °C and ice cover is rare (McGarrigle & Champ, 1999). Although the lake basin is spatially-heterogeneous and complex in terms of its physical nature (described in Section 2.2.1), studies of water circulation patterns in Lough Mask have shown that the open water part of the lake is well-mixed and that circulation is wind-driven (McCarthy *et al.*, 2001). Monthly temperature data for the period March 1996 AD to July 1996 AD indicated some transient summer stratification in summer (McCarthy *et al.*, 2001). No long-term, high resolution temperature records existed for Lough Mask prior to the current research project. A thermistor chain was installed in the deepest point in March 2007 as part of this research project (Figure 2.1; Appendix H), with loggers (ONSET TidbiT) placed at 15 depths between the surface and 50 m, and provided data to the end of the project. These data also indicated that several short-lived

periods of stratification occurred in the lake in the summer months of 2007 AD and 2008 AD, and that the lake was well-mixed during the rest of the year (Figure 2.7).

Contrary to the evidence of a well-mixed lake water from water circulation studies (McCarthy *et al.*, 2001), Lough Mask has also been described as complex in terms of its water chemistry. McGarrigle & Champ (1999) described the water chemistry of the embayments in the southwest part of the lake as having low ionic contents, while the open water of the lake is moderately hard with relatively low colour and good transparency (Flanagan & Toner, 1975). The most detailed water quality monitoring datasets for the lake were gathered as part of the BUFFER (EU Fifth Framework Programme) project for four different sampling sites (A, B, C and D) in Lough Mask (Figure 2.1), and were available for the current study from I. Donohue (Trinity College Dublin, pers. comm.). The BUFFER monitoring datasets, which comprise fortnightly to monthly monitoring for the period 2001-2003 AD, included pH, water temperature, alkalinity and secchi depth and showed little variation within the open water of Lough Mask, supporting previous descriptions of the well-mixed nature of the lake (Table 2.4; Appendix I).

At monitoring sites A (Keel), B (Robe) and C (south) lake water pH was in the alkaline range, had high carbonate buffering capacity and good transparency (Table 2.4), similar to the findings of McGarrigle & Champ (1999) based on monitoring of the lake between 1975-1995 AD. Although all four monitoring sites had similar mean values for physico-chemical parameters, the range of values at site D (the deepest point), the closest monitoring site to the western inflows, was larger with neutral to alkaline pH, low to high alkalinity and low to moderate conductivity (Table 2.4).

2.2.5.2 Lake nutrient conditions and trophic status

Measured trophic status, based on the modified OECD classification as described in S.I. No. 258 of 1998, indicates that Lough Mask is currently classified as mesotrophic (Toner *et al.*, 2005). Long-term TP and total chlorophyll *a* data from the Central Fisheries Board (CFB) (now Inland Fisheries Ireland, IFI) indicated that the lake has undergone deterioration since the mid-late 1980s in the form of a shift in trophic status from oligotrophic to mesotrophic (McGarrigle & Champ, 1999; Toner *et al.*, 2005) (Figure 2.8). Lough Mask was classified as being on the oligotrophic/mesotrophic boundary

Table 2.4 Summary of lake water quality monitoring data for 4 monitoring sites (see Figure 2.2) for Lough Mask (2001-2003 AD), showing ranges and means (in parentheses), available from the BUFFER project (EVK1-1999-00094), supplied by Dr. Ian Donohue and Dr. Ken Irvine, Department of Zoology, Trinity College Dublin. Full details are provided in Appendix I

Variable	Units	A (Keel)	B (Robe)	C (south)	D (deepest point)
pH	pH units	8.2-8.5 (8.3)	8.2-8.5 (8.3)	8.3-8.4 (8.4)	7.4-8.5 (8.2)
Temperature	°C	7-17 (12)	7-18 (11)	7-18 (14)	5-17 (12)
Alkalinity	mg CaCO ₃ l ⁻¹	103-110 (106)	105-113 (107)	103-104 (103)	16-108 (101)
Conductivity	µS cm ⁻¹	236-269 (252)	197-255 (239)	230-289 (251)	70-290 (234)
Turbidity	NTU	3-14 (8)	6-9 (7)	8-8 (8)	3-11 (7)
Colour	PtCo	0-22 (13)	19-29 (22)	15-15 (15)	10-94 (29)
Suspended solids	mg l ⁻¹	1-2 (1)	1-2 (1)	1-2 (1)	1-7 (2)
DOC	mg l ⁻¹	4-6 (5)	4-6 (5)	3-7 (5)	2-8 (4)
SRP	µg l ⁻¹	0-7 (2)	1-7 (2)	1-7 (3)	1-7 (2)
PP	µg l ⁻¹	2-32 (9)	1-17 (8)	4-12 (6)	1-16 (6)
TP	µg l ⁻¹	6-32 (14)	7-27 (14)	6-15 (10)	7-22 (12)
Nitrate	mg l ⁻¹	0.3-0.5 (0.3)	0.3-0.5 (0.3)	0.3-0.4 (0.3)	0.1-0.5 (0.3)
TN	mg l ⁻¹	0.5-0.8 (0.6)	0.5-0.8 (0.6)	0.6-1.1 (0.8)	0.5-1.6 (0.7)
Secchi depth	m	3-6 (4)	3-7 (4)	3-5 (5)	2-6 (4)
Chlorophyll <i>a</i>	mg l ⁻¹	1-10 (3)	1-9 (3)	2-11 (5)	2-10 (4)

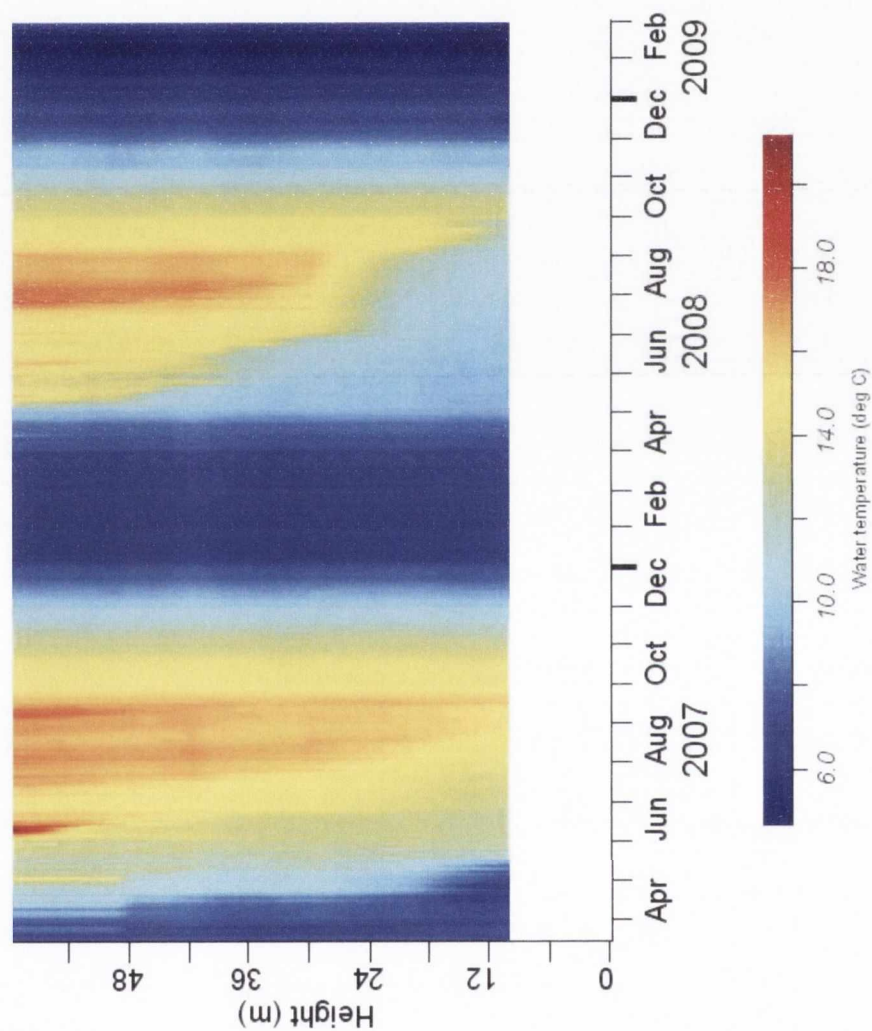
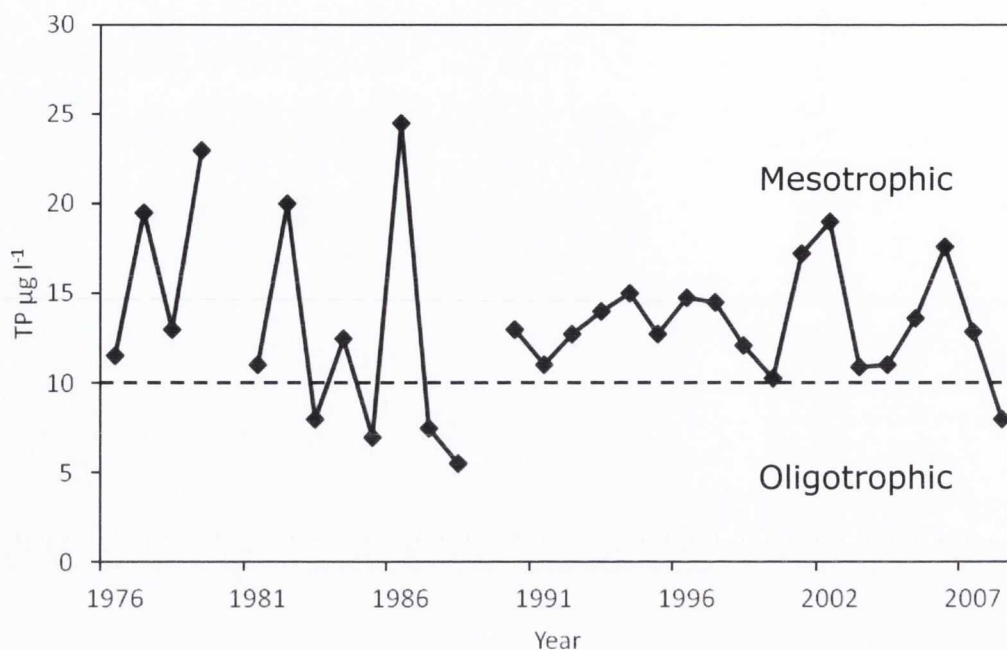
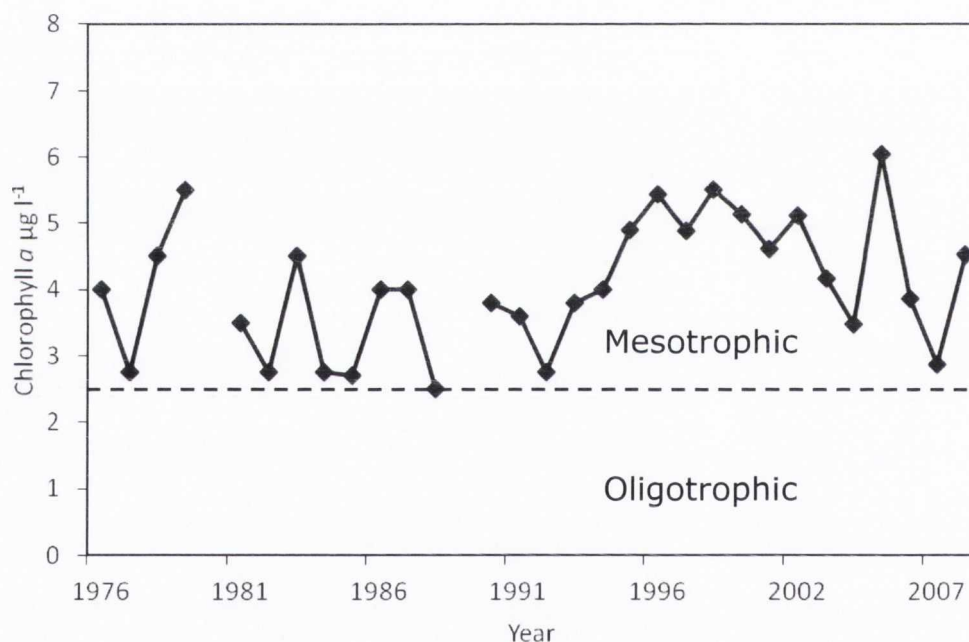


Figure 2.7 Daily measured temperature profiles for Lough Mask between March 2007 AD and February 2009 AD. See Appendix Q for full details



(a)



(b)

Figure 2.8 Annual mean total phosphorus (TP) and annual mean total chlorophyll a concentrations based monitoring from McGarrigle & Champ (1999) and the Central Fisheries Board (CFB)

during the period 1976-1995 A (McGarrigle & Champ, 1999) and oligotrophic between March 1996 AD to July 1997 AD (McCarthy *et al.*, 2001) based on chlorophyll a and TP levels. TP and total chlorophyll a data from the BUFFER dataset indicated that oligo-mesotrophic conditions persisted in the lake between 2001-2003 AD (Table 2.4).

Monitoring data from the EPA indicated mesotrophic conditions during the 2001-2003 AD period (Toner *et al.*, 2005).

Nutrient concentrations measured between 2001-2003 AD, including dissolved organic carbon (DOC), particulate P (PP), soluble reactive P (SRP), total dissolved P (TDP), total organic nitrogen (TON), total nitrogen (TN) and total P (TP) showed little or no variation between different lake monitoring sites, however, the highest values were consistently recorded at sites A and B (Table 2.4; Appendix I). Secchi depths indicated good transparency at all monitoring sites during the monitoring period, and were inversely correlated with chlorophyll *a* at all sites ($r^2 = 0.5-0.9$; $p < 0.05$; $v = 22$). P concentrations generally peaked in winter months, and reached up to $35 \mu\text{g l}^{-1}$ (Appendix I). The observed seasonal chlorophyll *a* concentration data in Lough Mask were variable and displayed an unusual annual pattern with two peaks during the year, the highest in spring or summer (up to c. $12 \mu\text{g l}^{-1}$) and a smaller one in winter (up to c. $7 \mu\text{g l}^{-1}$) during the 2001-2003 AD period (Appendix I), and this pattern was evident in both CFB and BUFFER monitoring datasets.

2.2.5.3 Lake ecology

2.2.5.3.1 Phytoplankton

Phytoplankton monitoring data in the form of unpublished algal counts were available from the CFB (T. Champ & J. King, pers. comm.). These data comprise monthly single-point samples from the deepest point collected during 1975, 1983, 1984, 1985 and 1986 AD. A full list of phytoplankton taxa, density and biomass data is provided in Appendix K. The observed seasonal trend in the phytoplankton community in Lough Mask was unusual (Figure 2.9 a-e). Diatoms were abundant for most of the year (c. 40-100 % of total phytoplankton assemblage). However, in 1975 AD and 1983 AD cyanophytes, and *Oscillatoria agardhii* in particular, were the most abundant taxa followed by diatoms (Figure 2.9 a-b). Cyanophytes exhibited peaks in summer and early autumn in 1975 AD and 1983 AD. Two peaks were also apparent in the diatom data, the highest in spring and a smaller peak in autumn. A shift in the phytoplankton assemblage was evident in the 1984-1986 AD dataset with diatoms outnumbering chlorophytes and cyanophytes in most months. Cyanophyte numbers were low for most of the year, but displayed a

distinct peak in late autumn, characterised by abundant *O. agardhii*. Chlorophytes were the next most abundant group and peaked in late summer, after the diatom peak, and again in late autumn, before the second diatom peak (Figure 2.9 a-e). *Asterionella*, *Melosira* and *Tabellaria* were the most abundant diatom taxa in the spring blooms, while *Fragilaria crotonensis* was prevalent in the warmer summer months. An increase in the planktonic *Stephanodiscus/Cyclotella* species, which peaked in spring and late summer, was evident in the dataset from 1985 AD onwards. The seasonal succession of *Melosira/Synedra* to *Asterionella* to *Fragilaria* to *Stephanodiscus* in some years is typical of seasonal silica (Si) depletion in the lake water column (Tilham *et al.*, 1982; Hecky & Kilham, 1988). The seasonal succession of phytoplankton evident in Lough Mask is similar to that of other lakes in Ireland, e.g. Lough Neagh (Jewson *et al.*, 1981).

Monthly phytoplankton monitoring was also carried out during between March 1996 AD and July 1997 AD as part of an EPA-funded project: Eutrophication Processes in the Littoral Zones of Western Irish Lakes (McCarthy *et al.*, 2001). However, these data were not made available for the current research project following consultation with both the project personnel and the EPA throughout the current research. McCarthy *et al.* (2001) summarises the data in the project final report. The findings presented in McCarthy *et al.* (2001) indicate that seasonal variation in phytoplankton populations was similar to that observed in the earlier monitoring datasets from the CFB, and were typical of mesotrophic conditions. There were two algal peaks evident during 1996-1997 AD, one (the highest) in spring and a second smaller and more prolonged peak in late summer/autumn. Diatoms were particularly abundant in the spring but subsequently declined owing to a depletion of SiO₂. McCarthy *et al.* (2001) also noted the persistence of the cyanophyte species, *O. agardhii* throughout the year, which exhibited an autumn peak.

During the 2001-2003 AD period instances of excessive algal growth were recorded in the littoral parts of the lake, while the open waters showed low or moderate levels of planktonic algae, thus highlighting the potential for localised nutrient enrichment (Toner *et al.*, 2005).

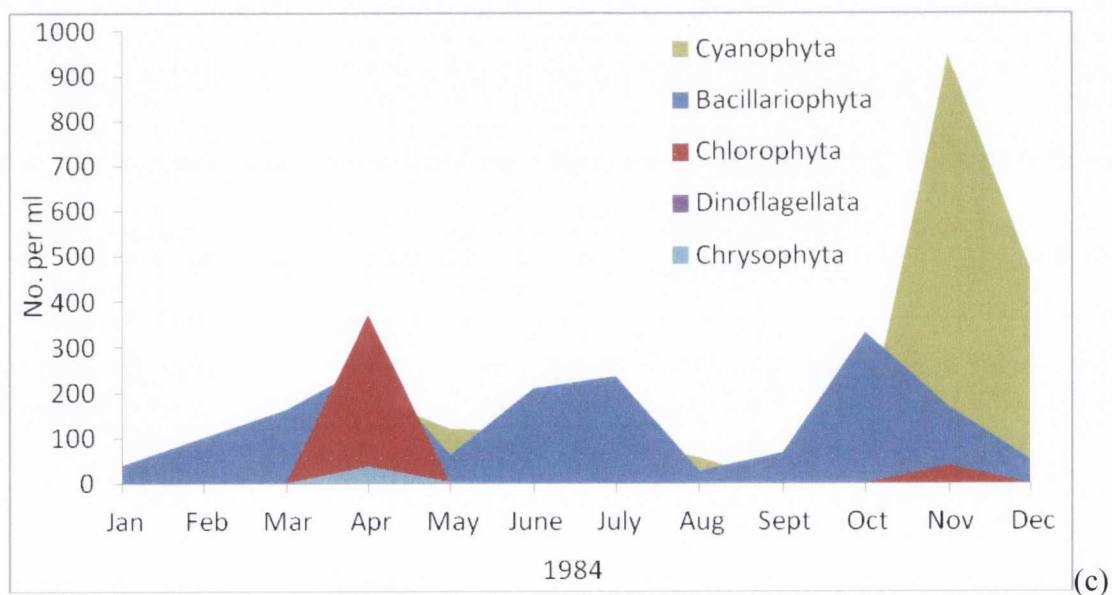
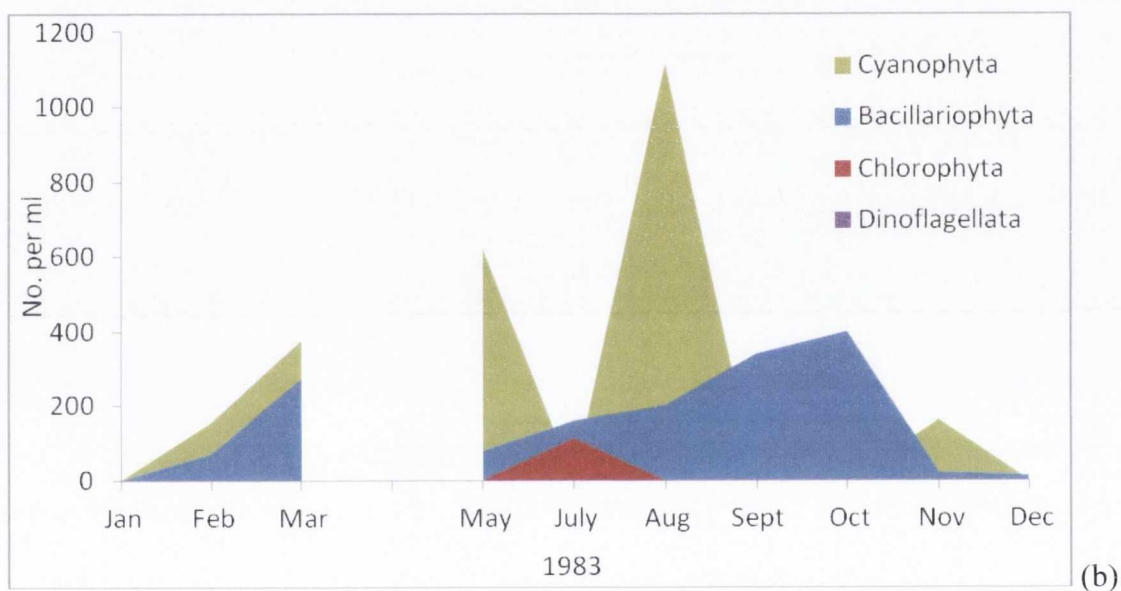
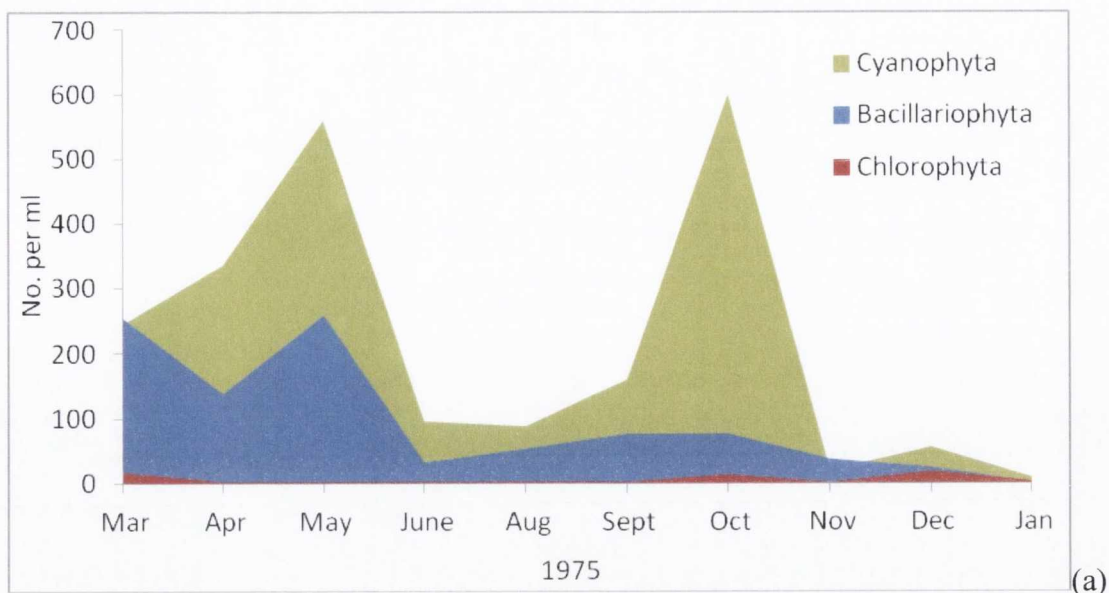


Figure 2.9 Monthly algal density (number of cells per ml) in (a) 1975, (b) 1983 and (c) 1984, and algal biomass (mg/m^3) in (d) 1985 and (e) 1986

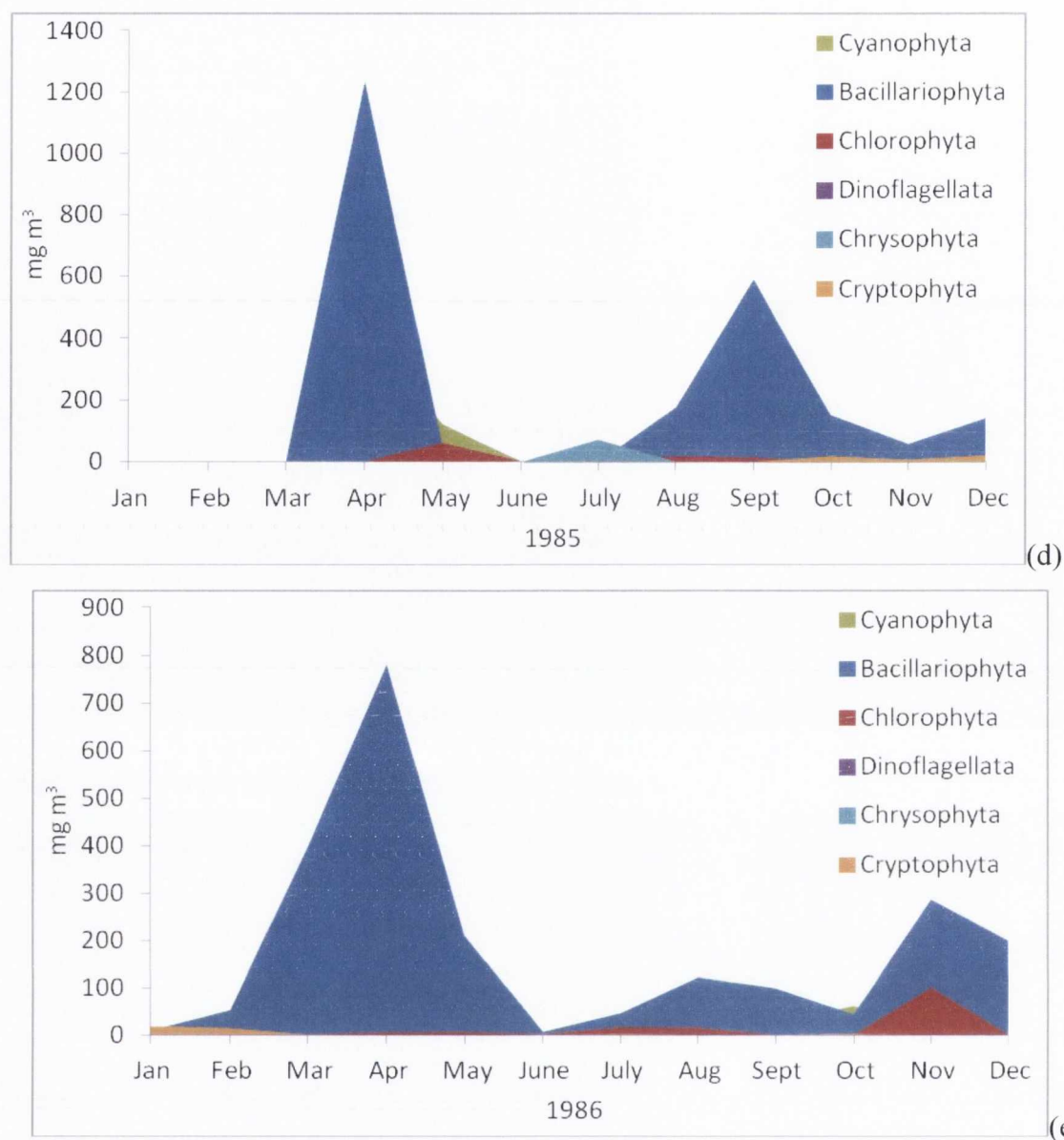


Figure 2.9 (continued)

2.2.5.3.2 Macrophytes

Geographically distinct macrophyte communities in the eastern and western parts of the lake have been described by McGarrigle & Champ (1999) and McCarthy *et al.* (2001). The macrophyte flora in Lough Mask are dominated by stoneworts (charophytes), which are widely distributed in Lough Mask with the densest communities occurring in the eastern embayments where they can extend to depths of 6 m (McGarrigle & Champ, 1999). The southwestern embayments of the lake are characterised by isoetid flora and some *Potamogeton* stands. The macrophyte community assemblage in Lough Mask has been deemed relatively unchanged in most parts of the lake since the early 1980s (McCarthy *et al.*, 2001).

2.2.5.3.3 Fish stocks

Lough Mask is one of the most important natural wild brown trout (*Salmo trutta* L.) fisheries in Europe (CFB, 2002), partly due to the retention of the locally rare species arctic charr (*Salvelinus alpinus* L.) (Maitland & Campbell, 1992; Maitland *et al.*, 2007). However, declines in brown trout stocks during the latter part of the 20th century are evident from fish surveys, and have been linked to pike predation and nutrient pollution via the River Robe (McGarrigle & Champ, 1999). Declines in fish stocks in more recent years are also evident and have been linked to localised nutrient enrichment, excessive algal growth (Toner *et al.*, 2005) and spawning habitat destruction in the inflows to the lake (IFI, 2010).

2.2.5.3.4 Lake management

Lough Mask is located in the WRBD, one of the water management units concerned with implementing the EU WFD in the west of Ireland. According to the EPA typology (Free *et al.*, 2007), Lough Mask is a type 12 lake (deep and large with high alkalinity). Lough Mask was classified as being at significant risk of failing to meet WFD good water quality requirements by 2015 (Anon, 2005). Although satisfactory conditions were measured in the open waters of the lake in recent years, the elevated trophic status highlights the need for the implementation of measures to reduce P inputs before major ecological deterioration occurs (Toner *et al.*, 2005).

The Carra Mask Corrib Water Protection Group was set up in 2000 AD by anglers, in response to the observed declines in water quality and decreased angling returns in Lough Mask, Lough Corrib and Lough Carra. The group are active in addressing water quality issues impacting the catchments, implementing policy relating to water quality, including the WFD, ensuring compliance with policy that has the potential to impact water quality, and increasing public awareness about water quality issues (O'Mealoin, 2005). Currently, the IFI and local angling clubs have plans to introduce specific conservation measures to protect trout spawning habitats in the inflows to Lough Mask (IFI, 2010).

2.2.5.4 Inflow water quality

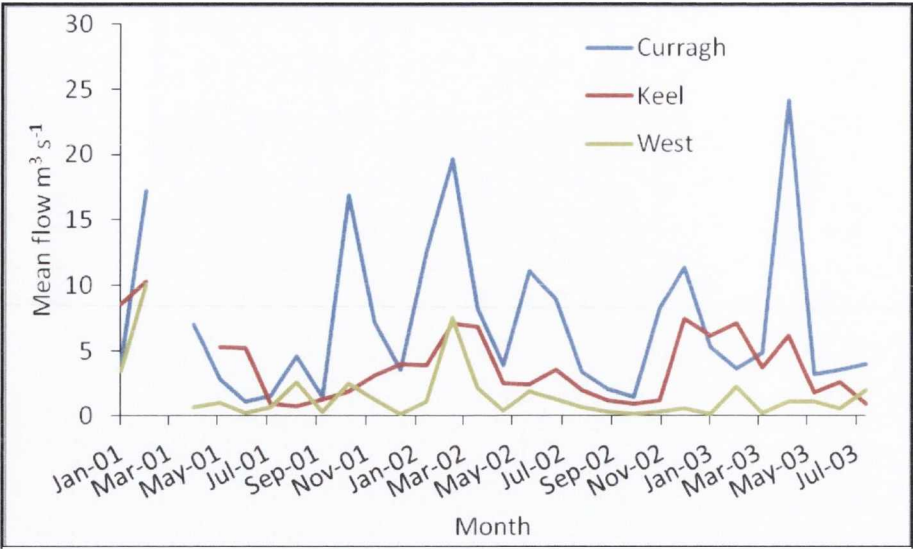
Flow rate data from the BUFFER (EU Fifth Framework Programme) project show that the River Robe is the largest inflow to Lough Mask followed by the Keel canal and the western inflows (Figure 2.10 a). Long-term daily flow records were also available for the main inflows from the Office of Public Works (OPW) and EPA (detailed further in Section 3.2.2.3.1 and Appendix L). A preliminary analysis of these data indicates that flow rates from all inflows closely track seasonal variations in precipitation.

Geological and edaphic disparities between the western and eastern subcatchments of Lough Mask are also evident in the inflow monitoring data from the BUFFER project (Table 2.5; Figure 2.10 b-f). Inflows in the west of the catchment are generally more acidic (pH in the range c. 6.5-8.6), with low to moderate buffering capacities (alkalinities in the range c. 3.9-73.2 mg l⁻¹ CaCO₃) and low ionic contents (conductivity in the range 42.0-87.2 µS cm⁻¹) (Table 2.5). The inflows in the east of the catchment have circumneutral to alkaline pH (in the range c. 7.7-8.2 in the Robe and c. 8-8.6 in the Keel), high ionic contents (conductivities in the range c. 190-336 mg l⁻¹ CaCO₃ in the Robe and c. 91-211 mg l⁻¹ CaCO₃ in the Keel) and high buffering capacities (alkalinities in the range c. 395-660 µS cm⁻¹ in the Robe and c. 245-441 µS cm⁻¹ in the Keel) (Table 2.5; Figure 2.10 b-d).

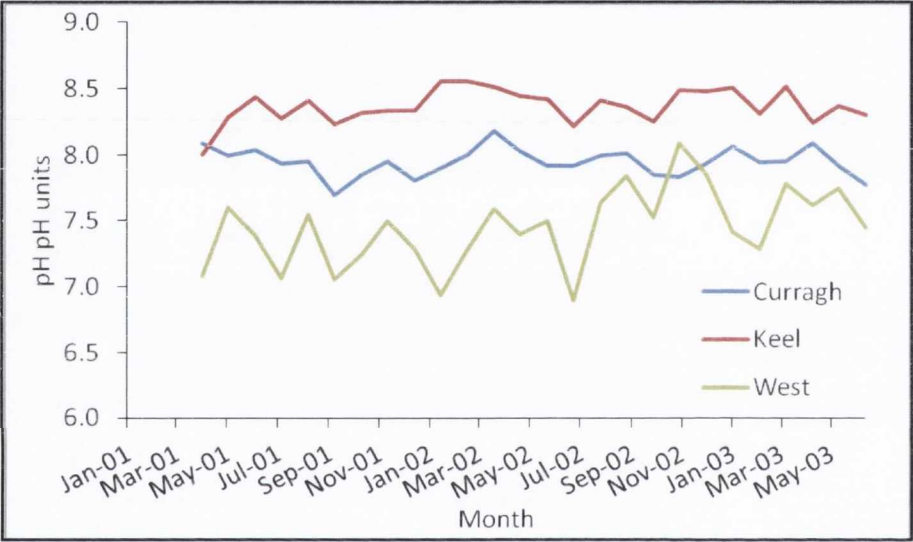
The River Robe generally had the highest DOC, suspended solids, turbidity and colour values (Table 2.5; Figure 2.10 b-f) followed by the western streams, although the western inflows drain a peat-dominated catchment which would be expected to have elevated inputs of organic material and therefore higher values for these parameters. Peak values for colour and suspended solids concentrations in the western inflows, however, were similar or higher to those of the Robe (Figure 2.10 f and 2.11 h). The lowest measurements for colour and suspended solids were recorded in the Keel canal. The western and eastern inflows to Lough Mask are also distinctive based on their nutrient levels. The River Robe had the highest nutrient concentrations (including SRP, PP, TP, nitrate, TON and TN) (Table 2.5; Figure 2.11), consistent with the findings of McGarrigle & Champ (1999) and Toner *et al.* (2005). Nutrient concentrations in the Keel canal were in a similar range to those evident in the western inflows (Table 2.5; Figure 2.11).

Table 2.5 Summary of inflow water monitoring data available for the main inflows to Lough Mask (see Figure 2.1) (2001-2003 AD), showing ranges and means (in parentheses), available from the BUFFER project (EVK1-1999-00094), supplied by Dr. Ian Donohue and Dr. Ken Irvine, Department of Zoology, Trinity College Dublin. Full details are provided in Appendix J. *West includes the Cloon, Srah, Glensaul, Cartron Bower, Owenbrin, Srahnalong and Finny subcatchments

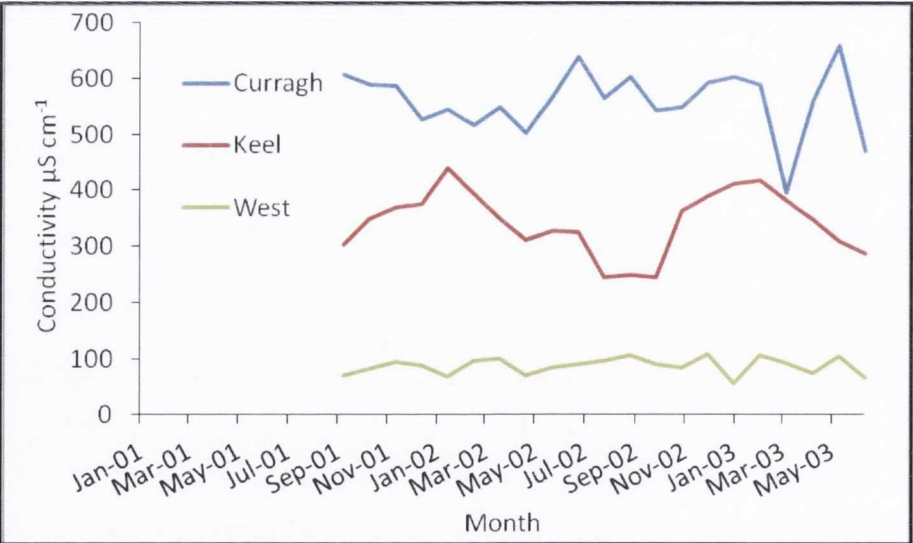
Variable	Units	Robe (Curragh)	Carra (Keel)	West (mean)*
Flow rate	m ³ s ⁻¹	1-24 (7)	1-10 (4)	0-18 (2)
pH	pH units	7.7-8.2 (7.9)	8.0-8.6 (8.4)	6.5-8.6 (7.4)
Alkalinity	mg CaCO ₃ l ⁻¹	190-336 (286)	91-211 (149)	4-73 (20)
Conductivity	µS cm ⁻¹	395-660 (560)	245-441 (343)	42-209 (87)
Turbidity	NTU	7-99 (22)	2-11 (6)	0-41 (10)
Colour	PtCo	29-181 (69)	0-254 (34)	8-230 (44)
Suspended solids	mg l ⁻¹	2-15 (5)	1-2 (1)	0-131 (4)
DOC	mg l ⁻¹	3-86 (18)	4-8 (6)	0-16 (4)
SRP	µg l ⁻¹	3-27 (11)	0-11 (3)	0-17 (3)
PP	µg l ⁻¹	10-56 (26)	2-10 (5)	0-44 (5)
TP	µg l ⁻¹	22-96 (44)	6-25 (11)	0-44 (10)
Nitrate	mg l ⁻¹	0.4-1.8 (1.0)	0-0.8 (0.2)	0-0.9 (0.2)
TN	mg l ⁻¹	1.0-2.6 (1.6)	0.5-1.6 (0.9)	0.1-1.4 (0.6)



(a)



(b)



(c)

Figure 2.10 Monthly inflow water physico-chemical data for Lough Mask, 2001-2003 AD: flow rate (a), pH (b), conductivity (c), alkalinity (d), turbidity (e) and colour (f) for Lough Mask available from the BUFFER project (EVK1-1999-00094) supplied by Dr. Ian Donohue and Dr. Ken Irvine, Department of Zoology, Trinity College Dublin

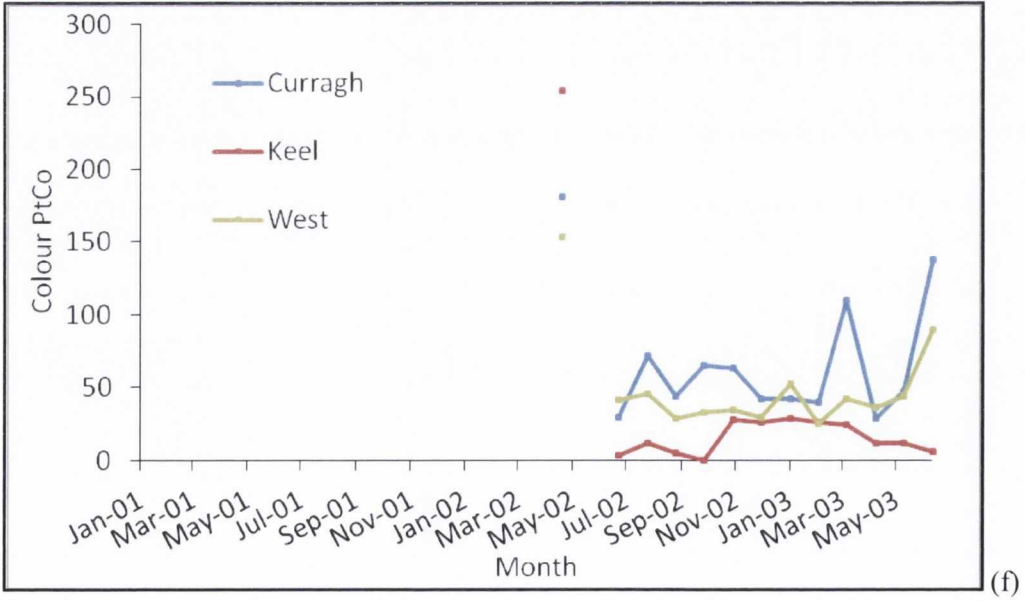
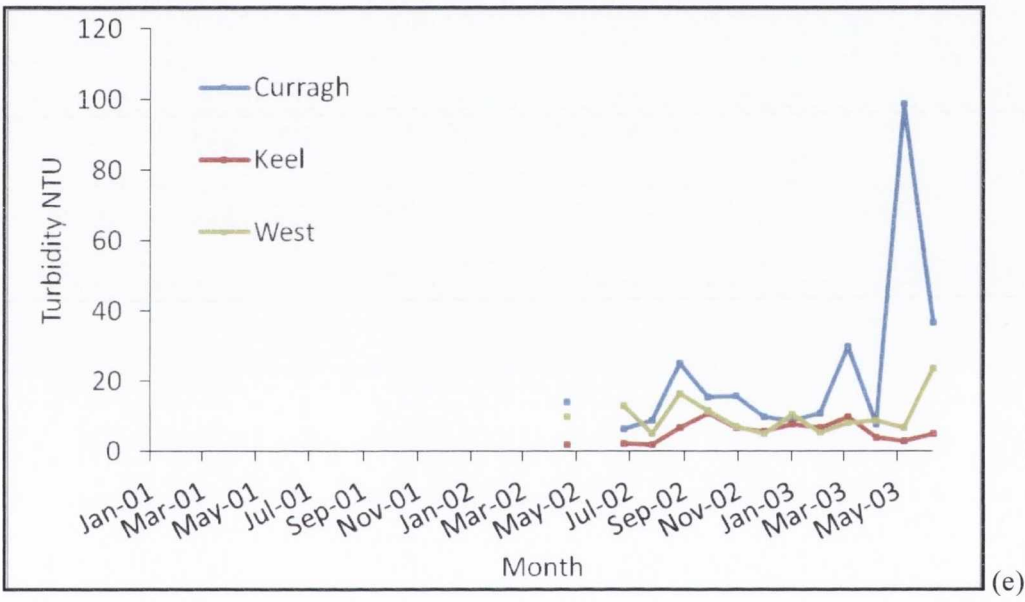
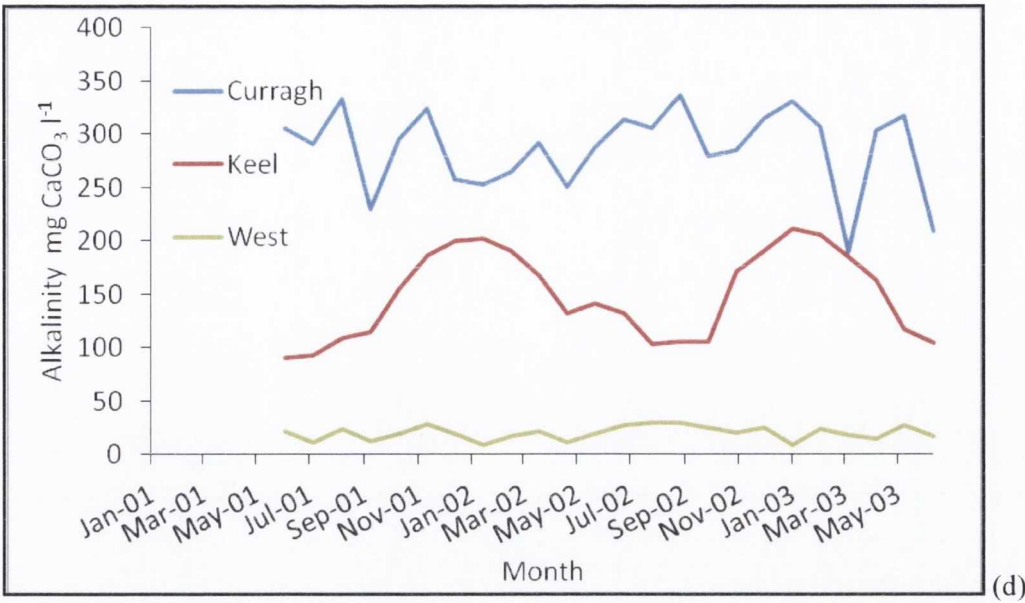


Figure 2.10 continued

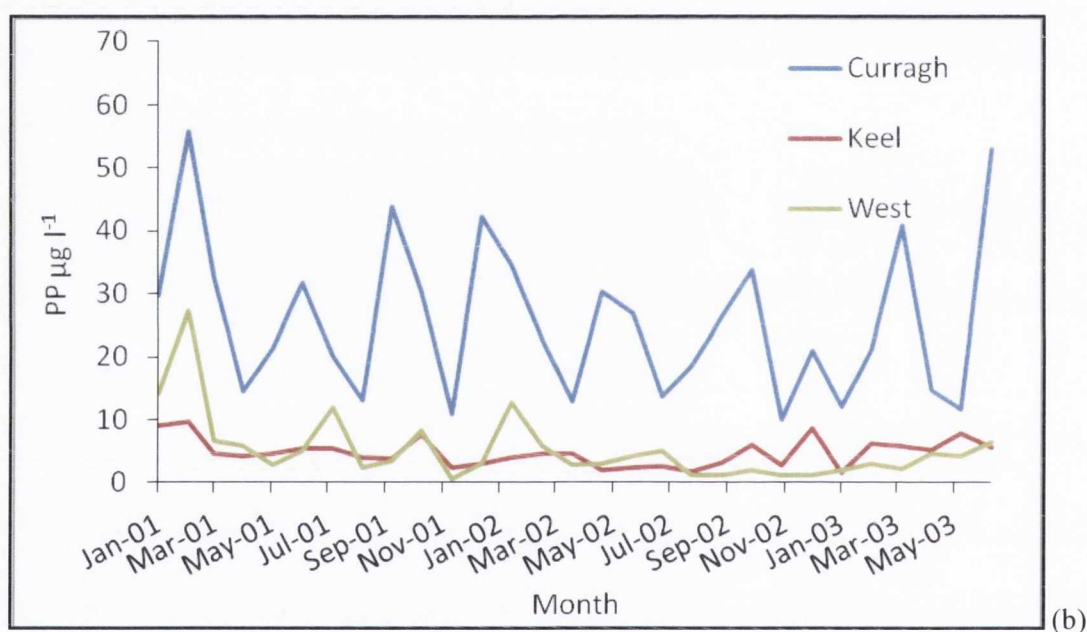
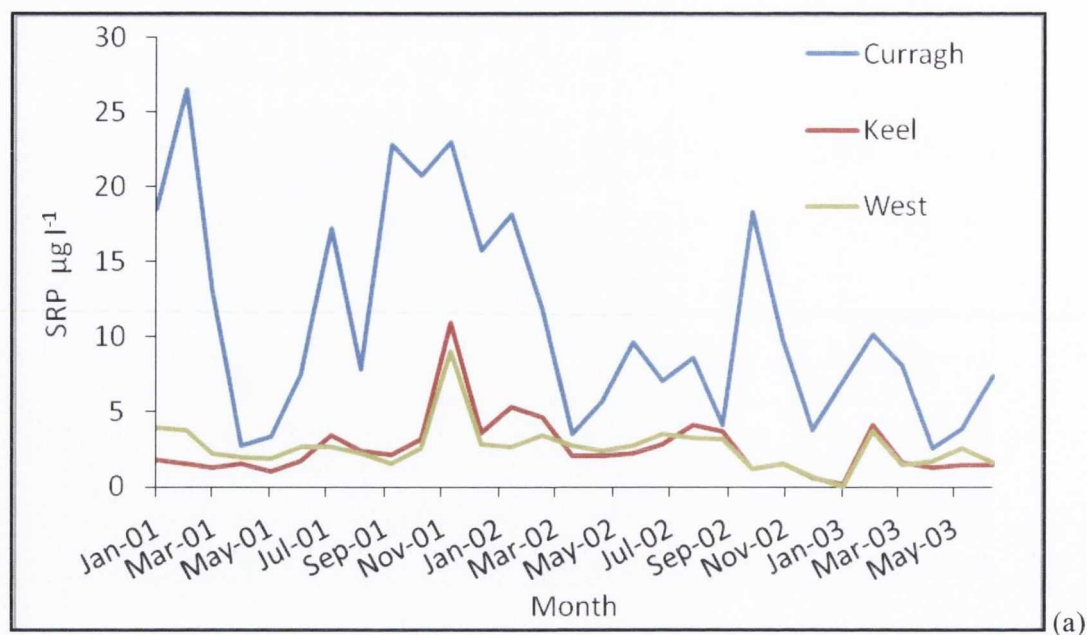
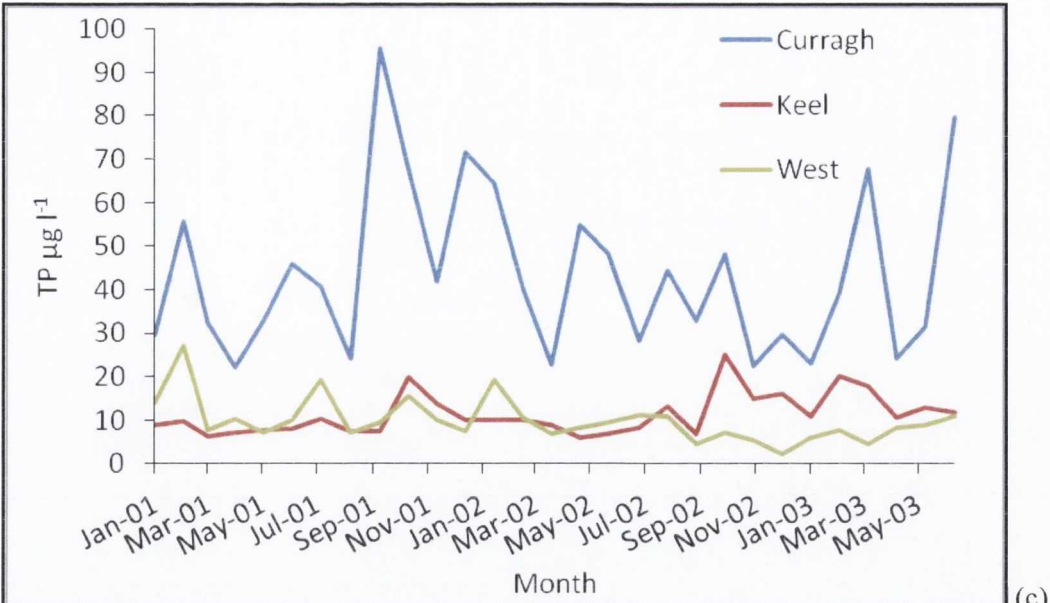
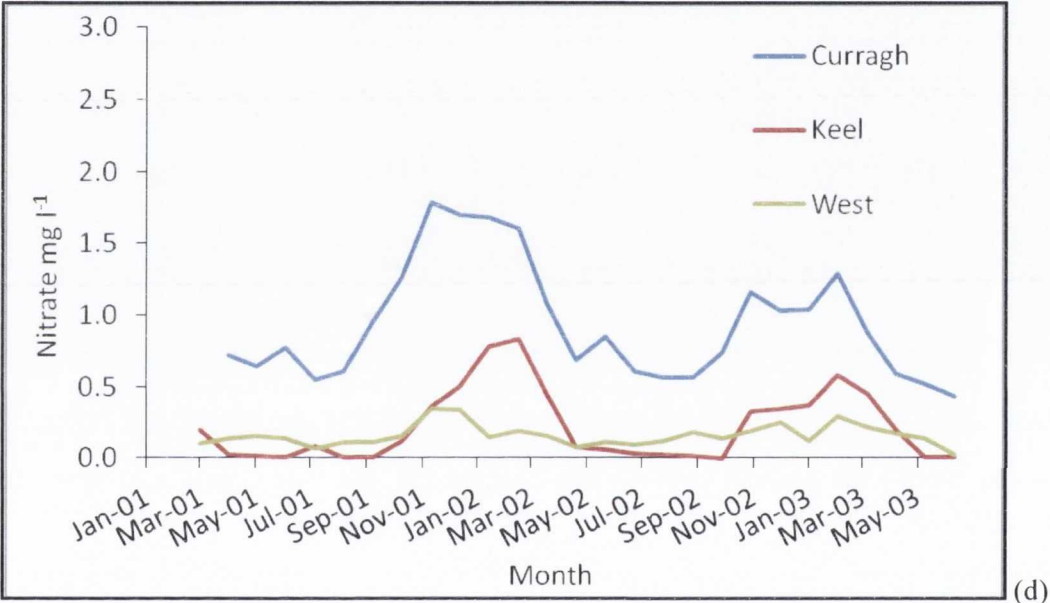


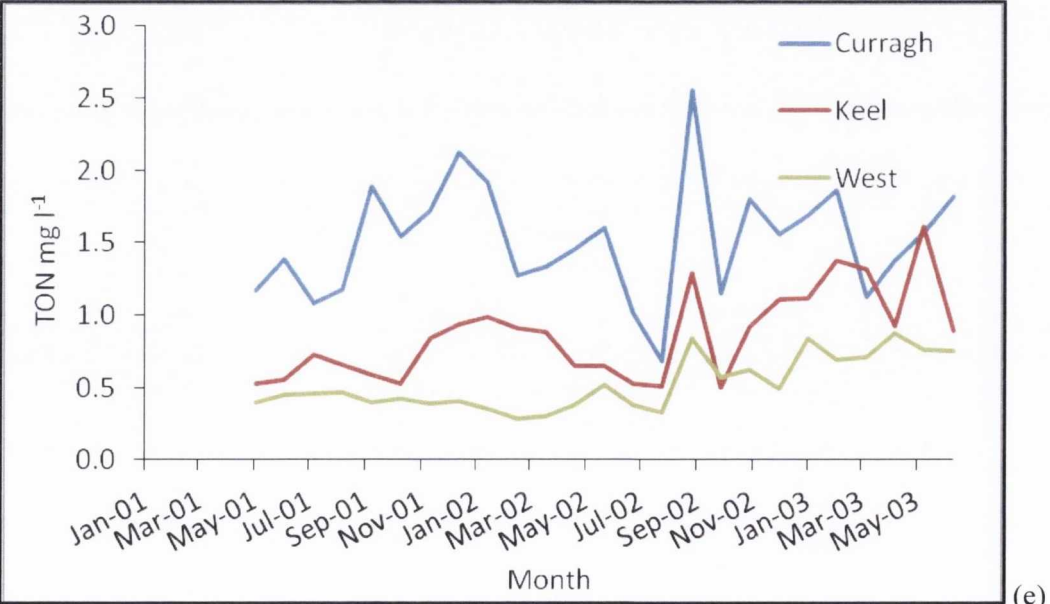
Figure 2.11 Monthly mean inflow water chemistry data: soluble reactive phosphorus (SRP) (a), particulate phosphorus (PP) (b), total phosphorus (TP) (c), nitrate (d), total organic nitrogen (TON) (e), total nitrogen (TN) (f), dissolved organic carbon (DOC) (g) and suspended solids (SS) (h) for Lough Mask available from the BUFFER project (EVK1-1999-00094), supplied by Dr. Ian Donohue and Dr. Ken Irvine, Department of Zoology, Trinity College Dublin. See Appendix J for raw data



(c)



(d)



(e)

Figure 2.11 (continued)

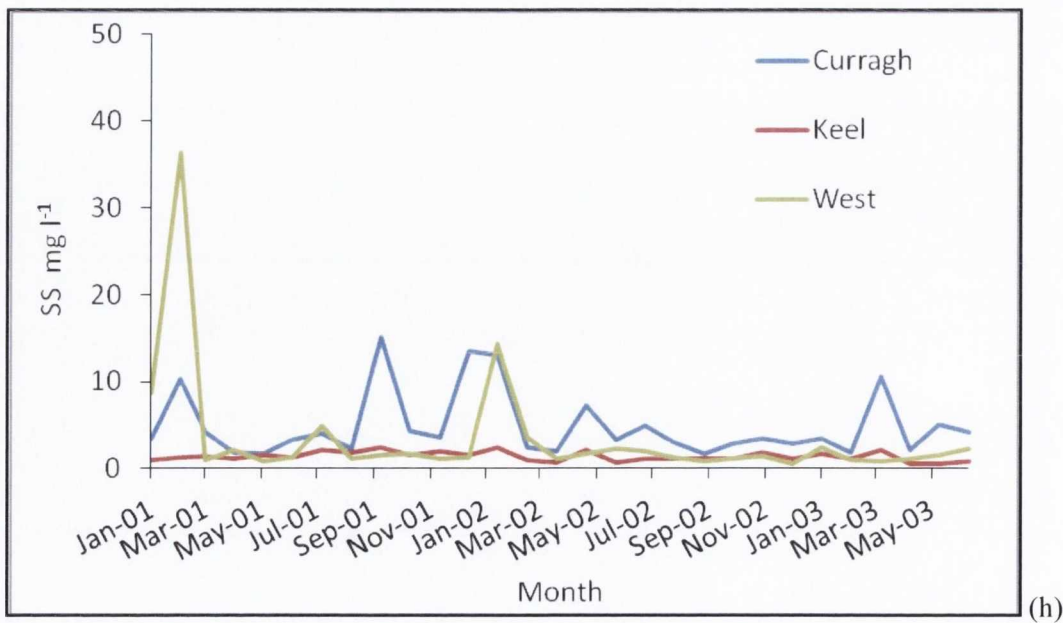
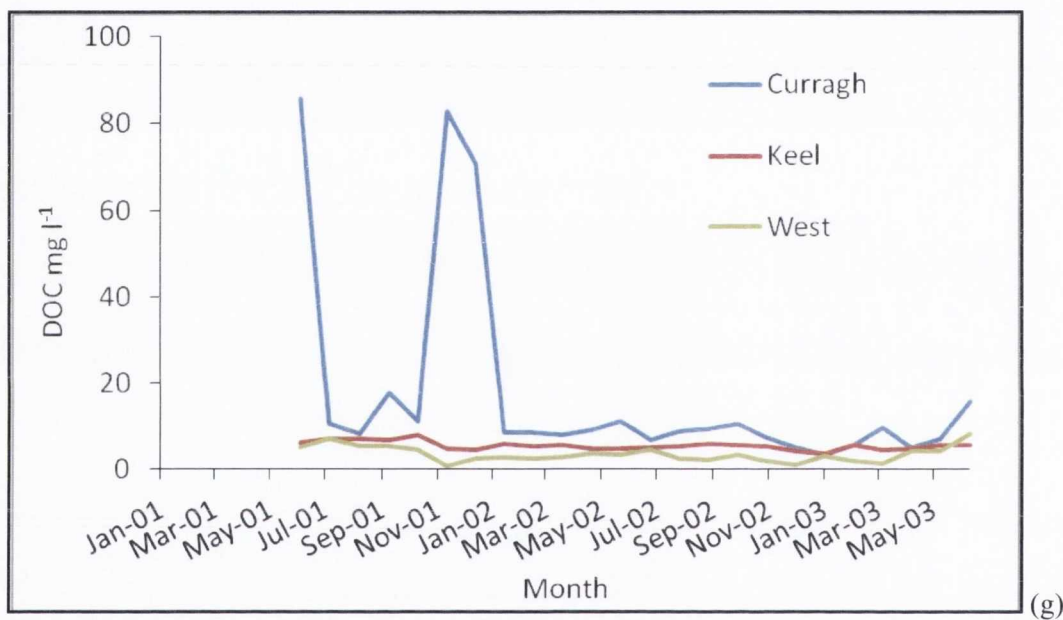
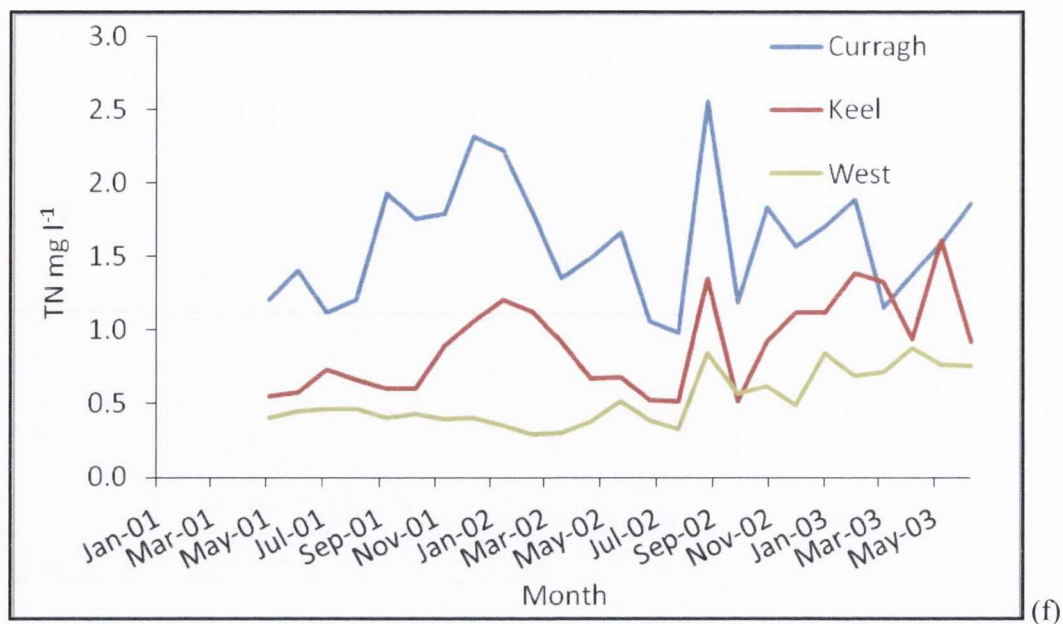


Figure 2.11 (continued)

Chapter 3

Methodological framework and techniques

3.1 Methodological framework

This project uses a multidisciplinary approach that combines expertise and knowledge from palaeolimnological and dynamic modelling techniques with a range of secondary historical and contemporary data. An outline of the methodological framework underpinning this research, including how the techniques were used to address each research question, and the stage of lake management that the techniques apply to, is presented in Figure 3.1 and described below. Detailed descriptions of the techniques and numerical methods used in this study are provided in Section 3.2.

- **Research Question 1:** How have trophic conditions varied over the long term in a lake with spatially-heterogeneous catchment characteristics?

Palaeolimnological data from multiple cores collected from two coring locations (see Section 3.2.1.1 for details) in Lough Mask were used to address the first research question. Variations in % Loss-on-ignition (LOI), sediment lithostratigraphy and sediment sodium (Na), potassium (K), calcium (Ca) and aluminium (Al) concentrations are indicative of major changes in sediment composition and possible changes in climate and catchment conditions that may have driven changes in lake trophic conditions. Sediment concentrations of TP were used to detect phases of nutrient enrichment in the lake, while concentrations of iron (Fe) and manganese (Mn) were used to detect redox-mediated changes in the ability of sediments to bind nutrients.

Diatoms, and reconstructions of diatom-inferred TP (DI-TP) and diatom-inferred pH (DI-pH), were used to assess long-term variations in trophic conditions and the possibility of climate-driven trophic variability. Variations in the remains of aquatic and terrestrial plants in the sediment cores were used to identify changes in trophic levels and productivity in the lake and changes in catchment conditions.

- **Research Question 2:** What are the relative roles of climate variability and human pressures in driving trophic changes in a west of Ireland lake during the 20th century?

A multidisciplinary approach combining sediment-based, modelling and historical records was used to address Research Question 2. Variations in trophic conditions

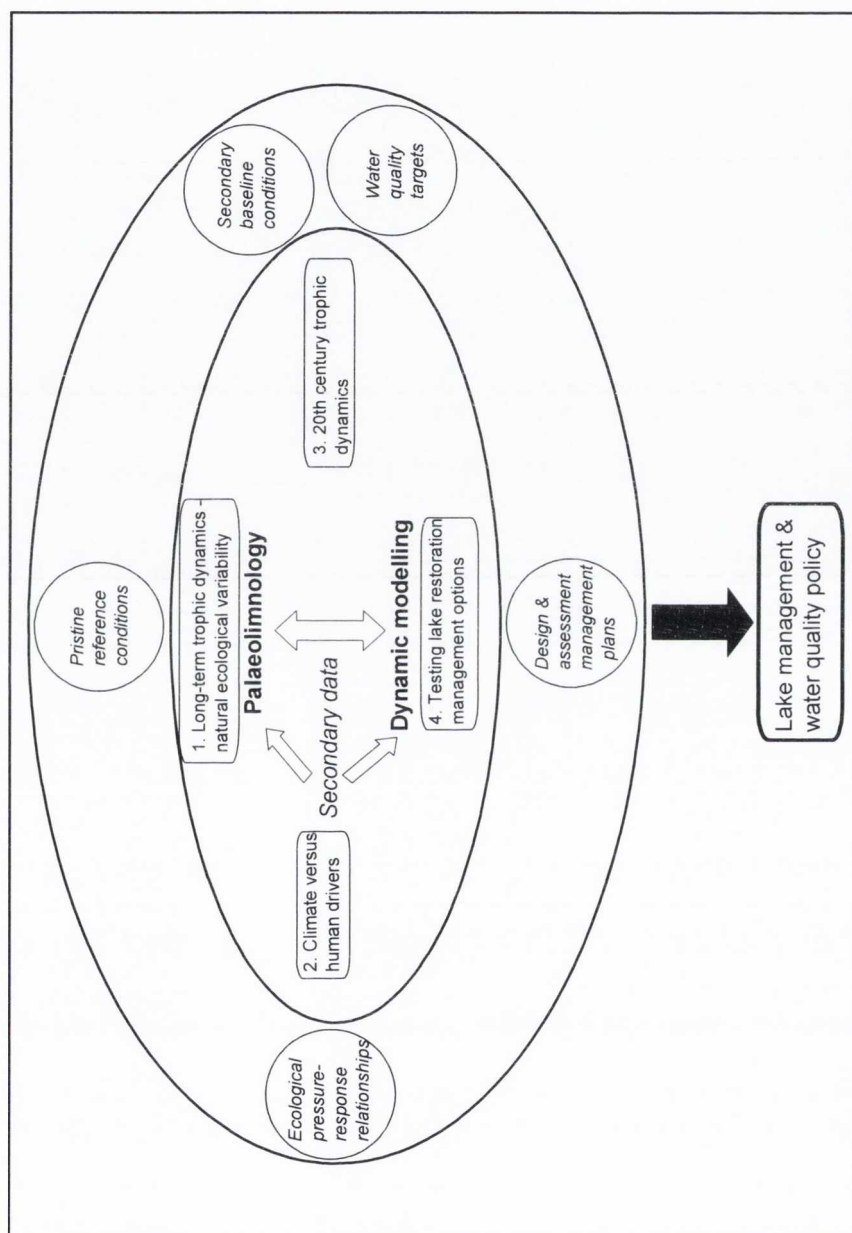


Figure 3.1 The methodological framework used in the current research. The inner circle indicates how the methods used relate to the 4 research questions addressed by this research. The outer circle indicates how the methods and research questions can potentially contribute to lake management

during the 20th century at Lough Mask were examined using sediment-based DI-TP and hindcast modelled in-lake TP concentrations. Variations in the levels of plant macrofossil remains and sediment concentrations of TP also indicated changes in nutrient and primary productivity levels in the lake. Sediment concentrations minor elements - Fe, Mn, Na, K, Al and Ca – were used to infer major changes in sediment composition and possible changes in climate and catchment conditions. Sediment concentrations of Fe and Mn were used to detect redox-mediated changes in the ability of sediments to bind nutrients. Potential changes in climate and human drivers of trophic changes in Lough Mask were examined using historical air temperature and precipitation data, human population data and agricultural census data (for further details see Section 2.2 and 3.2.2.2). Hindcast catchment nutrient and sediment loads were modelled using a dynamic catchment model (the Generalised Watershed Loading Functions model, GWLF) (Schneiderman *et al.*, 2002; Jennings *et al.*, unpublished). Ordination techniques were used to analyse the multidisciplinary (palaeolimnological, dynamic modelling, historical and climate) data for the last c. 100 years, and to decipher the relative roles of climate and human drivers of trophic variability in the lake during the 20th century.

- **Research Question 3:** Can a multidisciplinary approach, combining palaeolimnological and dynamic modelling methods, be used to elucidate long-term trophic dynamics?

Dynamic hindcast modelling and palaeolimnology were used to provide two independent reconstructions of lake water TP concentrations and total chlorophyll *a* concentrations, for the last c. 100 years. Statistical analyses, in particular time-series analysis, were used to assess baseline trophic conditions and deviation from baseline conditions in the lake during the 20th century. Comparisons between reconstructed datasets using the two independent methods also allowed limitations of both modelling and palaeolimnological methods to be identified.

- **Research Question 4:** Can dynamic modelling be used to design and test the effectiveness of water quality management plans?

Runs of GWLF allowed the contributions of different sources of catchment pressures to be distinguished (Schneiderman *et al.*, 2002; Jennings *et al.*, unpublished). Water quality

targets were established using 20th century baseline trophic conditions (see Research Question 3 above). A scenario-based dynamic modelling approach was used to identify the most effective and cost- and time-efficient management options for restoring baseline trophic conditions in Lough Mask. Scenarios incorporating the impacts of projected changes in catchment pressures and a range of potential management options for restoration, including basic measures already in place for addressing nutrient pressures, were tested and compared.

3.2 Methodological techniques

The following content describes the methods that were used in carrying out the research and the descriptions are not repeated in Chapters 4, 5, 6 and 7, which instead focus on particular research questions and associated results and discussions of these.

3.2.1 Palaeolimnological techniques

3.2.1.1 Sediment coring

Ideally palaeolimnological techniques are applied to accumulations of undisturbed, vertically continuous sediments that include an intact sediment-water interface (Glew *et al.*, 2001; Smol, 2008). Sediment records from the deepest parts of lake basins are often the most complete, as a result of sediment focusing and relatively quiescent underwater conditions, and subject to little spatial variability (Charles *et al.*, 1991). Sediments accumulating in the deepest parts of lakes are often assumed to provide the most representative record of conditions within the lake and its catchment, and are often the only part of a lake basin to be cored (Anderson, 1998).

A variety of types of sediment corers are available for palaeolimnological studies. The use of a particular type of corer depends on local environmental conditions (such as, ease of access to the site and depth of water, timescale of interest and the focus of the research undertaken (Dalton *et al.*, 2009). Gravity corers, such as the Hongve (Wright, 1990) or the Renberg (Hon-Kajak) (Renberg & Hansson, 2008), are usually the most suitable and most widely-used coring device for studying environmental changes over the last few decades or centuries (Glew *et al.*, 2001). The gravity corer consists of an open barrel (e.g. a polycarbonate tube) suspended from above the water column via a

wire or rope that is driven vertically into the sediment by gravity, often with the assistance of weights. After removal from the sediment, the barrel is sealed by a vacuum created by a closing mechanism at the top of the tube, preserving the sediment-water interface. The sediment cores can then be extruded onshore using a vertical push rod-type extruder. A prototype gravity corer (Renberg corer, HTH Teknik Varvagan 37, SE951 49 Lulea) (Renberg & Hansson, 2008) was used to extract sediment cores for the current study, in part because of the difficulties in using rod-based piston corers presented by local conditions (lake depth and frequency of large waves associated with strong winds and a long lake fetch). Cores were subsampled at 1-cm intervals from 5 cm to the base and at 0.5-cm intervals for the upper 5 cm, and stored in a cool box for immediate transfer to TCD.

3.2.1.2 Coring site selection

Optimal sediment coring locations in Lough Mask were initially chosen using bathymetric data from a 19th century admiralty chart (from 1846 AD), the only bathymetric map available for the lake basin at the time of preliminary fieldwork (R. Little, EPA, pers. comm.). The very sparse bathymetric data originally available were added to over the course of fieldwork (between 2006-2008 AD). A detailed bathymetric survey carried out in 2008 AD by the WRFB was made available for the current project (Figure 2.2). Water quality monitoring data for Lough Mask, from 2001-2003 AD, from the BUFFER (EU Fifth Framework Programme) Project were also used to choose appropriate coring locations. Test sediment cores obtained in November 2006 AD as part of the current project revealed considerable spatial variability in sediment type within the lake basin, with substantial differences evident between organic matter and lithostratigraphy profiles and between the eastern and western parts of the lake (Appendix M).

Inflow water quality monitoring data available from the BUFFER (EU Fifth Framework Programme) project (described in Section 2.2.5.2) revealed that inflow water chemistry differed substantially between the eastern and western parts of the catchment. However, lake water quality monitoring data from BUFFER showed generally well-mixed conditions and suggest very little spatial variability in physico-chemical and ecological characteristics. The embayments located in the southwest part of the lake were not monitored as part of the BUFFER project. Previous literature (McGarrigle &

Champ, 1999), however, suggested considerable differences in the water chemistry and ecology between the southwestern embayments and the open water of the lake. The BUFFER dataset also indicated greater variability in physico-chemical conditions at the deepest point, the monitoring site closest to the southwestern embayments of the lake (see Section 2.2.5.1; Table 2.4; Appendix I). Using the test sediment cores, together with the bathymetric and water quality data, three coring sites were chosen for the current research: the deepest point of the lake (09°22' W, 53°36' N; water depth = 62 m), a site in the eastern part of the lake (close to the mouth of the Robe) (09°18' W, 53°38' N; water depth = 13 m) and a site in the southwest part of the lake (09°26' W, 53°35' N; water depth = 20 m) (Figure 2.2). Eight sediment cores were collected from the three coring sites in March 2007 (cores MK-4 and MK-5 from the Robe site, cores MK-8, MK-9 and MK-10 from the deepest point, and cores MK-11, MK-12 and MK-13 from the southwest site). Details of the core locations, and analyses performed on each core, are provided in Table 3.1. A number of attempts were made to obtain additional sediment cores, from the southeast part of the lake and from shallower locations in the deepest channel on the western side, but were unsuccessful.

3.2.1.3 Chronological control

Establishing the time period represented by (or chronological control of) sediment cores is a crucial step in palaeolimnological research (Smol, 2008). Radiometric dating is one of the most frequently used methods for establishing chronological control for sediment profiles (Cohen, 2003). Chronological control in the current study was largely based on accumulation rates derived from the measurements of activity of radioactive isotopes (^{210}Pb , ^{137}Cs and ^{14}C). Estimated ages based on measured activities of radioactive isotopes were verified through counts of spheroidal carbonaceous particles (SCPs). One core from each of the three coring sites was used for radiometric dating (see Table 3.1 for details).

3.2.1.3.1 ^{210}Pb and ^{137}Cs dating

^{210}Pb and ^{137}Cs are commonly used to date material that accumulated in the last c. 100-200 years (Robbins, 1978; Appleby, 2001; Björck & Wohlfarth, 2001). Radiometric dating is based on the time dependant decay of certain naturally occurring isotopes. Knowledge of the rate of decay of the isotopes allows the age of the host material to be

Table 3.1 Summary of locational and hydromorphological details of the sediment coring locations for Lough Mask, Co. Mayo. Sediment cores are stored in the Geography, School of Natural Sciences, Trinity College Dublin. * MK = Mask

Location	Core code*	Date of collection	Location	Water depth (m)	Core length (cm)	Analyses
Deepest point	MK-8	14/03/07	09°22' W, 53°36' N	62	41	LOI, dating
	MK-9	14/03/07	09°22' W, 53°36' N	62	37	LOI, diatoms, geochemistry
	MK-10	14/03/07	09°22' W, 53°36' N	62	34.5	LOI, macrofossils
Robe site	MK-4	14/03/07	09°18' W, 53°38' N	13	32.5	LOI, diatoms, geochemistry
	MK-5	14/03/07	09°18' W, 53°38' N	13	23	LOI, macrofossils, dating
Southwest site	MK-11	15/03/07	09°26' W, 53°35' N	20	38	LOI, radiometric dating
	MK-12	15/03/07	09°26' W, 53°35' N	20	38	LOI, diatoms, geochemistry
	MK-13	15/03/07	09°26' W, 53°35' N	20	35	LOI, macrofossils

determined (Lowe & Walker, 1997). Due to its relatively short half life, the length of time that is required for a given quantity of the parent nuclide to be reduced by half, of 22 years, ^{210}Pb dating is one of the most widely used dating methods for recently deposited sediments (Cohen, 2003). ^{210}Pb occurs naturally in lake sediments as a radioisotope of the ^{238}U decay series (Battarbee, 1991). A part of the ^{238}U decay series involves the decay of ^{226}Ra to ^{222}Rn , which diffuses through soil into the atmosphere where it eventually decays to ^{210}Pb . ^{210}Pb is removed from the atmosphere by precipitation and dry fallout to the land surface, where it is retained in surface soils or transported to surface water (Appleby & Oldfield, 1983). ^{210}Pb that reaches lake waters is scavenged by sediments and deposited on the lake bed.

The ^{210}Pb activity of lake sediments has two components, a supported component derived from ^{222}Rn decay within the sediment column, and an unsupported (or excess) component derived from the atmospheric fallout of ^{210}Pb . In the absence of atmospheric fallout of ^{210}Pb , ^{210}Pb and ^{226}Ra would be in radioactive equilibrium. The unsupported ^{210}Pb concentration in sediment decreases exponentially over time in accordance with the radioactive decay law. This law can be used to calculate the sediment age provided that the initial unsupported ^{210}Pb concentration, when the sediment was deposited, was estimated in the same way (Appleby & Oldfield, 1983, 1992; Appleby, 2001).

SARs were used to calculate age using the constant rate of supply (CRS) and linear regression models (Appleby, 2001). Unsupported ^{210}Pb was calculated based on the distribution of total ^{210}Pb in the sediment core, by subtracting the background ^{210}Pb values obtained in lower samples of the cores. The CRS model assumes that the absolute flux of ^{210}Pb remains constant regardless of the SAR and that the sediment core is long enough to include all of the measurable atmospheric sources of ^{210}Pb (Appleby, 2001). Thus changes in SAR through time will result in changes in the initial concentration of excess unsupported ^{210}Pb . In such cases, dates for older sediments are based on the distribution of ^{210}Pb throughout the sediment core rather than on their present concentration (Appleby, 2001). The linear regression model estimates an approximate average SAR over the sediment core and is applied if the assumption of constant input of ^{210}Pb and SAR is met, based on the ^{210}Pb activity profile.

Atmospheric fallout of the artificial radionuclide ^{137}Cs (half life = 30.2 years) is associated with the history of development of nuclear-based weapons and nuclear power

generating technologies from the mid-1940s until c. 1980 AD and can be used to validate sediment ^{210}Pb activity profiles (Appleby, 2001; Leslie & Hancock, 2008). In the northern hemisphere there have been two pronounced peaks in atmospheric concentrations of ^{137}Cs that are also represented in lake sediments, at c. 1963 AD linked to the atmospheric detonation of nuclear weapons and just before the implementation of the Test Ban Treaty, and at c. 1986 AD linked to the Chernobyl nuclear power station accident in the Ukraine (Battarbee, 1991). Departures from the traditional ^{137}Cs sediment profile can be caused by sediment hiatuses or mixing resulting from bioturbation and sediment resuspension (Battarbee, 1991).

Radiometric ^{210}Pb and ^{137}Cs analysis was conducted at the laboratories of Flett Research, Winnipeg, Canada. Relative concentrations of ^{210}Pb were determined indirectly through the measurement of ^{210}Po , a granddaughter isotope of ^{210}Pb , by distillation from the sediment at a high temperature, acid digestion and plating onto silver discs for analysis by alpha spectrometry using Ortec 'Ortec' alpha spectrometry (Eakins & Morrison, 1978). Supported ^{210}Pb activities were estimated using measurements of ^{226}Ra , a proxy for supported ^{210}Pb in the sediment (Appleby, 2008), and were carried out using a bare photomultiplier tube and multi-channel analyser following the method of Mathieu *et al.* (1988). Analysis of ^{137}Cs activity was also carried out using gamma ray spectrometry using an HPGe coaxial detector.

Up-core irregularities in excess ^{210}Pb and dry bulk density were evident from the analysis of the MK-8 (from the deepest point) and MK-5 (from the Robe site) and, therefore, the CRS model was applied. MK-11 (from the southwest site) was not long enough to cover the entire measurable atmospherically-sourced ^{210}Pb and, therefore, the linear regression model was applied with background levels estimated from the analysis of ^{226}Ra . ^{137}Cs activity profiles were also examined for the three dated sediment cores (Table 3.1) to validate the ^{210}Pb profile data. The ^{137}Cs activity profile for MK-8 exhibited only one peak (c. 1963 AD), in the surface sediments, and was compatible with the ages predicted by the CRS model of the ^{210}Pb data. The ^{137}Cs activity profile for MK-5 exhibited a typical pattern expected in cores where the majority of the ^{137}Cs is derived from the catchment and also exhibited only one peak. Further validation of the ^{210}Pb chronologies for MK-5 and MK-8 was provided using SCPs. ^{137}Cs activity in MK-11 revealed a profile exhibiting 2 peaks and was comparable with the ages predicted by the linear regression model of the ^{210}Pb data.

3.2.1.3.2 SCPs

SCPs are anthropogenic in origin and released to the atmosphere as a result of the incomplete combustion of fossil fuels in power stations (Rose, 2001). The SCP record in lake sediments is reasonably reliable and robust as SCPs are resistant to changes in water and sediment chemistry once they are deposited in the sediment (Rose *et al.*, 1995; Rose, 2001; Rose *et al.*, 2004). Leira *et al.* (2006) outline how SCP profiles can be used to date lake sediment cores from Ireland, based on their very distinctive profiles of deposition in lake sediments in northwest Europe, linked to the commencement, expansion and increased regulation of power station emissions (Rose *et al.*, 1995). Throughout Ireland the SCP record generally begins between c. 1880-1890 AD (Rose *et al.*, 1995) and displays increases from the late 1940s (Leira *et al.*, 2006; O'Dwyer & Taylor, 2010). The peak in SCP concentration occurred between c. 1970-1980 AD, after which concentrations were reduced from the 1970s due to changes in the levels of atmospheric deposition across Europe, as a result of changes to more environmentally-friendly technologies and fuel types (Rose *et al.*, 1995; O'Dwyer & Taylor, 2010).

Concentrations of SCPs were measured using the method of Rose (1994) (detection limit of 100 SCPs g DM⁻¹), whereby sediment is treated with nitric acid (to remove organic material), HF_{aq} (to remove siliceous material) and HCl_{aq} (to remove carbonates), leaving carbonaceous material and a few persistent minerals. The final suspension is evaporated onto a coverslip and mounted onto a microscope slide using Naphrax mounting medium. The number of SCPs on the coverslip was enumerated following criteria outlined in Rose (2008). A Leica DM1000 research quality microscope at x 400 magnification was used for the identification of SCPs and the sediment concentration of particles was calculated as the number of particles g DM⁻¹ (Rose, 1994; Rose *et al.*, 1999). The results of the analyses were used in support of a radiometrically-based chronology (Rose *et al.*, 1995; Rose, 2001).

3.2.1.3.3 AMS ¹⁴C dating

The organic carbon component of lake sediments deposited over the last c. 40,000 years can be dated using ¹⁴C-based techniques (Björck & Wohlfarth, 2001). Samples of macrofossils extracted from the basal and mid-core sediment samples from MK-8 and the basal sample from MK-5 were dated by Beta Analytic, USA, using the AMS ¹⁴C

technique to ascertain a maximum age for the sediment cores from the deepest point and Robe sites. Approximately 5-10 g of terrestrial plant macrofossils were extracted with fine forceps and separated from the associated sediment matrix and wrapped in aluminium foil. AMS ^{14}C dating was carried out by Beta Analytic Inc., Miami, Florida. Calibrated ages were derived from the Calib 5.01 and the Intcal04.14c dataset (Stuiver & Reimer, 1993; Reimer *et al.*, 2004). A combination of $^{210}\text{Pb}/^{137}\text{Cs}$ and AMS ^{14}C dates were used to establish age-depth relationships for MK-5 and MK-8.

3.2.1.3.4 Age-depth modelling

Age-depth models range from simple models (e.g. linear interpolation) to more complex mixed-effects and Bayesian models (Blaauw & Heegaard, 2012). The greater the complexity of the model the greater the data requirements are. Bayesian models in particular require datasets with numerous dates and prior or additional information about the sediment sequence (e.g. layers of known ages) and, therefore, were not applicable in the current research. Where there is minimal information available the more basic models are preferred (Telford *et al.*, 2004).

The majority of age-depth modelling in palaeoecology uses simple linear interpolation between single data points (Blaauw & Heegaard, 2012). Though crude, the linear interpolation approach has provided reasonable estimates of age and gradients compared with more complex statistical modelling procedures (Bennett & Fuller, 2002; Blaauw & Heegaard, 2012). Many types of sediment accumulation can be regarded as essentially linear as a result of the effects of compaction on producing exponentially-decreasing SARs with age (e.g. Townsend *et al.*, 2002). However, simple linear interpolation is undeniably problematic for non-uniform sediment profiles. Changes in the gradients (representing SARs) at every measured age are unlikely to reasonably reflect SARs. Linear interpolation only incorporates the errors on the individual age estimates and assumes that the errors are completely independent of each other and that there are no systematic errors. Even small errors in estimated ages can greatly influence the slopes of the lines joining data points (Mahers, 1972), and thus polynomials and power functions may be more appropriate. However, the reliability of more complex and statistically exact models must also be questioned in light of the crudeness of dating data (single estimates of radiocarbon dates for a sample) (Press *et al.*, 1992; Blaauw & Heegaard, 2012). Many palaeostatisticians maintain that the most parsimonious model is

the most preferable (Blaauw & Heegaard, 2012). Blaauw & Heegaard (2012) recommend the application of more than one model and comparing the approximated ages and other sediment-based data.

Low sediment dating resolution meant that only simple models could be applied to estimate age-depth relationships in the Lough Mask sediment cores. Linear interpolation and a polynomial model were used to model the age-depth relationships for the Robe and deepest point sediment records. Linear interpolation involves plotting estimated age data against depth and connecting the points with straight lines; accumulation rates can be calculated from the gradients of the lines and intermediate interpolated ages can be read off (Blaauw & Heegaard, 2012). Polynomial models are of the form $y = a + bx$ (where x = depth; y = age; and a , b = regression coefficients to be estimated). A 2-term polynomial ($y = a + bx$) was also applied to the sediment record from the deepest point of Lough Mask.

3.2.1.4 Sediment core cross-correlation

For each sediment coring site a single, well-dated core acted as the master chronology; up-core variations in organic matter content, based on LOI (see Section 3.2.1.5), can be used as a basis for extending a chronology between adjacent cores from the same coring location in a lake (Carol *et al.*, 1998; Brancelj *et al.*, 2002). Sediment lithostratigraphy (see Section 3.2.1.5) also provides a basis for extending a chronology between adjacent lake sediment cores from the same coring site (Smol, 2008). Based on these data, SARs and ages for the master core were extrapolated to the other sediment cores from the same site.

3.2.1.5 Physical properties

The physical properties of sediment can be used to indicate sediment source and transport mechanisms, changes in catchment and limnological conditions, and palaeoclimatic and palaeohydrological changes in a catchment (Last, 2001). Lithostratigraphic analysis was carried out at 2-cm intervals on a sediment core from each coring site (MK-5, MK-8 and MK-11) using the Troels-Smith (1955) method. The Troels-Smith method is a widely used system in sediment-based studies that uses the physical properties of sediment to infer sedimentary conditions at the time of sediment

deposition, with a focus on changes in sediment composition, texture and macrofossil content. Laser particle size analysis was carried out on the organic matter-, metal oxide-, and carbonate-free sediment fractions using a Mastersizer2000 (Malvern Instruments, UK) following the procedure of Murray (2002), grouping grains into clay ($< 2.0 \mu\text{m}$), silt ($2.0 - 62.5 \mu\text{m}$) and sand ($62.5 - 2000 \mu\text{m}$) components. Up-core variations in organic and inorganic carbon content, which is mainly carbonate (Dean, 1981), and were determined using the standard LOI technique at 550°C and 1000°C , respectively (Dean, 1974; Heiri *et al.*, 2001) and used to indicate major changes in sediment composition.

3.2.1.6 Geochemistry

The chemical composition of sediments can provide a guide to past changes in lake and catchment conditions (Smol, 2008). P can occur in lake sediments in both authigenic and allogenic forms and as part of inorganic or organic compounds (Engstrom & Wright, 1984). Inorganic forms of P usually occur as components of Fe oxides, which provide the main source of exchangeable P with the water column. Sedimentary P profiles should reflect historical changes in lake productivity if a constant proportion of dissolved P accumulates in the sediment over time (Engstrom & Wright, 1984). However, sediment TP concentrations are often highly variable because of P mobility associated with changes in sediment conditions (Anderson *et al.*, 1993). In particular, sediment TP content is strongly influenced by redox conditions and the Fe content of sediment. If P and Fe or Mn are closely correlated then, rather than reflecting past P levels in the lake, the P profile mirrors changes in redox conditions at the sediment-water interface and P retention, or coprecipitation with Fe or Mn. If the overlying water becomes anoxic, for example, as a result of prolonged stratification, P can be released from the sediments (Engstrom & Wright, 1984). Sedimentary P can be influenced by other factors such as rates of mixing by currents and waves, the activity of benthic organisms and water temperature. Several palaeolimnological studies have found good agreement between sediment TP profiles and changes in lake productivity, and in some cases even where the surface sediment has been influenced by post-depositional migration (e.g. Bradbury, 1978; Ulen, 1978). However, more often than not, variations in sediment TP profiles are complex and only vaguely reflect changes in catchment TP loading and changes in redox conditions cannot be ruled out (Carignan & Flett, 1981; Engstrom & Wright, 1984; Anderson *et al.*, 1993). Sedimentary P profiles should therefore be interpreted with caution.

Fe and Mn in lake sediments are sourced from catchment soil and rock (Engstrom & Wright, 1984) and their input to lakes is controlled by changes in the composition of and redox conditions in catchment soils (Mackereth, 1966; Pennington *et al.*, 1972). Groundwater is another potential source of Fe and Mn, due to the low solubility of their oxidised forms. Fe and Mn can also be derived from clastic sediment derived from catchment erosion, shifts in catchment vegetation type or organic soil. In many lakes, however, because of the relatively high mobility of the elements under reducing conditions, variations in sediment Fe and Mn profiles reflect changes in redox conditions in the sediment over time (Engstrom & Wright, 1984). Fe and Mn that precipitate and accumulate in lake sediment can redissolve depending on the factors that control their solubility, such as the ionic content of the water, redox conditions, pH, temperature, light penetration and microbial activity. Other factors can influence the preservation of Fe and Mn in the sediment record, including pH and bioturbation (Engstrom & Wright, 1984). Diagenesis and migration within the sediment column can also result in changes in the Fe and Mn profiles. In the majority of lakes only the upper few cm of the bottom sediments are oxidised; below this conditions are reducing because of oxygen consumption by microbial activity and diagenesis of inorganic compounds. With burial, the change in oxygen conditions means that oxidised Fe and Mn forms undergo reduction and, as they are no longer stable, become more mobile and enter into solution. Upward migration and precipitation in surface sediment can occur as a result. This can result in Fe and Mn peaks at the top of a sediment profile that are caused solely by post-depositional migration (Carignan & Flett, 1981). This is a common feature of the sediment Fe and Mn profiles from numerous different types of lakes (Engstrom & Wright, 1984).

Studies attempting to assess recent human-induced changes must use lake sediment Fe and Mn profiles with caution, and preferably with additional independent evidence to support interpretations because of the numerous potential causes of their variations. Mackereth (1966) proposed a method for distinguishing between changes in the supply of Fe and Mn from the catchment and changes in the redox conditions of bottom waters in the sediment record. If the Fe:Mn ratio is negatively correlated with Fe levels, then changes in redox conditions in the hypolimnion are most likely responsible for the variations in the sediment profile, because concentrations of Fe will be lowest during strongly reducing conditions at the sediment surface and Mn would be even lower than Fe. If Fe levels and the Fe:Mn ratio in the sediment profile are positively correlated then changes in the supply (and redox conditions in catchment soils) are the most likely

cause of their variations. Furthermore, the redox-sensitive elements (Fe and Mn) can be used to detect redox-mediated changes in the ability of sediments to bind elements, such as P. Fe is important in the retention of P in the aerobic layer of sediments and therefore changes in the Fe:P ratio can provide a basis for assessing the ability of sediments to retain P (Mackereth, 1966; Engstrom & Wright, 1984). Relatively low Fe:P ratios indicate a reduced capacity of the sediment to bind P and therefore may indicate potential for internal loading of P from the sediment to the water column (Jensen *et al.*, 1992).

The concentrations of the alkali and alkali-earth elements, Na and K, in lake sediments can indicate the relative intensity of weathering and soil erosion in the catchment as they are usually associated with detrital clastic minerals (Mackereth, 1966). Levels of Al in lake sediments can indicate the extent of soil leaching and the intensity of erosion in the catchment (Engstrom & Wright, 1984). Analyses of Al, Na and K were used to assist in the reconstruction of phases of catchment inwash. Levels of Ca in lake sediment are often associated with organic matter input (Mackereth, 1966), and can reflect catchment inputs arising from soil disturbance (Engstrom & Wright, 1984), anthropogenic activity (e.g. land use change or agricultural activity) or eutrophication due to increased biological consumption of carbon dioxide (CO₂) and precipitation of CaCO₃ (Meyers, 2006).

Sediment concentrations of TP and minor elements - Fe, Mn, Na, K, Al and Ca - were determined at 2-cm intervals for a sediment core from each coring site (Table 3.1) using microwave nitric acid digestion (Boyle, 2001). Element concentrations were determined using Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) (Stefánsson *et al.*, 2007) at the Centre for the Environment, School of Natural Sciences, TCD. A pseudototal digestion method to determine P, rather than a sequential extraction method for determining several P fractions, was appropriate for the current study because this is the most commonly investigated P-related parameter in previous work on lakes in Ireland (e.g. Taylor *et al.*, 2006; Leira *et al.*, 2006; Jordan *et al.*, 2002), and therefore the most useful for comparison between sites and with other sediment-based proxies for nutrient loading. The method of pseudototal microwave-assisted digestion has been found to produce comparable results, i.e. with no significant differences detected, compared with the values obtained using the more complex sequential extraction method protocol (Gonzales-Medeiros *et al.*, 2005). Quality control

was assured through the use of validated and certified standard reference material of sediments (NCS DC 73307: stream sediment, China National Analysis Center for Iron and Steel), and sediment replicates and laboratory blanks in each digest batch. Results were corrected for blanks by subtracting the mean of the blanks (Boyle, 2001), ensuring that there were no anomalous values due to contamination or handling error.

Results of stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and total C and N analyses were used to determine sources of organic matter in the lake sediment. $\delta^{13}\text{C}$ values for organic C derived from C_3 plants generally range from -35 ‰ to -20 ‰ (Cerling, 1999). $\delta^{13}\text{C}$ values for C from C_4 plants is less well defined but is generally in the range -16 ‰ to -9 ‰ (Cerling, 1999; de Freitas *et al.*, 2001). $\delta^{13}\text{C}$ values for aquatic algae have values ranging from -23 ‰ to -12 ‰ (Smith & Epstein, 1971). Variations in $\delta^{15}\text{N}$ in lake sediments can be used to infer anthropogenic inputs of reactive N (Wolfe *et al.*, 2001). N can be an important pressure in oligotrophic lakes and in lakes enriched with P (Carvalho & Defew, 2005). Sediment C:N ratios were also used to distinguish allochthonous from autochthonous sources of organic matter inputs to a lake. C:N values < 10 indicate organic matter sourced from algal matter, while C:N values > 20 represent organic matter derived from terrestrial sources (Meyers, 2003). C:N ratios for sewage-derived organic matter are generally low (c. 4-6) (Brennan *et al.*, 1994). Stable isotope analyses were carried out at 2-4cm intervals on a sediment core from each coring site (Table 3.1). $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and total C and N analyses were carried out on oven-dried homogenised sediment samples, pre-treated with 1M HCl_{aq} for 2 hours in a water bath at 60 °C to remove inorganic carbon, using a Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) (Wolfe *et al.*, 2001).

3.2.1.7 Biological analyses

3.2.1.7.1 Diatom analysis

Diatoms, siliceous algae (Class Bacillariophyceae), are widely used as biological indicators of climate conditions (e.g. Drebler *et al.*, 2011) and water quality, including eutrophication (Bennion *et al.*, 2011a). Diatoms have well-defined optima for a range of environmental variables (Forrest *et al.*, 2002), and the relationships between assemblages of diatom species and environmental variables can be mathematically modelled using transfer functions (e.g. Chen *et al.*, 2008).

Diatom analysis was carried out on every sediment sample from a sediment core from each coring site (Table 3.1) using the method of Battarbee *et al.* (2001). Sediment samples were digested using $\text{H}_2\text{O}_{2\text{aq}}$ to remove organic material, washed with deionised water several times and 0.5 ml of polystyrene-co-divinylbenzene microsphere solution (6.35×10^6 microspheres ml^{-1}) was added to each to facilitate calculation of diatom concentrations. Each sample was mounted onto a glass slide using Naphrax mounting medium. Diatom concentrations were calculated using the following equation (Battarbee & Kneen, 1982; Battarbee *et al.*, 2001):

$$\text{Diatom concentration} = \frac{\text{no. of diatoms counted} \times \text{no. of microspheres added}}{\text{no. of microspheres counted}}$$

A Meiji ML2000 light microscope with a x100 oil immersion objective and a phase contrast condenser (giving a total magnification overall of x1000) was used for diatom enumerations. Diatom valves were counted in transects, offset by 2 mm, running horizontally along the microscope slide so that no diatom valve was encountered more than once. At least 300 valves were enumerated in each sample to obtain a good representation of the overall floristic composition of the sample. For samples with very low or no diatoms present, additional slides were mounted and checked for the presence of diatom valves.

Diatom taxonomy followed standard reference flora by Krammer and Lange Bertalot (Krammer & Lange-Bertalot, 1986, 1988, 1991a, 1991b). In addition, references including Foged (1977); Lange-Bertalot & Metzeltin (1996); Knie & Hübener (2007); Potapova & Hamilton (2007) and Lowe (2010), and databases including the European Diatom Database (EDDI) (2009) and AlgaeBase (Guiry & Guiry, 2012) were used to aid the identification of problematic taxa. The identification of problematic taxa was also aided by verification with colleagues at TCD and UL and at ILLUMINATE EPA/ERTDI Project # 2005-W-MS-40 diatom workshops held between 2007-2009 AD. DIATCODE (Hartley, 1986; Williams *et al.*, 1988) was used to check and update diatom nomenclature. Taxon names and authorities are listed in Appendix N.

The relative abundances (%) of diatom taxa were calculated, as were diatom concentrations (cells g^{-1}) and accumulation rates ($\text{cells cm}^{-2} \text{ yr}^{-1}$), and stratigraphically plotted using the C2 programme (Juggins, 2003). The ratio of planktonic to benthic taxa,

which can be a very sensitive indicator of eutrophication (Oldfield *et al.*, 1983; Battarbee, 1986), was calculated for the samples from the sediment core from the southwest site (MK-11), as this was highest resolved record of recent sediment accumulation in Lough Mask. A dissolution index (F), the proportion of non-dissolved valves to all classifiable valves counted, was calculated for all samples analysed for diatoms, according to Ryves *et al.* (2001). Diatom valves were classified into one of the two dissolution categories, visibly dissolved or not visibly dissolved under light microscopy. F was calculated for each sample as follows:

$$F = \frac{\sum_j n_{ij}}{\sum_j N_j} \quad (\text{Ryves } et al., 2001)$$

where n_{ij} is the number of pristine valves of species j , of m samples, counted in a sample i , compared with N_{ij} , the total number of classifiable valves of species j . F values range from 0 (all valves visibly dissolved) to 1 (perfect preservation).

Diatoms are widely used as biological indicators of water quality and can provide quantitative estimates of lake water TP concentrations and pH using the transfer function approach (Bennion *et al.*, 2005). Environmental reconstructions using DI-TP have been used extensively in eutrophication research. The most commonly used environmental reconstruction methods in palaeolimnology are transfer functions, using weighted averaging (WA) and weighted averaging partial least squares (WA-PLS) models, which provide a means of quantitatively estimating water quality, such as TP concentrations (Bennion *et al.*, 1996), and thus trophic conditions. WA and WA-PLS models assume a unimodal relationship between species and environmental variables (Racca *et al.*, 2001). In the WA regression model, the optimum for each taxon is estimated from the training dataset based upon the abundances of diatoms in the surface sediment and the measured environmental variable where the taxon is present (Racca *et al.*, 2001). A diatom's TP optimum is then calculated as the mean of all TP values for the lakes in which the taxon occurs, weighted by its relative abundance. A lake's inferred TP concentration is calculated as the weighted average of the TP optima of all the diatom taxa present in the lake (Birks *et al.*, 1990). The WA-PLS model is an extension of simple WA in which successive components are extracted from the training dataset (ter Braak & Juggins,

1993; Racca *et al.*, 2001). The performance of the transfer function is estimated using the root mean square error of prediction (RMSEP) value. This involves applying a number of transfer functions to the same fossil data using a range of cross-validation techniques (leave one out, bootstrapping and jack-knifing) and the model that provides the best estimate will have the lowest RMSEP value (Birks, 1995).

In the current study, DI-TP and DI-pH were established and calibrated using a diatom transfer function and training dataset (based on 72 lakes) developed specifically for the ecoregion of Ireland by Chen *et al.* (2008), using the programme C2 (Juggins, 2003). Several WA models were run by Chen *et al.* (2008); the best performing models, WA classical deshrinking for DI-pH ($r^2_{\text{jack}} = 0.89$; RMSEP = 0.32) and WA tolerance down-weighted and inverse deshrinking for TP ($r^2_{\text{jack}} = 0.74$; RMSEP = 0.21), were applied with leave-one-out cross validation in the current study. Modern Analogue Technique (MAT) is a palaeoecological method that employs a dissimilarity measure (chord distance or squared chord distance) to compare biological assemblages in fossil samples with biological assemblages in a training set of modern samples with associated environmental data (Birks, 1995). MAT was used to assess the suitability of the training set used for analysis. In general, the training set has good analogues where the minimum dissimilarity coefficients are 100-150 or less (Juggins, 2001). The TP optima for diatom species that were present in high abundances in the sediment cores were compared with optima from other training sets, including the Northern Ireland (Anderson *et al.*, 1993), southern England (Bennion, 1994), Central European (Wunsam & Schmidt, 1995), Welsh TP (Bennion *et al.*, 1996), northwest European (Bennion *et al.*, 1996) and the combined TP (EDDI, 2009) training sets, and a survey of modern epilithic algae in 32 lakes in Ireland (DeNicola *et al.*, 2004) (see Appendix O).

3.2.1.7.2 Plant macrofossil analysis

Plant macrofossils, the remains of plants found in sediments that are visible with the naked eye, provide a means of reconstructing catchment vegetation histories, climate and changes within lakes (Battarbee *et al.*, 2001; Birks, 2001; Birks & Bjune, 2010). Plant macrofossils were analysed for all sediment levels following the procedures of Birks (2001) and Wasylikowa (1986). Samples comprising 20 cm³ of wet sediment were disaggregated by soaking in a 10% Na pyrophosphate solution overnight, before being separated into different size fractions using sieves with 125 and 250 µm mesh sizes.

Macrofossils were separated using a binocular microscope at x12 magnification and examined and identified at x40 magnification through comparison with photographs, illustrations and identification keys (Birks, 2007; Mauquoy & van Geel, 2007), and following consultation with Prof. Hilary Birks, University of Bergen, Norway.

3.2.1.8 Analysis of palaeolimnological data

Numerical zonation is often used in palaeolimnology to aid the interpretation of up-core variations in data by categorising them into assemblage or stratigraphic zones (Birks & Gordon, 1985). There are two main methods of numerical zonation for stratigraphic data: agglomerative and divisive techniques. Stratigraphically-constrained agglomerative techniques, such as incremental sum of squares cluster analysis (CONISS), progressively group stratigraphically-contiguous samples with similar compositions in an agglomerative hierarchical fashion. The number of statistically significant groups or zones in each sediment profile can be determined using the broken stick model (Bennett, 1996). The broken stick model is based on the greatest reduction in the variance of a dataset; when the reduction in variance by the creation of a particular zone exceeds that expected from a random dataset then the zone is considered significant ($p < 0.05$). The procedure is repeated until the creation of a new zone is no longer significant. A dendrogram showing the order of groupings is produced to distinguish between zones and subzones (Gordon & Birks, 1972; Manly, 2005). Divisive techniques of data classification involve all samples placed in one group initially. Two groups of samples are then created based on a grouping that results in the least within-group variation in composition. The two groups thus produced are then successively split into smaller groups until there is little further reduction in the variance (Gordon & Birks, 1972; Bennett, 1996; Manly, 2005). The broken stick model can also be applied with divisive classification techniques to determine the number of statistically significant zones.

Major changes in geochemical, diatom and plant macrofossil data were delineated into zones using the agglomerative technique of CONISS (Grimm, 1987), and the computer software programme PSIMPOLL (Bennett, 2002). For each coring site, taxa comprising at least 2 % abundance at any one level were included in the dataset. Taxa present in lower proportions have little numerical importance for zonation; however, they can be of considerable value in interpretation (Gordon & Birks, 1972;

Bennett, 1996). The broken stick model was used to determine the number of statistically significant zones. Zone boundaries were plotted using the C2 programme (Juggins, 2003).

3.2.2 Modelling techniques

A major distinction in the classification of mathematical models is the division into empirical-based models or process-based models (Irvine *et al.*, 2005). Empirical models simulate relationships between variables without accounting for the dynamics of the processes involved and are based solely on statistical or judgemental summaries of data (Reckhow & Chapra, 1998). Empirical models usually simulate the magnitude of a response variable to a change in a driving variable either by not incorporating time-dependent processes or by amalgamating time-dependent processes into long time-steps (e.g. annual means). Process (also known as dynamic or deterministic) models, however, focus on changes in variables over time and generally depend on detailed mathematical descriptions of the processes (described typically by scientifically reasonable equations) involved (Irvine *et al.*, 2005). Model complexity and data requirements increase with the increasing spatial and temporal resolution of a model. Dynamic models can provide better indications of causal relationships and can be more useful for water quality management (Irvine *et al.*, 2005). However, their extensive data requirements can be unfeasible because of their high time, cost and resource requirements (Håkanson & Peters, 1995).

Models of catchment nutrient export range from those based on simple regression equations (e.g. Håkanson & Peters, 1995; Daly *et al.*, 2002; Donohue *et al.*, 2006) and export coefficient functions (e.g. Clesceri *et al.*, 1986; Johnes, 1996) to complex process-based models such as SHETRAN (e.g. Ewen *et al.*, 2000), Hydrological Simulation Program-Fortran (HSPF) (Bicknell *et al.*, 1997) or the Soil and Water Assessment Tool (SWAT) (e.g. Arnold *et al.*, 1998). Catchment nutrient export models can also be distinguished by the spatial resolution of the modelled data with the broad distinction between lumped and distributed models, which describe the extent to which they address areas, such as land-use categories as homogenous units as opposed to modelling spatial units separately (Irvine *et al.*, 2005). Irvine *et al.* (2005) outlines a decision framework for identifying appropriate catchment modelling options relating transfer from source to water body and the timescale of interest and catchment type (rural, urban or mixed - that

is both rural and urban). From this decision framework and the requirements of the current study, including a focus on long-term ecological dynamics and a mixed catchment, the options of a mid-range semi-empirical model, GWLF, and the Better Assessment Science Integrating Point and Non-point Sources (BASINS), one of the most advanced integrated process-based complex catchment models, were available.

Semi-empirical nutrient loading models offer a compromise between empirical export coefficients and more complex models with intense data requirements. Semi-empirical models mechanistically simulate the hydrologic and sediment components and estimate nutrient loads based on relationships between flow and concentration. A version of the semi-empirical model, GWLF (Haith & Tubbs, 1981; Haith & Shoemaker, 1987; Haith *et al.*, 1992; Schneiderman *et al.*, 2002), was used in the current study to simulate daily values for catchment discharge, sediment and nutrient loading. GWLF was originally developed and applied on the West Branch Delaware River at Walton, New York, the main tributary to the Cannonsville Reservoir of the New York City water supply (Haith & Tubbs, 1981; Haith & Shoemaker, 1987). The model is now widely used in the US, for example, in the Hudson River Basin in New York (Howarth *et al.*, 1991) and the Choptank River Basin, Maryland (Lee *et al.*, 2000). GWLF is employed frequently by the US EPA in the setting of total maximum daily loads (TMDLs) (Schneiderman *et al.*, 2002). GWLF has also been applied successfully in modelling climate change impacts on catchment nutrient loading in several European catchments in the CLIME project (2003-2006), including in Ireland (Moore *et al.*, 2010; Pierson *et al.*, 2010), and the ILLUMINATE project (*EPA/ERTDI Project # 2005-W-MS-40*) (Jennings *et al.*, 2009).

Different versions of the model with particular modifications of the original version, but comprising the same GWLF conceptual framework, have been developed and used for a variety of applications (e.g. Dai *et al.*, 2000, Evans *et al.*, 2002; Schneiderman *et al.*, 2002). The version used in the current study was developed by New York City Department of Environmental Protection in the Vensim visual modelling software package (Ventana Systems Inc.) (Schneiderman *et al.*, 2002) and subsequently in the CLIME project (Moore *et al.*, 2010; Pierson *et al.*, 2010) and the ILLUMINATE project (Dalton *et al.*, 2010; Jennings *et al.*, unpublished).

Models of in-lake responses also range from simple empirically-based models, based on relationships between nutrient loading and chlorophyll *a* (e.g. Vollenweider, 1968; OECD, 1982; Foy, 1992), to more complex models of in-lake productivity that include equations for a range of physical, chemical and biological processes (e.g. Elliot *et al.*, 2006; Trolle *et al.*, 2008). Dynamic Reservoir Simulation Model (DYRESM) – Computational Aquatic Ecosystem Dynamics Model (CAEDYM) (DYCD) is a dynamically coupled hydrodynamics-ecological response model of in-lake physical, chemical and biological processes (Hipsey *et al.*, 2006). GWLF and DYCD were used to explore past ecological pressures and responses in Lough Mask.

3.2.2.1 Model descriptions

3.2.2.1.1 GWLF

GWLF is a lumped-parameter model (Leavesley, 1999) that simulates a daily water balance and partitions water among the different pathways of the hydrological cycle (Schneiderman *et al.*, 2002). The model is driven by daily temperature and precipitation data and water balances are calculated on a daily timestep. Streamflow comprises surface runoff and fast and slow groundwater flow components (an unsaturated soil zone and a deeper saturated zone). Diffuse nutrient loads are calculated as a function of land use and runoff. Dissolved nutrient loads are derived by multiplying runoff by a land use-specific nutrient concentration. Sediment loading is based on the Universal Soil Loss Equation (USLE) (Wischmeier & Smith, 1978). Particulate nutrient loads are calculated according to streamflow on that day using information on sediment yield and a soil nutrient concentration for each land use. The contribution of nutrients from septic systems is based on population and estimates of system performance. Nutrient loadings from point sources, for example STPs, are also input and accounted for in the overall estimates of catchment nutrient flux. Output can be produced in daily, seasonal, event and annual time steps. The strength of the approach lies in its fairly robust hydrologic formulation of a daily water balance, and in the flexibility of the model, which can be adjusted in accordance with increasing knowledge and data on the factors that influence nutrient export from a catchment via streamflow (Irvine *et al.*, 2005).

The version of the model used in the current study was developed during the CLIME project (Moore *et al.*, 2010; Pierson *et al.*, 2010) to include an optimisation

procedure for the hydrology component of the model that improves the fit of the modelled to measured streamflow (Schneiderman *et al.*, 2010). Land use classification in the model was also changed to permit use of European CORINE level 3 land cover classes (European Economic Area, 2000). The land class pasture was further divided into high, mixed and low productivity; peat bogs were classified as unexploited or exploited, and farmyards were also included. Further development of the CLIME version of GWLF during the ILLUMINATE project (Jennings *et al.*, unpublished; Dalton *et al.*, 2010) to incorporate available historical catchment pressure data (including human population, land use and livestock numbers on approximately a decadal basis) for catchments in Ireland and to hindcast more realistic long-term catchment nutrient and sediment loads included the following changes:

1/ the use of time series inputs for land use, human population and livestock populations:

- data for the ‘unsewered population’ and the ‘seasonal unsewered population’ (population plus tourists) in the septic tank component of the model were changed from fixed values to variables,
- land use areas, used in calculating runoff, evapotranspiration, sediment yield and nutrient concentrations were changed from fixed values to variables, and

2/ the inclusion of a new dynamic livestock nutrient load module for sheep and cattle was created so that spreading of livestock slurry and manure on land could be accounted for:

- the calculation of dissolved nutrient loads based on an a simple increase in the dissolved nutrient concentration values applied to specified land uses, as in the original model, was not used in hindcast load estimates. Livestock numbers, as total and overwintering, were input as time series input to the livestock module. Livestock that remain on land over winter are referred to as grazers,
- sheep were assumed to overwinter on the land,
- nutrient output per head for sheep and cattle were assumed to have changed over time with introduction of concentrated feedstocks. Historical nutrient output per head was based on dietary manipulation literature (Cerosaletti *et al.*, 2004; Maguire *et al.*, 2007), while recent nutrient output per head was based on that specified in S.I. 101 of 2009 (E. Jennings, Dundalk Institute of Technology, pers. comm.),

- the number of grazing livestock was multiplied by the nutrient output per head to give a potential livestock load. A portion of this load was lost during grazing in surface runoff based on the loss rates for cattle and sheep assumed for export coefficient calculations (Johnes, 1996; Johnes & Heathwaite, 1997). All nutrients from over-wintering cattle were added to a slurry load that accumulated over the winter housing period. The dates for the start and end of the winter housing period were set in the module using a lookup table, and
- the slurry spreading season was based on the dates specified in S.I. 610 of 2010; on wet days, losses from slurry were related to any slurry spread in the previous days. A loss rate was applied to the slurry load based on available literature (Stevens *et al.*, 1997; Withers *et al.*, 2001; Hyde & Carton, 2005; Vadas *et al.*, 2007). Losses were also proportional to runoff on that day. The loss rate on dry days was set to zero. Both daily slurry and livestock loads were apportioned into particulate and dissolved forms based on published values (Stevens *et al.*, 1997; Withers *et al.*, 2001).

3.2.2.1.2 DYCD

Thermal stratification occurs in lakes during periods of warm, calm weather; increases in wind speed or precipitation can result in mixing of the water column (Imberger & Patterson, 1989; Wetzel, 2001). Most lakes in Ireland are either monomictic, in that they experience one period of stratification and one of mixing in any year, or polymictic, with several short-lived periods of stratification and mixing during summer months. The intensity and duration of thermal stratification and the mixing depth are inherently linked to phytoplankton productivity and seasonal succession (Wetzel, 2001). Diatoms are usually abundant in spring before or in the early stages of stratification, and in autumn when stratification breaks down. Cyanophytes usually dominate phytoplankton assemblages during warmer, calmer weather conditions and more intense thermal stratification (Jöhnk *et al.*, 2007; Wilhelm & Adrian, 2008). As the temperature structure of the water column is important for phytoplankton growth, simulation of the physical structure of a lake is a vital requirement for simulating in-lake biological responses.

DYRESM is a one-dimensional process-based hydrodynamics model used for predicting the vertical distribution of temperature, salinity and density in lakes (Imerito, 2007), and has been successfully applied and validated to simulate the seasonal thermal

and ecological dynamics of lakes over several years (e.g. Trolle *et al.*, 2011). DYRESM can be coupled to an ecological model, Computational Aquatic Ecosystem Dynamics Model (CAEDYM), which models in-lake processes including primary production, secondary production, nutrient cycling and oxygen dynamics. The DYRESM model and software are currently available at no charge, for research purposes, from the Centre for Water Research (CWR), University of Western Australia (Imberger & Patterson, 1981). The models are applied and interpreted using a graphical user interface, Modeller, also available from CWR, which has graphing capabilities for input and output data and measured data. The model can be run at daily or subdaily timesteps. Model input data requirements are, however, more extensive than for GWLF and include daily solar radiation, cloud cover, wind speed, vapour pressure, air temperature, precipitation, lake bathymetry, inflow volume and inflow water temperature (Table 3.2). DYRESM model outputs include water temperature and density, which can be interpolated to provide a high resolution two-dimensional output of changes in modelled water temperature at the deepest point in a lake over time. Parameterisations in the model are derived from detailed process studies including field and laboratory data. The model is unique in that reliable predictions are obtained without calibration (Imerito, 2007).

The linked ecological model CAEDYM is a process-based model of the major processes influencing lake water quality (Hipsey *et al.*, 2006). CAEDYM is nutrients-phytoplankton-zooplankton based, but also simulates the C, N, P, and Si cycles along with inorganic suspended solids, phytoplankton, and optional biotic compartments (e.g. bacteria, fish and zooplankton) (Imberger & Patterson, 1981; Hamilton, 1999). The model was developed by CWR and the software is also available free of charge from the CWR, University of Western Australia (Imberger & Patterson, 1981). The model can be dynamically coupled to models of hydrodynamic drivers, including DYRESM. Seven phytoplankton groups can be simulated, including freshwater diatoms, cyanophytes, chlorophytes, cryptophytes and dinoflagellates. The model operates on any subdaily time step, but is generally run at the same time interval as the hydrodynamics model. Additional model data requirements include time series data on inflow concentrations for nutrients and a range of other parameters (Hipsey *et al.*, 2006). Compulsory state variables include dissolved and particulate labile nutrient concentrations for C, N and P, together with dissolved oxygen concentrations and, if diatoms are simulated, Si. The model produces simulations of the selected parameters for each timestep for a profile at the deepest point in the lake.

Table 3.2 Lough Mask modelling data availability and sources. * BUFFER (EVK1-1999-00094)), supplied by Dr. Ian Donohue and Dr. Ken Irvine, Department of Zoology, Trinity College Dublin. **Western Regional Fisheries Board, supplied by Dr. Cathal Gallagher, Central Fisheries Board, CFB. *** Data supplied by Mr. T. Champ and Mr. J. King, CFB

Data	Source	Time period (years AD)
Climate air temp (°C)	MET Éireann	daily, 1901-1913, 1917-1920,
rainfall (mm/day)	Claremorris station (1950-	1930-1938, 1942-2006
cloud cover (fraction)	2006)	daily, 1905-1914, 1931-1942,
wind speed (m/s)	&	1950-2006
relative humidity (%)	Blacksod point (1901-1950)	daily, 1980-present
solar radiation		daily, 1950-1979
(W/m ²)	MET Éireann, Claremorris &	daily, 1905-19
sunshine hours	calculation from sun hours	
Inflow total volume	OPW, EPA, BUFFER* project	daily: Robe -1955 - 2006, Keel 2002-2006, western inflows - 1970-2006, 1990s-2006.
water temp (°C)	BUFFER* project	fortnightly, 2001-2003
nutrient concentration		
Lake temperature profile	thermistor chain (see Section 2.2.5.1)	hourly, 2006-present.
chlorophyll <i>a</i>		monthly/quarterly, 1997-
nutrient	CFB**	2008
	CFB**	fortnightly/monthly, 2001-
	BUFFER*	2003
phytoplankton groups	CFB***	monthly, 1975, 1983-1986

3.2.2.2 Model application

3.2.2.2.1 GWLF

GWLF driving data (daily air temperature and precipitation) were available from Claremorris synoptic station (from 1950-2006 AD) and Blacksod Point meteorological station (for the periods 1901-1914 AD, 1918-1921 AD, 1932-1938 AD and 1941-2006 AD) (Table 3.2). The hydrology subroutine of GWLF includes a precipitation correction factor, which is optimised during the calibration process to correct input precipitation data based on differences between modelled and measured streamflow. The precipitation correction factor was recalibrated to account for the use of precipitation data from each station. Air temperature data were also compared and corrected where required. Population data (human, cattle and sheep) for the catchment were available from the CSO for the DEDs within the catchment for all census years from 1901 AD to present. An annual increase in summer populations due to the tourist population was based on published estimates for the west of Ireland available from the Irish tourist board (Failte Ireland). Houses outside of sewerred urban areas were assumed to have septic tanks in the model. In GWLF septic tanks are assigned to one of the following categories; normal, short-circuited, ponded and direct (Schneiderman *et al.*, 2002). The depth of overburden, determined to be the critical factor controlling the loss of nutrients from septic tank soak-away areas in the west of Ireland (Kirk McClure Morton, 2003), and soil type (Daly & Styles, 2005) were used to classify septic tank categories. Septic tanks in areas with <3 m soil depth were classified as short-circuit and those in areas with >3 m soil depth were classified as normal (Kirk McClure Morton, 2003; Jennings *et al.*, 2009). Septic tank systems were first introduced to Ireland in the early 20th century but were rare until the 1960s (Patrick, 1988); therefore the use of privy vaults/cesspits or other small on-site treatment systems, with nutrient losses classed as for septic soak-away systems, was assumed during the early part of the simulation period.

CORINE land cover values were available from the EPA (Ireland) for 1990 and 2000. Additional data were available for agricultural land use from years in which agricultural censuses were undertaken from 1900 AD. Coefficients of soil erodibility and vegetation cover, required for USLE calculations in the model, were based on Wischmeier & Smith (1978). Average slope length and slope gradient were calculated for each land use using ordnance survey maps. Soil and runoff nutrient concentrations

for different land uses were based on published values for the Lough Mask catchment, or a nearby catchment with comparable soil types and land uses, from Daly (1999), Cummins & Farrell (2003), Daly *et al.* (2002), Styles *et al.* (2006) and Pierson *et al.* (2010) (Appendix P). Dissolved P losses after experimental application of slurry range from 0.29 to 34.0 mg dissolved P l⁻¹, with relative increases in concentrations of between 5- and 60-fold (Withers *et al.*, 2001; Kleinman & Sharpley, 2003; McGechan *et al.*, 2005; Vadas *et al.*, 2007). A value of 0.42 mg dissolved P l⁻¹, representing an average relative increase in concentration, was applied to runoff events during the slurry season in the model by an increase in the concentration applied to high productivity pasture. The slurry spreading period was set to the dates stipulated in the Good Agricultural Practice for Protection of Waters Regulations 2010 (S.I. 610 of 2010), which prohibits slurry spreading between 15th October and the following 15th January.

3.2.2.2.2 DYCD application

In-lake daily temperature, nutrient and total chlorophyll *a* concentrations and phytoplankton community composition were hindcast for the deepest part of the lake, for the period 1905-2006 AD, using the coupled DYCD models. Hindcast annual mean TP, mean chlorophyll *a* and maximum chlorophyll *a* concentrations were used to assign trophic status according to a modified version of the OECD classification system (OECD, 1982) adopted in Ireland (Table 3.3). Although air temperature and precipitation data were relatively continuous, discontinuities in other climate data required to run the model meant that in-lake response modelling could only be carried out for the following periods: 1905-1914 AD, 1931-1942 AD and 1950-2006 AD. Daily output streamflow, sediment and nutrient loading data from GWLF were used to drive the in-lake hydrodynamics model, DYRESM, and ecological response model, CAEDYM. Seasonal mean surface and deep (50 m) water temperatures were calculated from the modelled daily data. The extent of thermal stratification, which has implications for primary productivity and trophic conditions (Wetzel, 2001), is described by the difference between modelled surface and deep water temperatures.

CAEDYM was used to demonstrate the potential of a dynamic model to simulate in-lake biological responses and as a tool in lake management. The model was used to hindcast past in-lake responses to changes in meteorological drivers and nutrient loading,

and to explore potential impacts of projected changes in catchment management. CAEDYM (v 4.0.0-b2) was run in nutrients-phytoplankton-zooplankton configuration on a daily time step. Where inflow nutrient data were not available, data based on the output from GWLF was used for suspended solids and dissolved and particulate nutrient concentrations. Particulate organic C concentrations were estimated based on simulated levels of suspended solids using GWLF. Published values for soil and runoff Si concentrations were limited and measured Si data for calibration and validation were non-existent for the Lough Mask catchment. Among the model requirements for CAEDYM are Si concentrations in inflows. In GWLF, Si loads are a simple function of flow and an applied concentration, which was based on the values for soil and nutrient runoff from the CLIME project.

Table 3.3 The modified OECD classification scheme for lake trophic status (OECD, 1982)

Trophic status	Annual mean TP ($\mu\text{g l}^{-1}$)	Annual mean chlorophyll <i>a</i> ($\mu\text{g l}^{-1}$)	Annual maximum chlorophyll <i>a</i> ($\mu\text{g l}^{-1}$)
Oligotrophic	≤ 10.0	≤ 2.5	≤ 8.0
Mesotrophic	10 - 35	2.5 – 8	8 - 25
Eutrophic	35 - 100	8 – 25	25 - 75

3.2.2.3 Model calibration and validation

All modelling approaches are restricted by the availability of historical input and validation data. An overview of the availability of suitable data for the model calibration and validation, and model driving data is shown in Table 3.2. Both GWLF and DYCD were successfully calibrated and validated against available lake and catchment monitoring data.

3.2.2.3.1 GWLF

The GWLF hydrology model was calibrated and validated for the main subcatchments using measured flow data from the OPW and the EPA for a range of time periods between 1955-2006 AD (Table 3.2). Flow data were quality controlled by the OPW and EPA; indicated quality was taken into account when selecting data for model calibration

and validation. Simulated nutrient loads were validated using inflow monitoring data from 2001-2003 AD available from the BUFFER (EU Fifth Framework Programme) project (described in Section 2.2.5). Quality control standards were within acceptable ranges for all BUFFER water quality analyses (Donohue & Irvine, 2003). Hydrology and nutrient constants in GWLF were calibrated as described in Schneiderman *et al.* (2002). Seven adjustable parameters are included in the GWLF hydrology model: a coefficient for scaling the retention in runoff, a snowmelt coefficient which determines rates of melt as a function of temperature, a runoff recession coefficient which describes the recession of direct runoff, two rate parameters (a recession and a slow recession coefficient) and a baseflow (or groundwater) storage capacity that control the baseflow output from the saturated zone, and a precipitation correction factor to correct for any bias in the precipitation measurements (Schneiderman *et al.*, 2010). Direct runoff and baseflow were simulated based on daily streamflow data using the baseflow separation technique of Arnold *et al.* (1995), where a low flow threshold is defined as the 20th percentile of the daily flow values. An iterative calibration of the model was then performed to minimise the mean square error between the simulated values and the measured variables. Optimisation of the hydrology parameters was performed as follows: the precipitation correction factor was optimised using cumulated streamflow; the curve number adjustment in relation to the cumulated runoff; the runoff recession coefficient in relation to the daily runoff; the melt coefficient in relation to the daily streamflow; the recession coefficient in relation to the daily separated baseflow; and the slow recession coefficient and baseflow storage capacity in relation to the baseflow on the days when flow was less than the low flow threshold. A similar iterative approach was also used to calibrate the curve numbers for the different land cover types. The resulting parameters are shown in Table 3.4.

The NS coefficient of model efficiency (NS), a statistical measure of the degree of correlation between measured and modelled data (Nash & Sutcliffe, 1970), was used to assess model performance:

$$NS = \frac{1 - \sum(\text{measured} - \text{modelled})^2}{\sum(\text{measured} - \text{modelled})^2}$$

Table 3.4 Optimised GWLF hydrology parameters for the main Lough Mask subcatchments

	Precipitation correction factor (unitless)	Recession coefficient (1/day)	Slow recession coefficient (1/day)	Runoff recession coefficient (1/day)	Soil water capacity (cm)	Deep groundwater capacity (cm)	Unsaturated leakage coefficient (unitless)
Robe	1.37	0.10	0.01	0.31	12	4.7	0.03
Carra	1.20	0.03	0.01	0.07	12	6.8	0.11
Owenbrin	1.46	0.28	0.01	0.29	12	8.4	0.03

The percent cumulative error, a measure of the bias of model predictions (Thomann, 1982), was also used to measure model performance. Ideally, model performance is characterised by a value of NS close to 1 and percent cumulative error close to 0 (Schneiderman *et al.*, 2002). Values of NS for daily and monthly stream flow indicated a good model fit for catchment hydrology for all three subcatchments and ranged from 0.69 to 0.83 (Table 3.5; Figure 3.2 a-c).

The NS values indicated a reasonable model calibration and validation for all the subcatchments and were comparable to those reported from other studies based on a variety of different hydrological models in comparable European catchments, e.g. Perrin *et al.* (2001), Parajka *et al.* (2005) and Schneiderman *et al.* (2010). Some high or extreme flow events in the Keel inflow, which drains the Lough Carra subcatchment, during the 2001-2003 AD period were overestimated by the model. The Keel river is the sole outflow from Lough Carra and an expected dampening effect of the lake on flow in the river would be expected and this may not be fully captured by the model. The lowest NS values for the streamflow calibration and validation were for the Owenbrin inflow, for which the model tended to underestimate high flow events. This may be linked to the spatey nature of the rivers in this part of the catchment, where water movement is known to be highly dynamic over relatively short timescales (Donohue *et al.*, 2005). Moreover, lower NS values would be expected for these inflows because of the shorter length of the flow monitoring dataset available for calibration (Table 3.2).

Estimates of sediment yield and sediment P concentration were optimised as described in Schneiderman *et al.* (2002). Comparison of the modelled TP data compared well with measured data, indicating a good model fit for all subcatchments. Values for NS, ranging from 0.61 for the Owenbrin subcatchment to 0.81 for the Robe subcatchment (Figure 3.2 and Table 3.5), were consistent with those quoted for other applications of GWLF and nutrient loading models (e.g. Schneiderman *et al.*, 2002; Dalton *et al.*, 2010; Pierson *et al.*, 2010). The NS values for the western inflow were lower than those obtained for the other subcatchments (Table 3.5). This is likely to be related to the relatively small size and low resolution of the calibration dataset. Moreover, optimisation of the nutrient component of the catchment model is not expected to perform as well as that of streamflow. This is because the streamflow component of the model is dynamically-simulated on a daily timestep, whereas the nutrient loading component, though greatly improved with developments described in

Section 3.2.2.1.1, is not designed to simulate fully the processes that contribute to variations in P concentrations (Pierson *et al.*, 2010). Interpreting the fit of nutrient simulations using the NS statistic is difficult unless the sampling frequency for the calibration/validation period is sufficiently high enough to ensure adequate estimates of loading, including during storm events.

Table 3.5 Model calibration and validation statistics for modelled daily streamflow and monthly TP loads for the main subcatchments (a) and daily mean surface water temperature, monthly water column TP concentrations and total chlorophyll *a* concentrations (b) for Lough Mask. NS = Nash-Sutcliffe r^2 ; n = sample size; cum bias = cumulative bias

(a)

	Streamflow (daily)			TP load (monthly)		
Subcatchment	Robe	Carra	West	Robe	Carra	West
Calibration						
NS (n)	0.82	0.79	0.70	0.80	0.71	0.61
	(2850)	(360)	(440)	(12)	(11)	(12)
cum bias	0.020	0.002	0.040	0.030	0.004	0.020
Validation						
NS (n)	0.79	0.76	0.55	0.67	0.61	0.57
	(9131)	(336)	(365)	(24)	(12)	(16)
cum bias	0.020	0.002	0.090	0.030	0.004	0.030

(b)

Lake model	Surface	TP	Total chlorophyll
validation	temp	concentration	<i>a</i> concentration
NS (n)	0.98	0.78	0.65
	(617)	(60)	(60)
cum bias	0.03	0.03	0.04

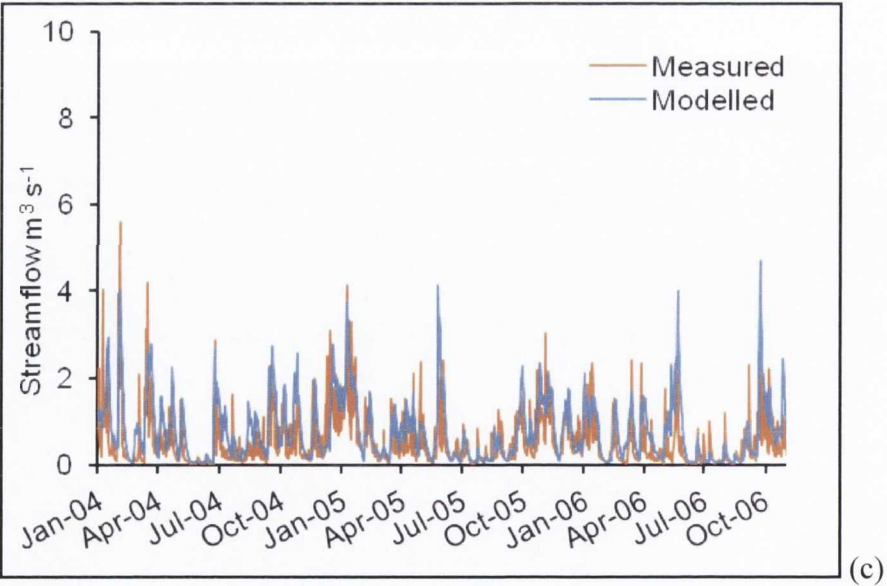
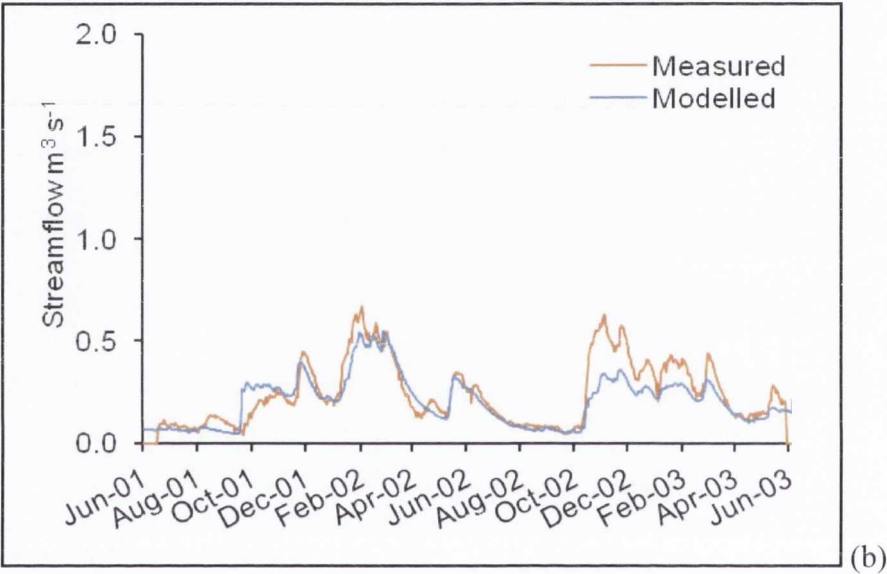
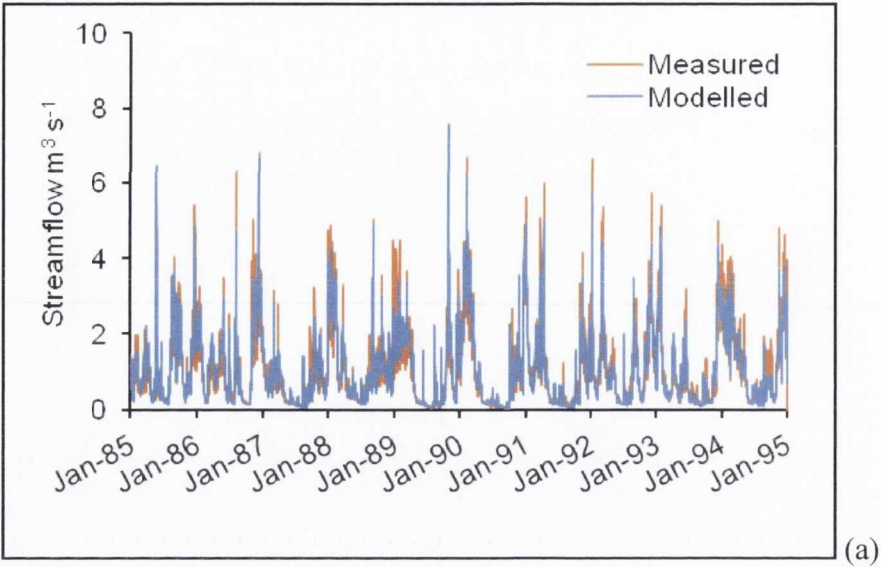


Figure 3.2 GWLF-modelled versus measured catchment modelled daily streamflow: Robe (a), Carra (b) and Owenbrin (c), and monthly TP load: Robe (d), Carra (e) and Owenbrin (f)

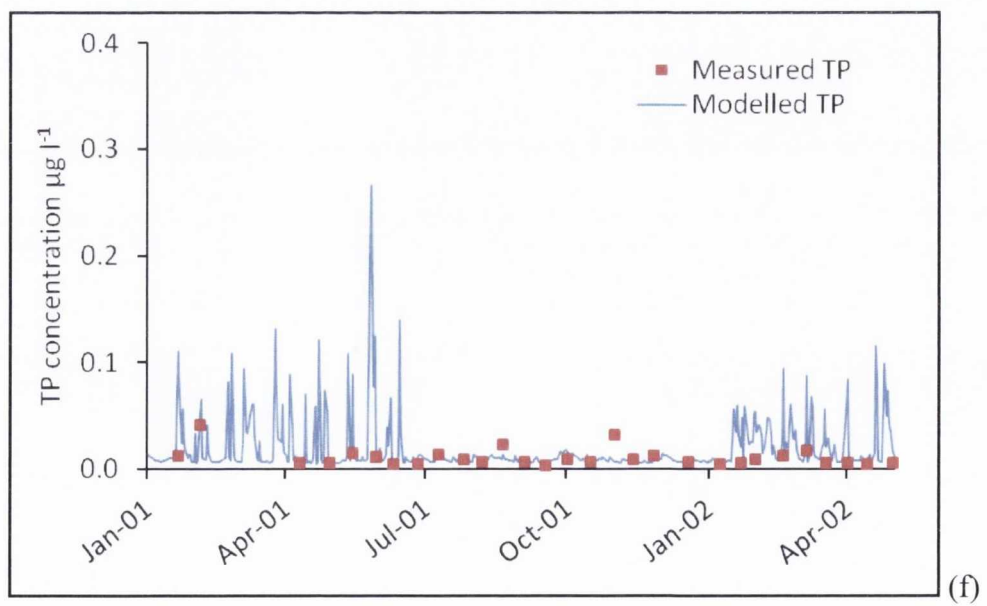
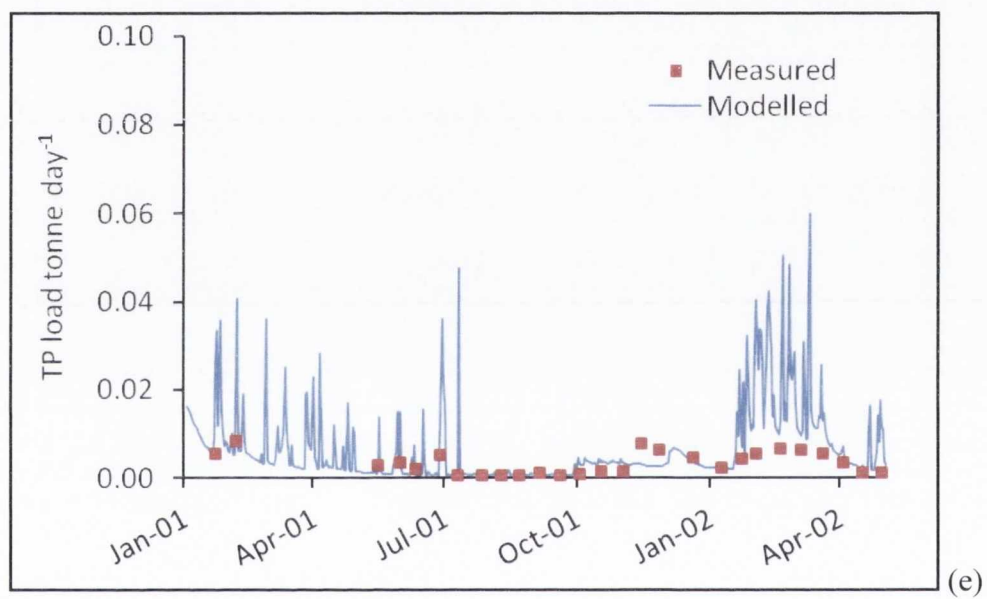
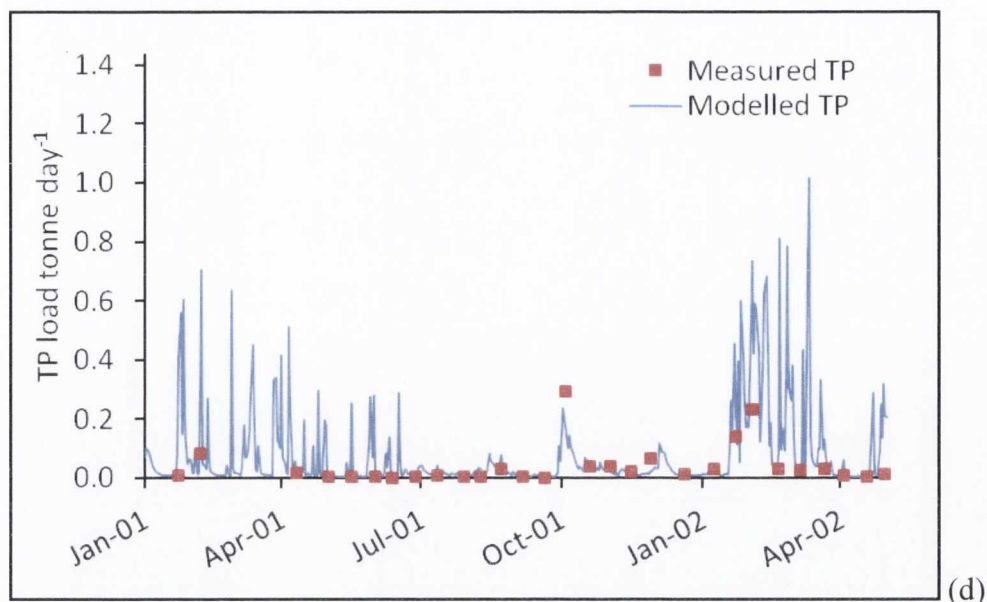


Figure 3.2 (continued)

3.2.2.3.2 DYCD

Parameters used in DYCD relating to phytoplankton growth and nutrient uptake were calibrated following the method of Trolle *et al.* (2008), using available in-lake monitoring data (described in Section 2.2.5). DYRESM is based on a description of internal physical processes in a body of water and does not therefore have constant values that are calibrated. Validation of DYCD simulations of in-lake temperature, TP and chlorophyll *a* for Lough Mask was carried out by comparison with monitoring data, available for the deepest point in the lake (Table 3.2). Hindcast lake surface and deep water (50 m) temperature data were successfully validated using two years (March 2007 to March 2009) of high resolution measured temperature profile data (averaged to daily) from a thermistor chain (Figure 2.7; Appendix Q), described in Section 2.2.5.1. A good fit, with a NS of 0.98, was evident between modelled and measured long-term surface water temperature data (Table 3.5 b; Figure 3.3 a).

Validation data for Lough Mask included fortnightly to monthly chlorophyll *a* data from 2001-2003 AD from the BUFFER project (described in Section 2.2.5.2), and 1996-2003 AD (C. Gallagher, CFB, pers. comm.). Hindcast in-lake TP concentrations also compared reasonably well with measured values (Table 3.5 b; Figure 3.3 b). Hindcast chlorophyll *a* values were close to measured data from late spring to early autumn (March to September) but the model did not replicate the winter chlorophyll *a* peak evident in the monitoring data (Table 3.5 b; Figure 3.3 c). Hindcast phytoplankton community composition data were validated using unpublished monthly data on phytoplankton species composition in Lough Mask for the period 1975-1986 AD from the CFB (see Section 2.2.5.3.1 for further details). The hindcast data compared best with measured data for spring and autumn (Figure 3.4). Hindcast data for the winter months, however, did not replicate measured phytoplankton composition well.

3.2.2.3 Scenario-based modelling

Scenarios are plausible stories about how the future might unfold (Biggs *et al.*, 2007). Scenario-based modelling provides a useful means for exploring potential responses to complex changing environments, and can inform decision making by providing a basis for exploring possible alternative management frameworks (Sutherland, 2006). In the

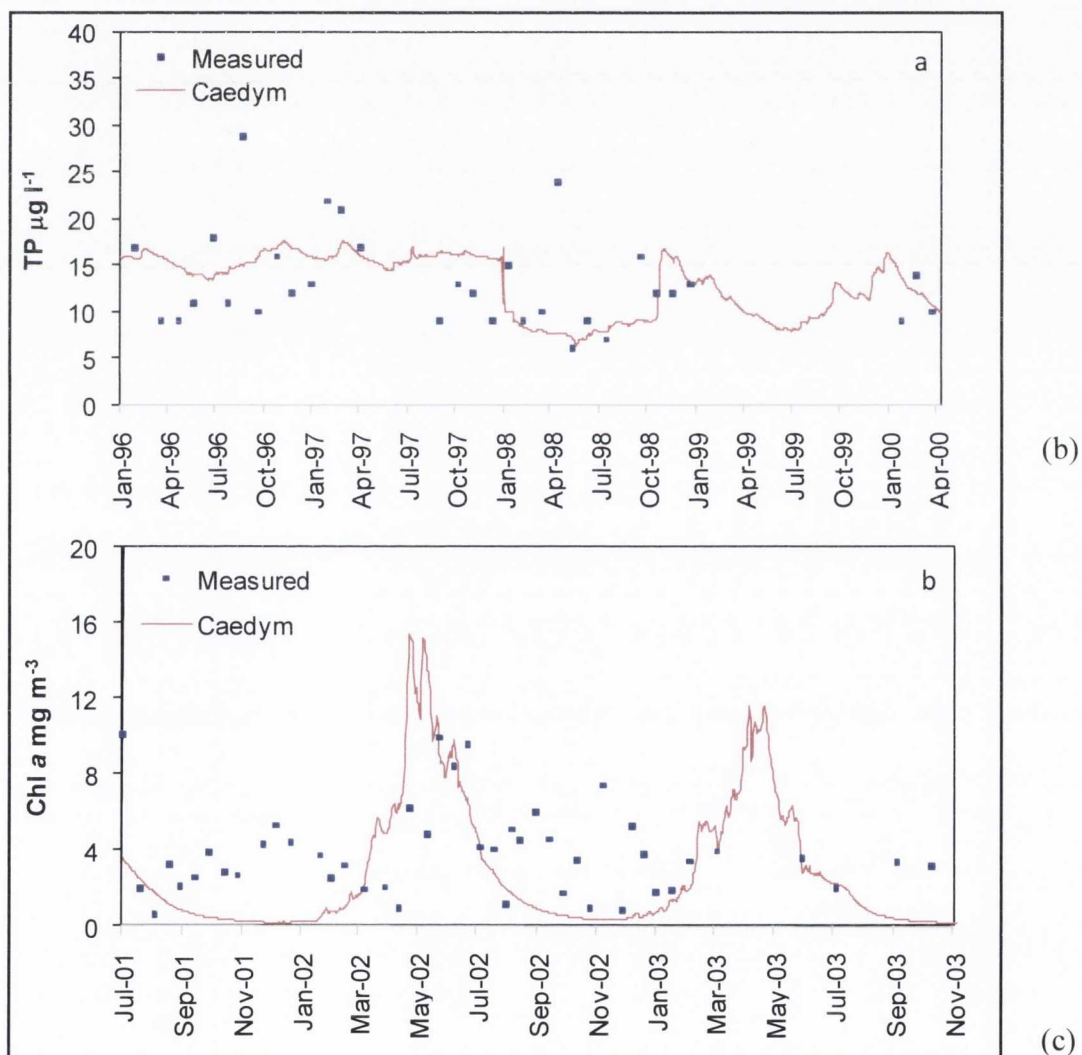
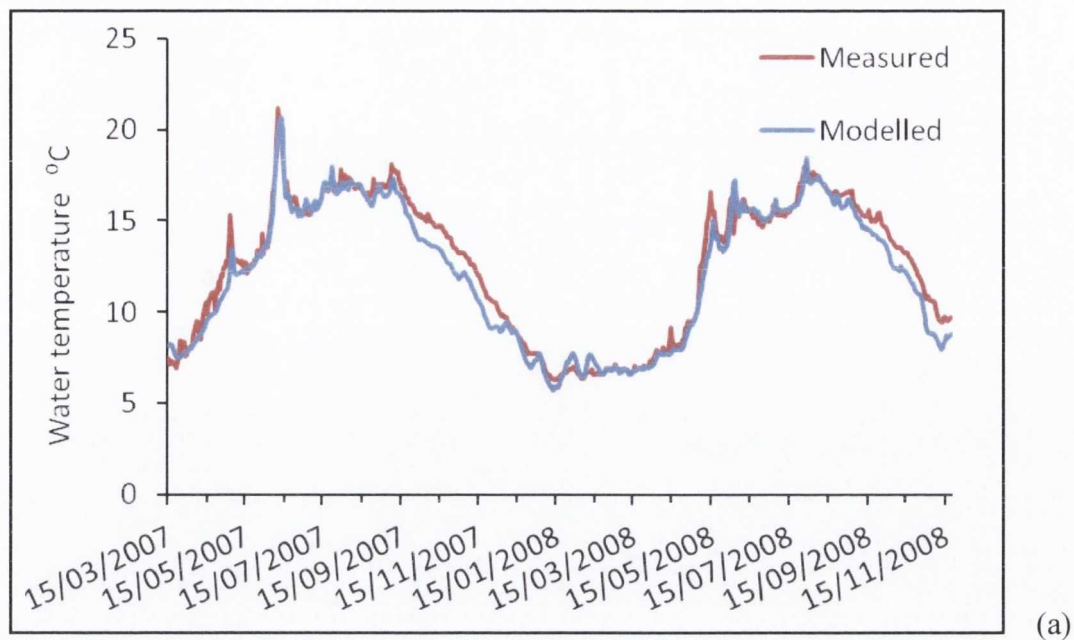


Figure 3.3 DYRESM-modelled versus measured surface water temperature (a), monthly water column TP concentrations (b) and total chlorophyll *a* concentrations (c) for Lough Mask

current study, scenario-based modelling was used to explore the possible impacts of potential changes in catchment pressures on trophic conditions in Lough Mask over a 6-year RBD management period, and the usefulness of potential management measures for water quality restoration. A broad range of management scenarios was derived to assess potential impacts of changes in catchment pressures (including variations in human and livestock population levels, land use change, septic tank performance and slurry spreading period) and were based on analysis of the relative contribution of sources of hindcast nutrient loading for the catchment, existing measures set out in the WRBD management plan (Canney, 2009) and relevant literature (detailed below).

Scenario 1 involved a decrease in catchment livestock numbers by c. 13 %, and was based on EU agricultural policy and projections for agricultural markets (Binfield *et al.*, 2008). Scenario 2 involved almost complete destocking of cattle (92 %) and a 50 % increase in sheep numbers, and was based on the 2003 Mid Term Review of the Common Agricultural Policy (European Commission, 2003), and data from the Irish National Farm Survey and Census of Agriculture, and associated decoupling of all direct payments to farmers from 2005 (Shrestha *et al.*, 2007). Scenarios 3 and 4 involved more moderate reductions of 25 % and 50 % in the catchment livestock population, based on Howley *et al.* (2010). Scenario 5 involved a reduction in the P output per head of livestock to pre-1980 levels, which was implemented in the model by reducing the P concentration of cattle feed (Cerosaletti *et al.*, 2004). Scenario 6 combined a reduction in P output per head of livestock to pre-1980 levels and a reduction in catchment livestock numbers by 50 %.

Scenario 7 included conversion of 50 % of high productivity grasslands to low productivity grasslands, based on Shrestha *et al.* (2007). Scenario 8 involved a change from predominantly high productivity grasslands to non-irrigated arable land, based on predictions by Sweeney (2003) that alternative land uses may be desirable as increases in grassland productivity in the west of Ireland together with stable livestock numbers will mean that less grassland is required per head of stock. Scenario 9 assumed that all septic systems in the catchment were upgraded to operating correctly, a requirement of the EU Directive on Waste (2008/98/EC). Scenario 10 involved P reduction of cattle slurry before application to land, for example, by treatment with magnesium source (e.g. Burns & Moody, 2002) or by physical removal of slurry to local anaerobic digesters (e.g. Northern Ireland Environment Agency, 2008). Scenario 11 involved an increase in the

average annual human population by 1.5 % per year, based on projections by the CSO (2008).

Scenario 12 involved an increase in grassland productivity, based on projections by Sweeney (2003) for the west of Ireland, by conversion of 25 % of low productivity grassland area to high productivity grassland and a 10 % increase in cattle numbers. Scenario 13 was based on Government objectives to increase forest cover to 17 % of land area by 2030 (Jennings *et al.*, 2009), with at least 20 % of this area consisting of broad-leaved forest (Department of Agriculture, Food and Forestry, 1996). Half of the additional forestry was deducted from low productivity grassland and half from unexploited bog (Jennings *et al.*, 2009). Scenario 14 included a change in the slurry spreading period to 1st April to 30th September, i.e. the optimum period identified for slurry spreading in Ireland (Hyde & Carton, 2005; Jennings *et al.*, 2009).

3.2.3 Statistical data analysis

3.2.3.1 Trend analysis

Long-term changes, such as linear trends, in time series data can be found using regression analysis where the data are regressed against time (Shumway & Stoffer, 2011). Regression analysis is a statistical method whereby a mathematical equation is developed to relate one or more independent or predictor variables to the value of a single variable, called the dependent variable. Where time is used as the independent variable, a number of assumptions of regression analysis (e.g. normal distribution of the data and independent error structure) may not be met because the time series data may have an internal structure (such as autocorrelation, trend or seasonal variation) and, therefore, may not be mutually independent. However, these assumptions can be tested for prior to time series analysis (Bianchi *et al.*, 1999).

Trends in meteorological and modelled datasets in the current study were analysed using regression analysis using the software package PAST v. 4.5 (Hammer *et al.*, 2001). As the test assumes normal distribution of data and independent error structure, all datasets were first checked for normality and serial correlation using, respectively, the Ryan-Joiner and Durbin Watson tests in MINITAB 13.1. Historical changes in nutrient loading to lakes are driven by changes in nutrient sources. Significant

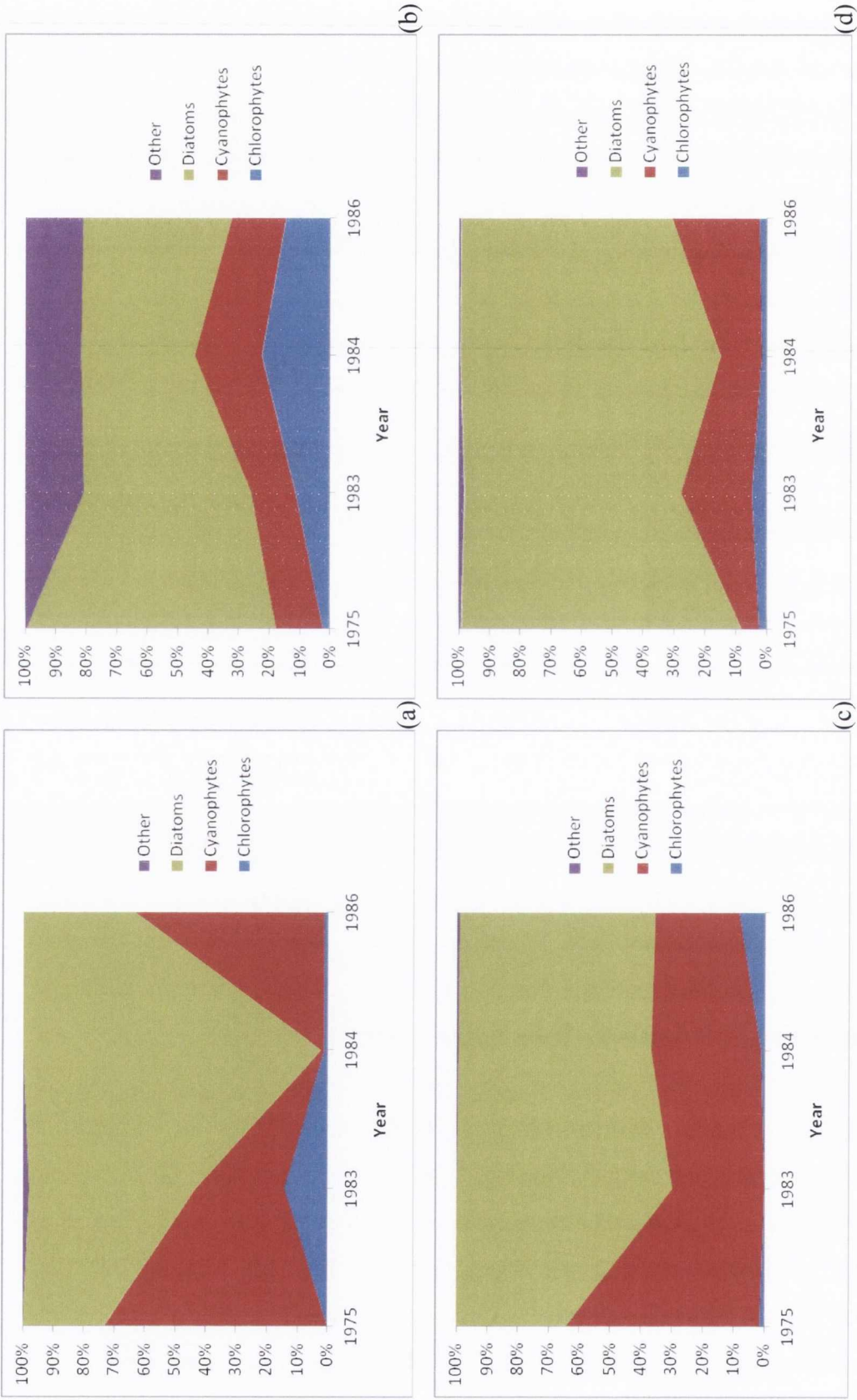


Figure 3.4 Comparison of measured and CAEDYM-modelled phytoplankton assemblage composition (%): spring measured (a) spring modelled (b) autumn measured (c) and autumn modelled (d)

change points in the hindcast catchment TP loading data were identified using cumulative deviations plots (Buishand, 1982) using the software Change-Point Analyzer version 2.3 (Taylor, 2003). In this test, the cumulative deviations from the overall mean are calculated and are rescaled using the overall standard deviation. Change points in a plot of these values are indicated by an alteration in direction. The statistical significance of the change point with the maximum cumulative score can be assessed as a Q value, as defined by Buishand (1982). Correlation analysis, using the Spearman's rho test (Hammer *et al.* 2001), was used to assess the degree of association between sediment-based and hindcast datasets.

3.2.3.2 Multivariate data analysis

Ordination, or gradient analysis, techniques allow the reduction in dimensionality of multivariate environmental datasets and permit description by a small number of new axes that make the greatest contribution to the variance in the data (ter Braak, 1995). The information is then expressed as a reduced number of ordination axes that are, by definition, orthogonal and uncorrelated (Birks & Birks, 2006). Ordination is useful for large environmental datasets as it can reduce the complexity and make patterns in the dataset more obvious (Birks & Birks, 2006). Moreover, the new ordination axes can be treated individually and can be plotted in combination with sediment core data against depth/estimated year. Each new axis produced is described by an eigenvalue, which indicates the relative amount of total variation in the data that is summarised by that particular axis, and an eigenvector, a set of scores for each object in the original data matrix (Kovach, 1995; Manly, 2005). Ordination (or indirect gradient analysis) can be used to find the axes of greatest variability of a dataset and for visualising the similarity structure of the samples and species in a dataset (ter Braak & Prentice, 1988).

PCA is a linear form of ordination and is an extension of multiple (least squares) regression (ter Braak & Prentice, 1988). The first PCA axis will explain most of the variance and will have the largest eigenvalue. Subsequent axes are obtained in the same way as the first axis with the exception that they are uncorrelated with the previous PCA axes and will account for lower proportions of variance in the dataset (Kovach, 1995). In the standard form of PCA, or species-centred PCA, each variable is implicitly weighted by the variance of the values. Variables with high variance dominate the PCA solution; those with low variance have minor influence on the solution (Lepš & Šmilauer, 2003).

Detrended Correspondence Analysis (DCA) is the unimodal form of PCA. The results of ordination analysis are often commonly displayed as a bi-plot where samples are marked by points and variables by arrows. Samples that plot close together are similar in composition; sites that plot far apart are less similar in composition (ter Braak & Prentice, 1998). The species arrows point in the direction of maximum variation in the variable quantity and the length of the arrow is proportional to its maximum rate of change.

3.2.3.2.1 Ordination analysis

Ordination was conducted on data collected for each individual sediment proxy (diatoms, macrofossils and geochemistry) for each site and the resulting primary ordination axes were used to summarise the main patterns of variation in aquatic ecological pressures and responses using the computer software programs CANOCO (version 4.5) (ter Braak & Šmilauer, 2002) and PAST (Hammer *et al.*, 2001). Variations in sediment biological data were investigated using non-linear ordination, i.e. DCA. Taxa with > 2% abundance in at least two samples in the diatom datasets or > 3% abundance in at least one sample in the macrofossil datasets were included in the analyses in order to minimise the influence of rare species (ter Braak & Prentice, 1988). An initial DCA indicated gradients of < 2.5 standard deviation units for geochemical concentration datasets indicating that linear ordination methods were applicable (ter Braak & Prentice, 1988), and therefore PCA was used to investigate variations in the sediment geochemistry data. Geochemical concentration data were square-root transformed to minimise variance.

3.2.3.2.2 Constrained ordination analysis

Constrained ordination analysis (also called direct gradient analysis) can be applied to find the variability in species composition that can be explained by measured environmental variables (Lepš & Šmilauer, 2003). Canonical Correspondence Analysis, CCA, is a form of constrained ordination analysis that can be used to establish links between potential explanatory variables (such as environmental pressures) and response variables (such as aquatic ecological responses) in palaeolimnological studies (Legendre & Birks, 2012). CCA eigenvalues can also be interpreted as variances. Thus

partitioning of variance between potential explanatory variables can be carried out based on CCA eigenvalues (Borcard *et al.*, 1992, Økland & Eilertsen, 1994).

CCA was applied to sediment geochemistry, diatom and macrofossil response datasets separately using climate and catchment data and modelled catchment loads as potential explanatory variables (drivers of ecological responses) for Lough Mask for the period 1901-2006 AD, using CANOCO for Windows version 4.5. Potential explanatory variables included climate (annual and seasonal mean air temperatures, annual and seasonal total precipitation, a continentality index and the North Atlantic Oscillation, NAO) and human pressure data (human population, cattle population, sheep population, modelled annual and seasonal catchment flow, modelled annual and seasonal nutrient and sediment loads, modelled seasonal mean surface water temperatures, modelled seasonal mean deep water temperatures and modelled seasonal stratification). The climate and catchment datasets are detailed further in Section 2.2. All environmental variables were tested for collinearity ($p < 0.05$) and variables that showed high collinearity were not included in the analysis. Taxa with $> 2\%$ abundance in at least two samples in the diatom and macrofossil datasets or $> 3\%$ abundance in at least one sample in the macrofossil datasets were included in the analyses in order to minimise the influence of rare species (ter Braak & Prentice, 1988). The CANOCO for Windows version 4.5 program centres and standardises all environmental variables to bring their means to zero and their variances to one (Lepš & Šmilauer, 2003).

The annual timing of seasons was based on the meteorological definitions, i.e. spring: March, April and May; summer: June, July and August; autumn: September, October and November and winter: December, January and February. The difference between surface water temperature and deep water temperature was used to describe long-term changes in lake thermal stratification. The winter (December through March) NAO index (Hurrell, 1995) was available from the Climate and Global Dynamics Division of the US National Center for Atmospheric Research, and the continentality index was defined as the absolute difference between summer and winter temperature (Battarbee *et al.*, 2002).

Climate (annual and seasonal mean air temperature and total precipitation), human population, agricultural census and modelled catchment data had varying sampling intervals, ranging from daily (climate and modelled flow and loads) to decadal

(human population). The relatively low temporal resolution of sediment data when compared with model output data meant that sediment-based DI-TP levels and sediment TP concentrations could only be calculated at 2 to 10 year intervals. In order to retain the maximum information in the climate and modelled data, human agricultural census data were linearly interpolated on an annual timestep, and annual data were used in the CCA analysis. A dataset of 11 independent variables (human population, cattle population, sheep population, modelled annual catchment TP loads, summer mean air temperature, winter mean precipitation, winter mean air temperature, spring mean thermal stratification, summer mean thermal stratification, continentality index and NAO index) were used in the CCA analysis.

3.2.3.2.3 Partial CCA analysis

Partial CCA analysis can be used to investigate the extent to which two or more different groups of independent variables explain unique aspects of the response data. Moreover, the procedure of partitioning variance using partial CCA analysis can be used to quantify the role of different groups of independent variables in explaining variance in the response dataset (Bocard *et al.*, 1992). Partial CCA involves carrying out separate CCA analyses, initially with all independent variables and then with separate groups of independent variables with the other groups used as covariables. Eigenvalue analysis for 2 groups of independent variables allows for the estimation of:

- the variance uniquely described by the first group (but not explained by the second),
- the variance uniquely described by the second group (but not by the first),
- the variance jointly described by both groups, and
- the variance that is unexplained.

The hypothesis of non-significant ($p = 0.05$) deviation of variation explained by a variable, compared with that explained by a random variable, was tested with the Monte Carlo permutation method in CANOCO 4.5 (ter Braak & Šmilauer, 1998) with 99 unrestricted permutations of the constraining variable.

Chapter 4

Middle to late Holocene environmental changes in western Ireland inferred from fluctuations in preservation of biological variables in sediment

4.1 Abstract

Knowledge of natural variability in aquatic ecosystems is vital for assessing the form and level of human-induced change, and for predicting the likely impacts of future anthropogenically-induced changes. Distinguishing between natural and anthropogenic variability in sediment records can be problematic, however, because of the potential for similar ecological effects. Standard sediment-based approaches for reconstructing past environmental changes tend to focus on qualitative and quantitative variations in palaeoenvironmental indicators, with little significance attached to their absence.

This chapter is based on radiometrically-dated, multiproxy palaeolimnological data from two coring sites in Lough Mask, Co. Mayo, a lake located close to the Atlantic seaboard in western Ireland. Although low SARs and non-uniform sediment accumulation is evident, these data suggest that aquatic, including sedimentary, conditions in Lough Mask may have been sensitive to climatic change, especially levels of precipitation, over the mid-late Holocene. Variations in the presence of siliceous microfossils and calcareous macrofossils from aquatic sources, sediment lithology and geochemistry indicate a quasi-cyclical response to oscillations in climate conditions, with the timing of the latter appearing to correspond largely with findings from elsewhere in northwest Europe, including other sites in Ireland. This chapter posits that the sedimentological variations may be linked to variations in the precipitation and the resulting influx of Si in inflows, which may be linked to the relative influence of groundwater versus surface water in streamflow. Ground-water dominated flow during relatively dry climatic conditions can be relatively enriched in Si, whereas during wetter climatic conditions high surface water runoff can lead to dilution of Si levels in streamflow and result in reduced Si concentrations. Depleted Si can facilitate Si recycling from the surface sediments and thus post-depositional dissolution of diatoms. The variations in subfossil preservation in lake sediments are, however, also likely to be complicated by in-lake processes (such as variable SAR and sediment mixing), the effects of which are not well-understood, and are also likely to be affected by variations in climate conditions. The impacts of relatively early human impacts are also evident in the sedimentary record. Overall, the results highlight the aquatic and taphonomic effects of interactions between past variations in catchment conditions, climate and in-lake processes. The complexity of these interactions and their effects, mediated through the characteristics of Lough Mask and its catchment, poses severe problems for the

conventional analysis of palaeolimnological data and their use in dynamic simulations of future changes in aquatic ecological pressures and their impacts.

4.2 Introduction

Variability in aquatic ecosystems is influenced by both natural (climate and catchment) and anthropogenic drivers. Lake ecosystems are under increasing pressure from human activity since the onset of the Anthropocene, c. 200 years ago (Oldfield, 2005), and this has impacted significantly on ecological quality, structure and functioning (Woodward & Shulmeister, 2005). Knowledge of natural variability in aquatic ecosystems, or of baseline or reference (pre- or minimum human impact) conditions, is vital for assessing the form and level of human impacts and for predicting the likely impacts of future anthropogenically-induced changes (Bennion & Battarbee, 2007).

Palaeolimnology is widely used to reconstruct past environmental changes and to distinguish the effects of natural and anthropogenic drivers (Bennion & Battarbee, 2007). Sedimentary biological proxies are particularly effective tools for reconstructing long-term environmental changes (Smol *et al.*, 2005; Smol, 2008). Though highly-sophisticated statistical quantitative techniques have been developed to assess palaeoenvironmental data and to investigate the role of different environmental pressures (Simpson & Anderson, 2009), distinguishing between natural- and anthropogenic-driven variability in sediment records can be problematic, because of the potential for similar ecological effects (Bennion *et al.*, 2011b; Battarbee *et al.*, in press). For example, the effects of climate change and anthropogenic nutrient pollution on lake ecology can be identical (Jeppesen *et al.*, 2010; Moss *et al.*, 2011). Moreover, the hydrological impacts of changes in precipitation and human-induced catchment disturbance are often similar (e.g. Austin *et al.*, 2007).

Determining aquatic reference conditions can be problematic owing to difficulties in separating human from natural causes of variation, and because of the confounding influence of local factors (Taylor *et al.*, 2006). Furthermore, reference conditions are generally not static but vary on short (interannual to decadal) and long (centennial to millennial) timescales (Bennion *et al.*, 2011b). During the Holocene, significant decadal- to millennial-scale fluctuations in climate conditions have been recorded in western Europe (Schettler *et al.*, 2006), linked to solar forcing and changes in the North

Atlantic surface water current system (Richter *et al.*, 2009), and these have impacted aquatic conditions (Charman, 2010). Changes in climate conditions can result in changes in lake levels (Magny, 2007), which have direct implications for ecological conditions (including water chemistry, light penetration and primary productivity) (Smol *et al.*, 2005). Catchment characteristics and lake hydromorphology also influence natural aquatic ecological variability. In lakes with complex bathymetries and catchments with varied geology and topography, spatial differences in ecological responses to external drivers are likely to exist (Gilbert, 2003).

Palaeolimnological approaches to reconstructing past drivers of aquatic ecological changes and their effects generally focus on qualitative and quantitative variations in biological proxies and geochemical components that are present. Relatively little attention is paid to the absence or degree of preservation of subfossil data upon which environmental reconstructions are based (Ryves *et al.*, 2006; 2009). Biological proxies can be absent or poorly preserved in sediment records and little work has been carried out to investigate the effects of preservation on the accuracy of environmental reconstructions (Ryves *et al.*, 2009). The aims of this chapter are to use a multiproxy palaeolimnological approach (including independent sediment proxies) to:

1. examine the relationship between variations in the preservation of sedimentary biological proxies and Holocene environmental changes,
2. elucidate the effects of different drivers of ecological changes (both natural and anthropogenic) during the middle to late Holocene, and
3. establish the controls on preservation of biological proxies,

in a complex lake (Lough Mask) in the west of Ireland over the last c. 6000 years. Lakes located on the Atlantic seaboard, such as the study site, provide an ideal opportunity to study the influence of climatic fluctuations, particularly fluctuations in precipitation, on aquatic environments, as they are highly sensitive to ocean circulation patterns (Holmes *et al.*, 2010), an important control on regional climate variability (Holmes *et al.*, 2007). The current chapter is based on sediment-based analyses from cores collected from the Robe (MK-4 and MK-5) and the deepest point (MK-8, MK-9 and MK-10) coring sites

(see Table 3.1 and Figure 2.2) in March 2007. Details of the palaeolimnological methods used in the research are described in Chapter 3.

4.3 Results

4.3.1 Sediment chronology

Levels of ^{210}Pb and ^{137}Cs were only above background levels (2.5 DPM g^{-1} and 0.41 DPM g^{-1} , respectively) in the uppermost 1.5 cm of the core from the deepest point and calculated SARs were very low ($< 0.01 \text{ g cm}^{-2} \text{ yr}^{-1}$). The ^{210}Pb activity measurements for the top 1.5 cm of the core showed an approximate exponential decrease with depth (Table 4.1; Figure 4.1 a, b; Appendix R). Below 2 cm, ^{210}Pb activities were variable with depth but remained low ($< 3 \text{ DPM g}^{-1}$). Levels of ^{137}Cs activity decreased gradually between 0.5-5 cm and below 6 cm activity remained constant (Figure 4.1 c; Appendix R). The maximum fallout of atmospheric ^{137}Cs from nuclear testing is expected to peak at c. 1963 AD or later and therefore resides in either the 0.5 cm or 1 cm sample. Application of the CRS model to the ^{210}Pb data predicted that the bottom of the 0.5 cm sample dates to c. 1964 AD, which was reasonably compatible with the prediction of the maximum ^{137}Cs peak. A low rate of sediment accumulation was supported by the AMS ^{14}C dates where sediment samples 40-41 cm and 20-21 cm, were dated at, respectively, $5370 \pm 60 \text{ BP}$ ($\delta^{13}\text{C} = -27.5 \text{ ‰}$) (6125 to 6290 cal BP) and $3830 \pm 40 \text{ BP}$ ($\delta^{13}\text{C} = -26.6 \text{ ‰}$) (4184 to 4406 cal. BP) (Table 4.1).

^{210}Pb activity declined with depth between 0-8 cm in the sediment core from the Robe site (Table 4.1; Figure 4.1 d, e). Below 8 cm, ^{210}Pb activity remained low ($< 3 \text{ DPM g}^{-1}$) and relatively stable to the base of the core. Measured ^{137}Cs activities exhibited a profile typical of that where the majority of the ^{137}Cs is derived from the catchment (Walling & Qingping, 1992), with no clearly defined subsurface peaks, associated with atmospheric input, evident (Figure 4.1 f). Application of a linear regression model ($y = -1.08 \ln(x) + 2.96$; $r^2 = 0.97$) (Figure 4.2) to the ^{210}Pb data in the uppermost 9 cm of the sediment core suggested a mean accumulation rate of $0.033 \text{ g cm}^{-2} \text{ yr}^{-1}$ and an estimated age for the sample at 3.5 cm of c. 1967-1985 AD. Concentrations of SCPs in four and five sediment core samples from, respectively, MK-8 (deepest point) and MK-5 (Robe site) were used to verify SARs and ages based on the radiometric dating techniques (Table 4.2). In both cases, up-core variations in concentrations of

Table 4.1 Estimated rates of sediment accumulation (SARs) and ages of the basal and mid-samples for sediment cores based on radiometric (^{210}Pb and ^{137}Cs) and AMS ^{14}C analyses for MK-5 and MK-8 (see Appendix R for raw data)

Site	Core (sample depth, cm)	Core length (cm)	Beta ID	CRS estimated age (years)	Linear regression estimated age (years)	Cal. radiocarbon age years BP (1 sigma)*	SAR ($\text{g cm}^{-2} \text{ yr}^{-1}$)
Deepest point	MK-8 (0-0.5)	41	Beta-251237 Beta-245605	42.92	—	—	0.0075
	MK-8 (0.5-1)			85.85	—	—	0.0075
	MK-8 (1-1.5)			128.77	—	—	—
	MK-8 (20-21)			—	—	4184 - 4406	—
	MK-8 (40-41)			—	—	6125 - 6290	—
Robe	MK-5 (0.5-1)	25	Beta-251239	8.67	9.34	—	0.0360
	MK-5 (1-1.5)			16.73	16.90	—	0.0314
	MK-5 (2-2.5)			25.68	27.91	—	0.0411
	MK-5 (3-3.5)			37.44	39.84	—	0.0339
	MK-5 (4-4.5)			63.86	63.79	—	0.0303
	MK-5 (6-7)			—	113.39	—	0.0303
	MK-5 (8-9)			—	157.42	—	—
	MK-5 (24-25)			—	—	2618 - 2757	—

* According to Calib 5.01 and the Intcal04.14c dataset (Stuiver & Reimer, 1993; Reimer *et al.*, 2004).

Table 4.2 Concentrations of Spheroidal Carbonaceous Particles (SCPs) for sediment core samples from MK-8 (deepest point) and MK-5 (Robe site)

Coring site	Core	Core depth (cm)	SCP concentration (no. g ⁻¹)
Deepest point	MK-8	0 - 0.5	3056
		2 - 2.5	0
		3 - 3.5	0
		6 - 7.0	0
		20 - 21	0
Robe	MK-5	0 - 0.5	2047
		2.0 - 2.5	2784
		11 - 12	0
		20 - 21	0

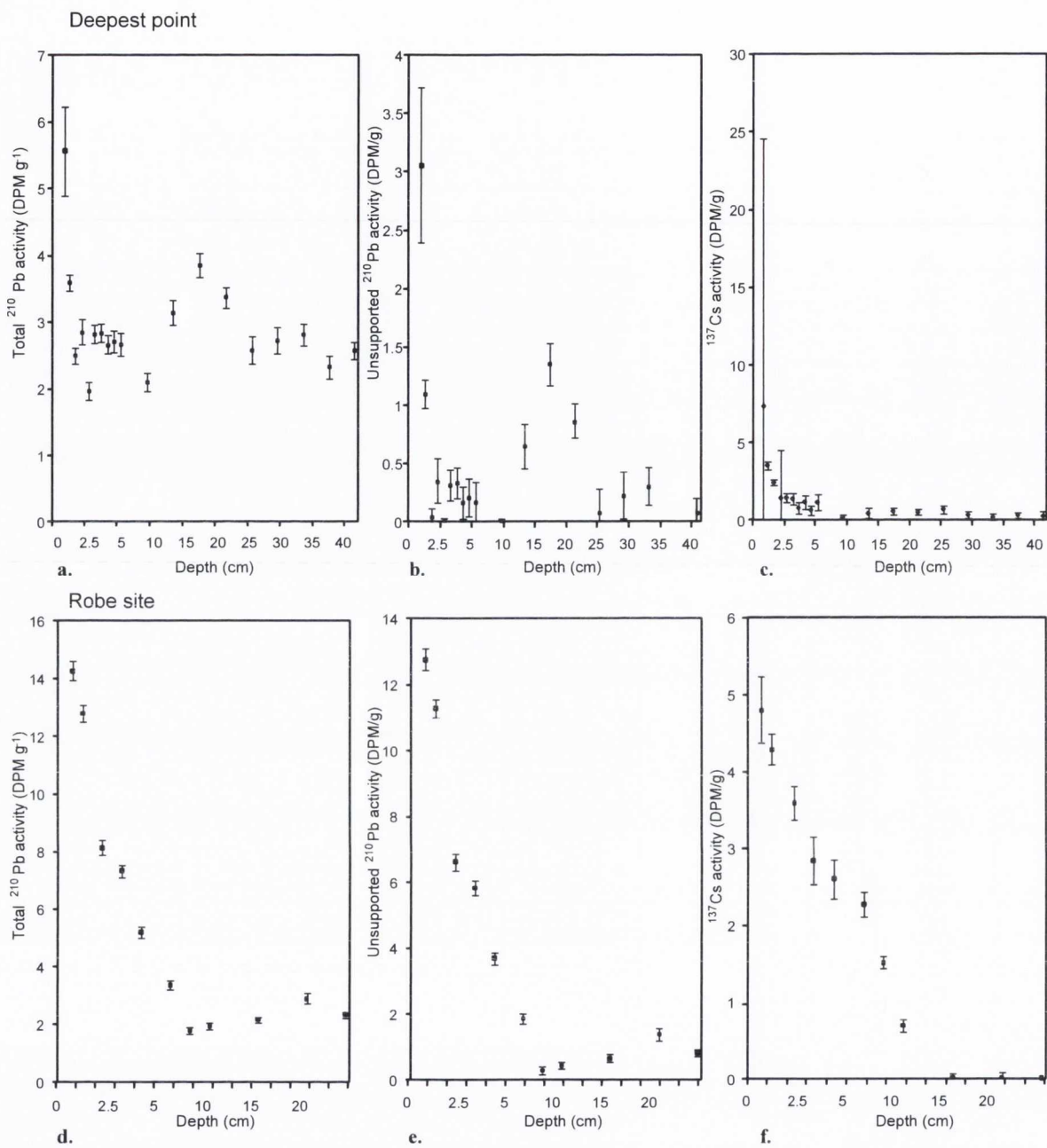


Figure 4.1 Fallout radionuclides at the deepest point (MK-8) (a-c) and Robe site (MK-5) (d-f) coring sites showing total and supported ^{210}Pb and ^{137}Cs concentrations versus depth

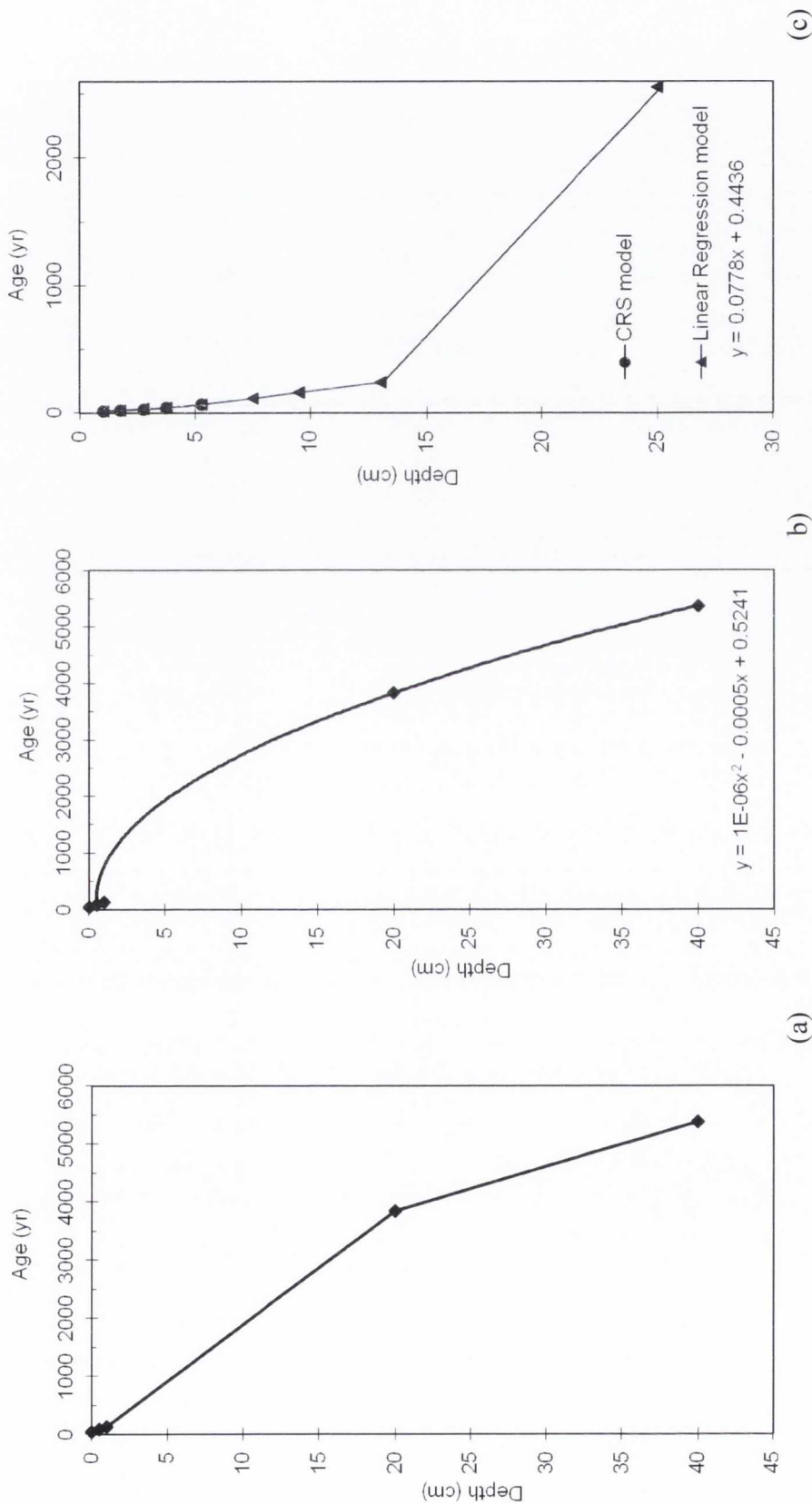


Figure 4.2 Age-depth models for the deepest point (MK-8), based on linear interpolation (a) and a 2-term polynomial (b); and the Robe site (MK-5) showing both CRS and linear regression models for the ^{210}Pb dates (c). Note that the age depth profile and SARs were estimated using a combination of radiometric ages and AMS ^{14}C calibrated ages (BP)

SCPs were in agreement with the chronologies established through AMS ^{14}C , ^{210}Pb and ^{137}Cs analyses.

4.3.2 Sediment stratigraphy, LOI and stable isotopes

Sediments from both coring sites exhibited considerable lithological variation (summarised in Figure 4.3). The basal unit of MK-8 comprised a mixture of brown silt and clay and intermittent sand-rich horizons and some terrestrial plant remains. LOI values varied in the range 7-27 % (Figure 4.3). Above the basal unit is a 13-cm unit of brown silt, containing four sand-rich horizons. The uppermost unit had a higher sand content, particularly between c. 7-10 cm and c. 0-3.5 cm. Macrofossil abundances increased between c. 9-12.5 cm. Sediments from MK-5 comprised pale marl with no macrofossil remains, in the basal part (15-25 cm) of the core. LOI values were very low (c. 3-4 %) in the basal unit. Between 12-15 cm there was a distinct sand- and organic-rich interval, macrofossil remains were abundant and LOI values increased sharply. Overlying this was a mixture of marl and silt with few macrofossils. The carbonate content, though low throughout the sediment core, of the uppermost sediments was reduced (Figure 4.3), while LOI values and silt content increased. The sand content of this uppermost horizon was variable and increased dramatically between c. 10-12 cm and c. 3-6 cm.

C:N ratios, levels of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ indicated that sources of organic matter in the deepest point below 4 cm were mainly terrestrial (Figure 4.4 a). Organic matter comprised a mixture of material from terrestrial and aquatic sources between 4-2 cm, and mainly aquatic sources from 0-2 cm. At the Robe site, the C:N ratios and levels of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ indicated substantial inwash of terrestrial material at c. 21 cm and a mixture of material from terrestrial and aquatic sources between 21 cm and the top of the core (Figure 4.4 b). Up-core variations in $\delta^{15}\text{N}$ and C:N ratios reflected an increased influence of autochthonous sources of organic matter in the lake in more recent times, particularly between 0-9 cm.

4.3.3 Core correlation and age-depth modelling

Up-core variations in organic matter content, based on LOI, can be used as a basis for extending a chronology between adjacent cores from the same coring location

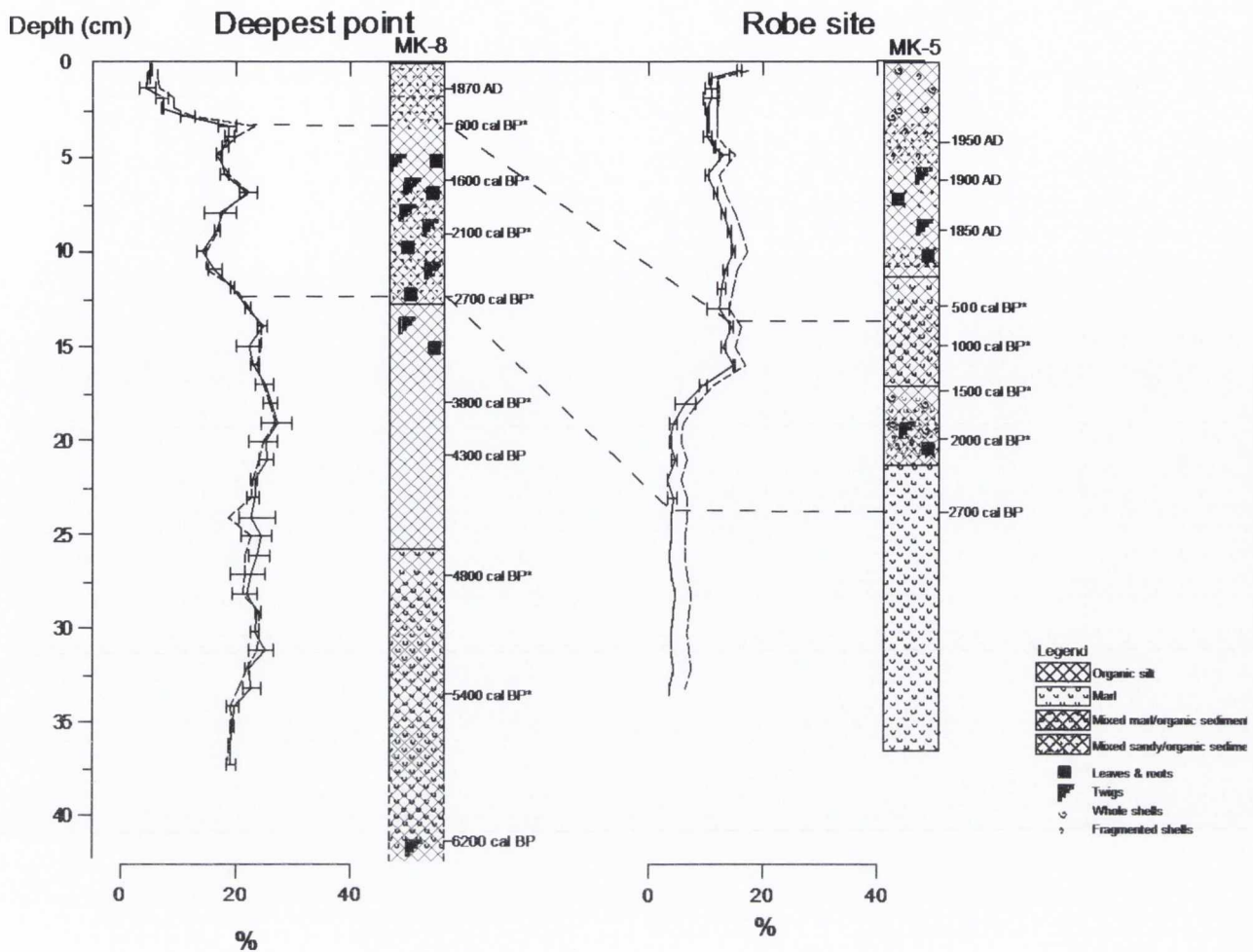
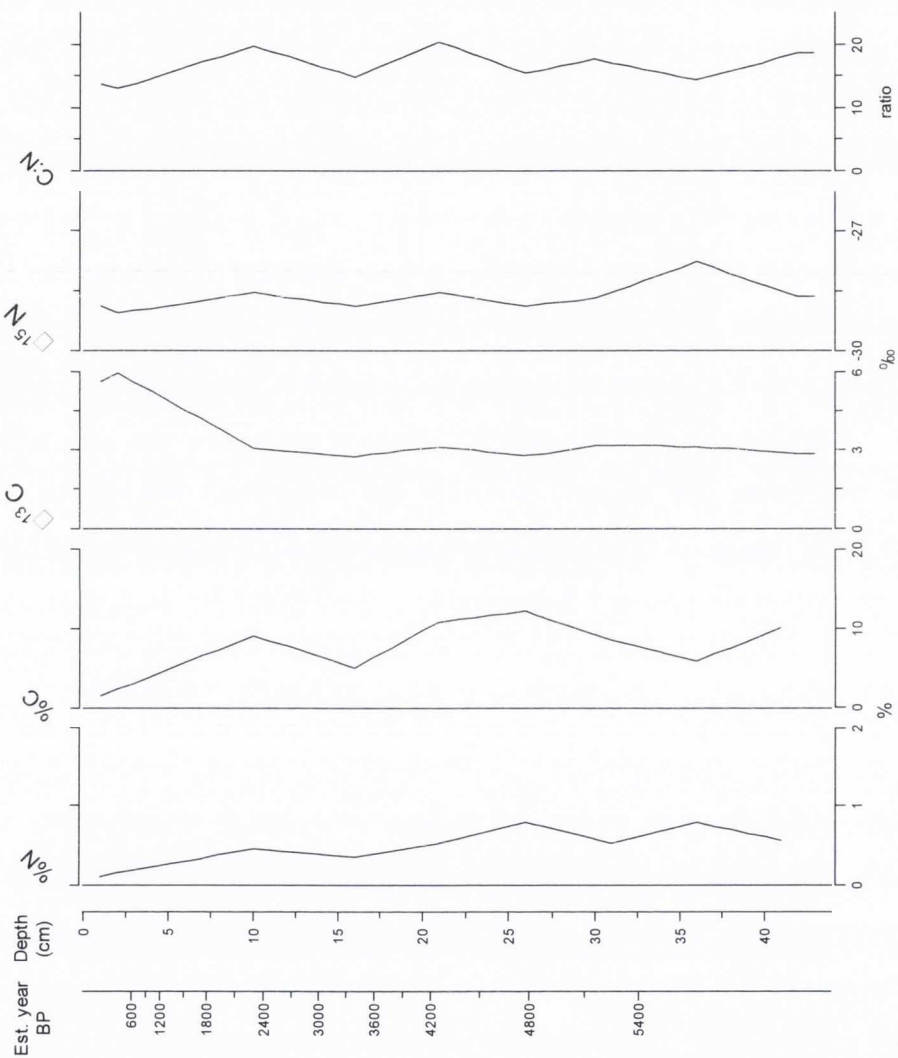


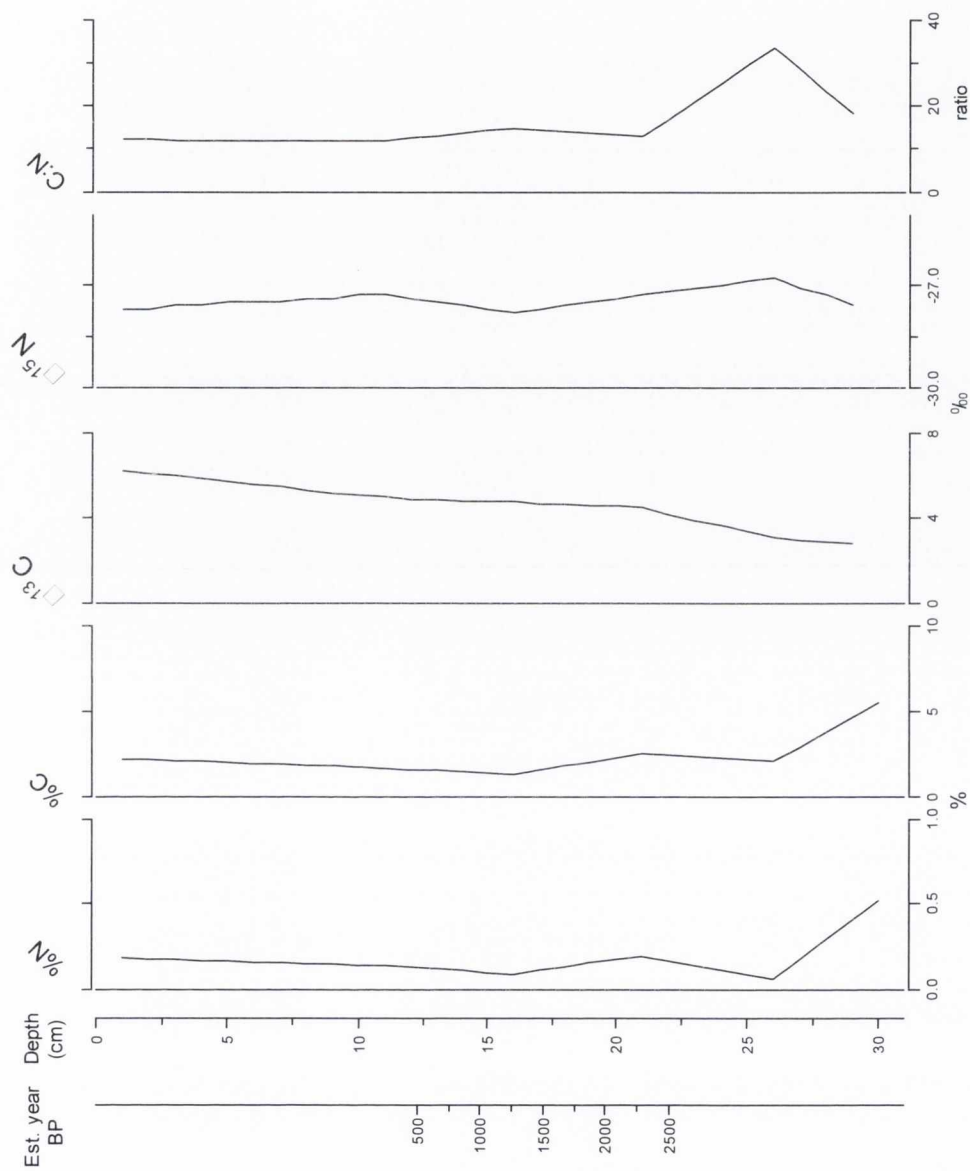
Figure 4.3 Up-core variations in % organic matter content, LOI (solid line = mean of triplicate measurements), % carbonate (dashed line) and lithostratigraphy: a. the deepest point and b. the Robe site

in a lake (Carol *et al.*, 1998; Brancelj *et al.*, 2002). Comparison of LOI data for the sediment cores from the deepest point and Robe sites showed very different profiles (Figures 4.3), but were strongly correlated for sediment cores within each of the three coring sites (deepest point sediment cores: $r^2 = 0.88-0.92$, $v = 40$, $p < 0.01$; Robe site sediment cores: $r^2 = 0.86$, $v = 26$, $p < 0.01$; southwest site sediment cores: $r^2 = 0.92-0.93$, $v = 38$, $p < 0.01$). There were 2 distinct units evident in the LOI profiles for both coring sites from major changes in LOI occurring between c. 1.5-4 cm in the deepest point profiles and between c. 12-16 cm in the Robe site (Figures 4.3). LOI in sediment cores from the deepest point was relatively high in the lower unit (below 4 cm; mean = c. 21.7 %; $\sigma = 3.2$) and relatively low in the upper parts (above 4 cm; mean = c. 9.6 %; $\sigma = 6.0$).



(a) deepest point

Figure 4.4 Up-core variations in %N and %C content, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ and ratios of C:N for the sediment cores from: the deepest point (MK-9) (a) and the Robe site (MK-4) (b)



(b) Robe site

Figure 4.4 (continued)

The LOI profiles for the sediment cores from the Robe site displayed contrasting patterns of variation. LOI was very low (ranging between c. 3-9 %) below c. 14 cm and increased to between c. 10-16 % above c. 14 cm. According to the radiometric data, the changes in the LOI profiles did not occur contemporaneously.

Percent carbonate content was very low in the sediments from both the deepest point and Robe sediment cores. Although little variation was evident in the carbonate profiles, the amount decreased upcore at both sites. Sediment lithostratigraphy also provides a basis for extending a chronology between adjacent lake sediment cores from the same coring site (Smol, 2008). Sediment lithostratigraphy at both coring sites also revealed highly variable sediment composition and different upcore profiles (Figure 4.3). The high variability in lithostratigraphy is likely to reflect non-uniform sediment accumulation and the presence of sediment hiatuses. Together with the low dating resolution, this means that any inferences made for periods between AMS dates are subject to considerable error.

According to the radiometric dating data, the sediment cores from the deepest point and Robe sites represent different time periods: c. 6000 years at the deepest point and c. 2700 years at the Robe site. The lithostratigraphic and LOI data suggested that sediment accumulation at these sites may be non-uniform. There were no consistent patterns of variation between the radiometric dating, lithostratigraphic, LOI/carbonate and stable isotope profiles in the sediment cores from the deepest point and Robe coring sites and, therefore, identification of hiatuses with any certainty was not possible. All age-depth models are alternative interpretations of a site's unknown true sedimentation history (Blaauw & Heegaard, 2012). Bayesian modelling was deemed not applicable in the current research as no additional information, such as layers of known age, were available for the sediment cores. Basic models, specifically linear interpolation and a polynomial model, which are the most appropriate where there is minimal information available (Telford *et al.*, 2004), were applied to produce age-depth models for the deepest point sediment core (Figure 4.2 a, b). The polynomial model produced older dates than linear interpolation for the upper c. 20 cm of the core. The accuracy of the polynomial model cannot be determined in this case, however, as the number of data points is close to a number of terms in the polynomial. As there was only one AMS ^{14}C date for the Robe sediment core, linear interpolation was applied to the lower section of

the core (between the lowest ^{210}Pb radiometric date and the AMS ^{14}C date) (Figure 4.2 c).

Other age-depth models, such as splines, LOESS smoothers or mixed-effects, were not utilised as they require more data points than that available. Moreover, the variability of the lithostratigraphic (and other) data did not indicate distinct horizons that could be interpreted as hiatuses in order to carry out age-depth modelling using the uniform sections. Simple linear interpolation is undeniably problematic for non-uniform sediment profiles. The approach has been criticised for generating inaccurate estimates of SARs for a number of reasons: the gradient changes at every measured age, the age errors are assumed to be completely independent of each other and the model assumes that there are no systematic errors (Blaauw & Heegaard, 2012). Even small errors in estimated ages can influence the gradients of the lines between data points (Mahers, 1972), and thus polynomials and power functions preferred by some as a result. However, the reliability of more complex and statistically exact models is also questionable in light of the crudeness of the dating data (single estimates of radiocarbon dates for a sample) (Press *et al.*, 1992; Blaauw & Heegaard, 2012). Moreover, the lithostratigraphy and LOI data generally indicated increased SARs in Lough Mask over the time period represented by the sediment cores, in contrast to the outcome of the polynomial-inferred dates. Therefore, the decision was made to use estimated ages based on those generated using linear interpolation for dated samples between the sediment samples dated based on $^{210}\text{Pb}/^{137}\text{Cs}$ activities and the calibrated AMS ^{14}C dates from the basal and mid-core sample (Figure 4.2 a). Estimated ages, and the inferences that depend on the dating models being correct, based on an assumption of linearity are treated with caution because of the assumptions inherent in the linear interpolation model, the shortcomings of the dating model (in part due to the lack of radiocarbon dates) and the fact that there are many unknown possibilities for the age-depth models.

4.3.4 Sediment geochemistry

The lowermost sample from MK-9 analysed for geochemical composition dates to c. 5820 BP. Up-core variations in concentrations of chemical elements are illustrated in Figure 4.5 a. These data were grouped into 3 zones using the broken stick model: G-MK1-1 (c. 5820 BP to c. 5520 BP); G-MK1-2 (c. 5520 BP to c. 1500 BP) and G-MK1-3 (post-c. 1500 BP). G-MK1-1 was characterized by low levels of K, Mn and P. G-MK1-

2 had increasing levels of all measured elements with peaks in TP and K concentrations at, respectively, c. 4300 BP and c. 2850 BP. Al and K concentrations were relatively high in G-MK1-3 and G-MK1-2 to c. 2100 BP, when they declined before levelling off. Fe and P, which were relatively stable for much of the period represented by the core, peaked at c. 1500 BP. Declines in all major, trace and nutrient elements were evident prior to G-MK1-3 and further decreases are evident after c. 1180 BP.

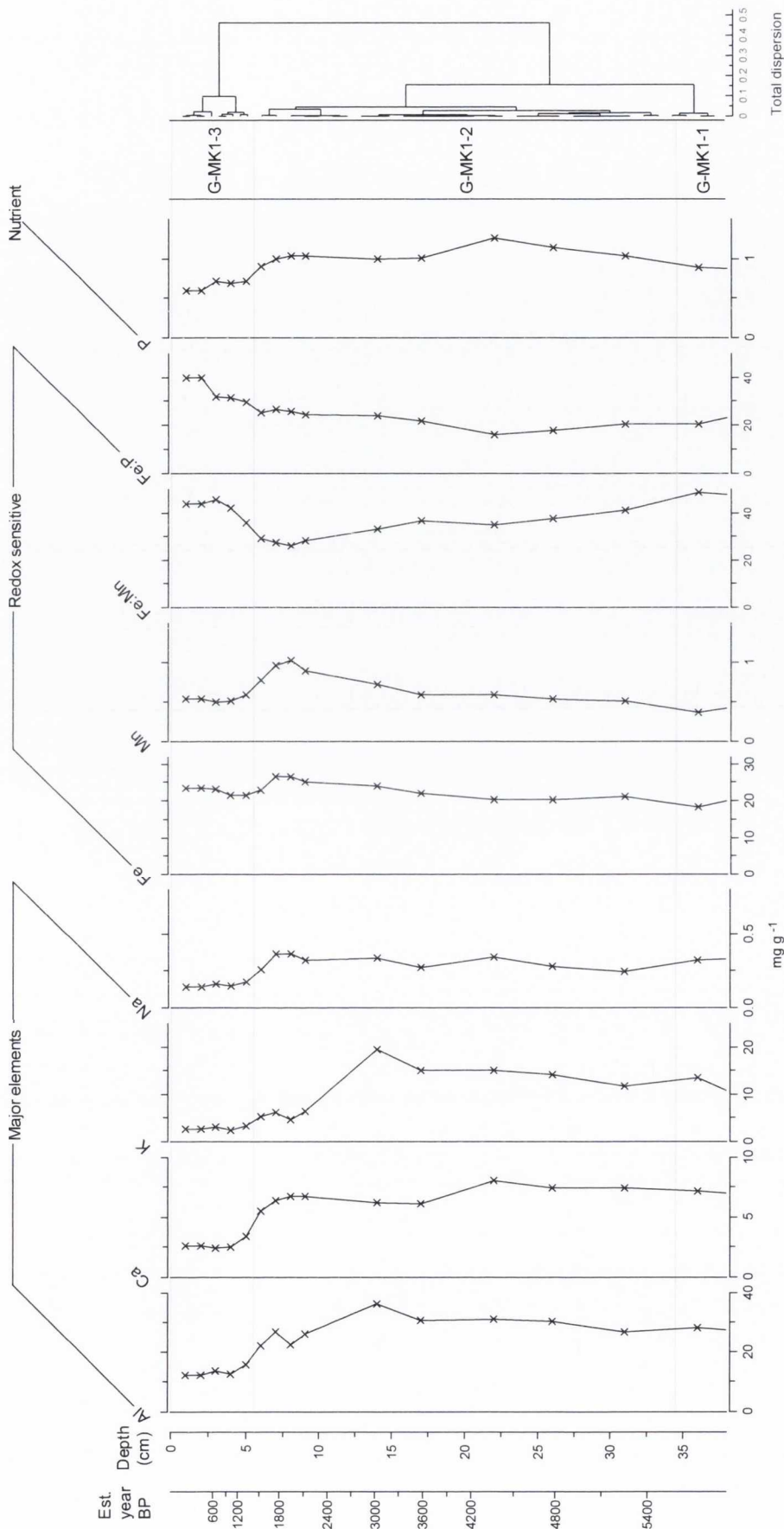
Up-core variations in concentrations of chemical elements in MK-4 are illustrated in Figure 4.5 b. These data were also grouped into 3 zones: G-MK2-1 (pre-c. 2700 BP to 435 BP) had declining levels of trace and major elements with the exception of Ca, P and Mn. Sediment TP concentrations increased from c. 2000 BP and continued to rise along with Ca and Mn levels in G-MK2-2 (c. 435 BP to c. 1980 AD) and G-MK2-3 (post-c. 1980 AD).

The sediment Fe:Mn ratio was negatively correlated with Fe concentrations in sediment cores from the deepest point (MK-9) ($r^2 = -0.59$; $p < 0.05$; $v = 14$) and Robe sites (MK-4) ($r^2 = -0.25$; $p < 0.05$; $v = 15$), indicating that changes in the redox conditions at the sediment-water interface are most likely responsible for the variations in these elements. The Fe:P ratio declined substantially upcore in MK-4 but did not reach low enough levels to indicate internal P loading. In contrast, the Fe:P ratio increased upcore in MK-9, indicating increased potential for P retention in the sediment.

4.3.5 Diatom analysis

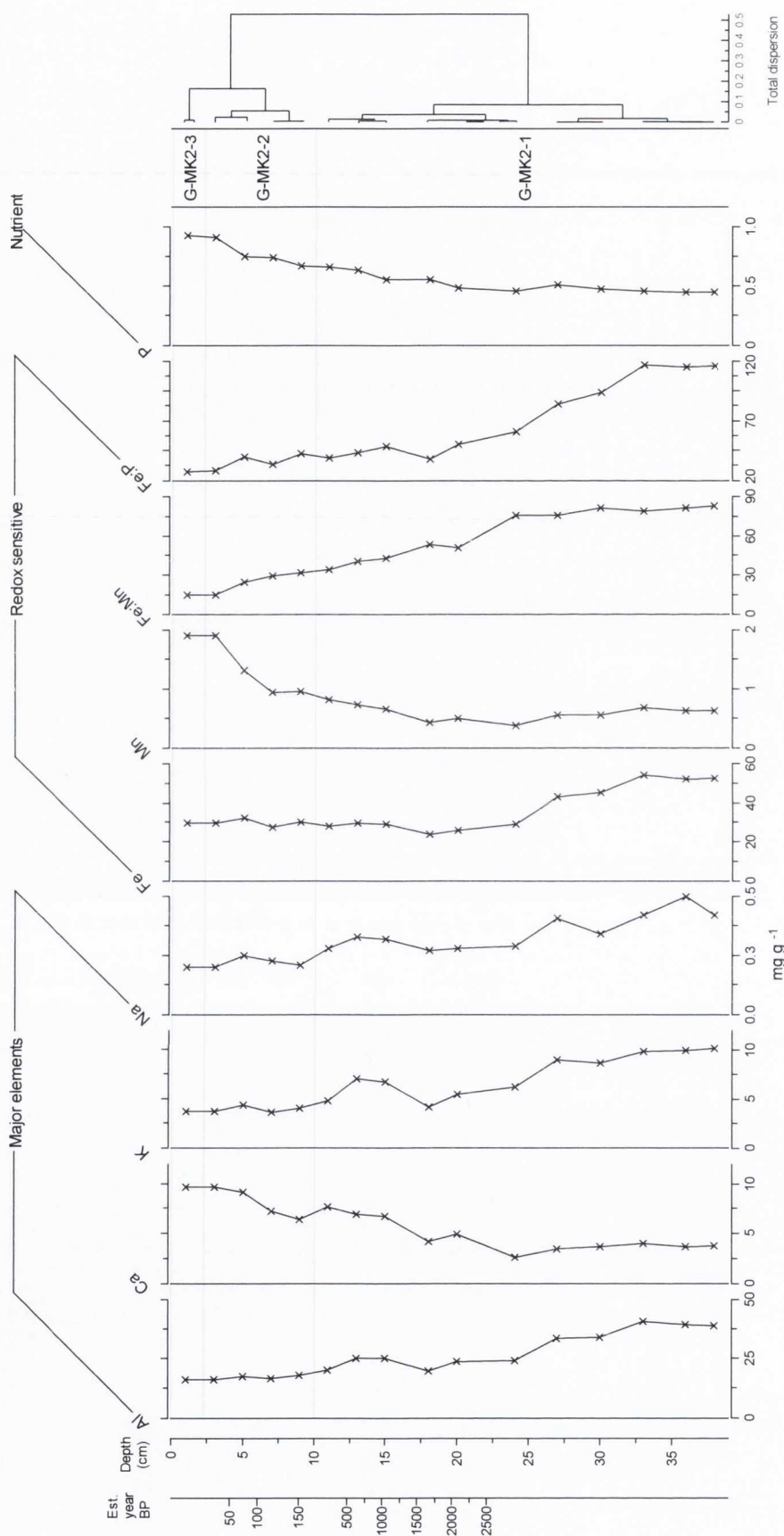
Diatom stratigraphies for the deepest point and Robe sites are summarised below and in Figure 4.6 (a, b), and a full list of species identified is provided in Appendix S. A total of 61 diatom taxa were identified in the 42 sediment samples in MK-9, 21 samples of which showed relatively good preservation. Seventy diatom taxa were identified in the 37 sediment samples from MK-4, with relatively good preservation a characteristic of 14 samples. Up-core variations in diatom concentrations at both coring sites showed a quasi-cyclic pattern, from zero to relatively high.

The 'broken-stick' model identified five diatom assemblage zones for MK-9:



(a) deepest point

Figure 4.5 Up-core variations in concentration of geochemical elements: the deepest point (MK-9) (a) and the Robe site (MK-4) (b)



(b) Robe site

Figure 4.5 (continued)

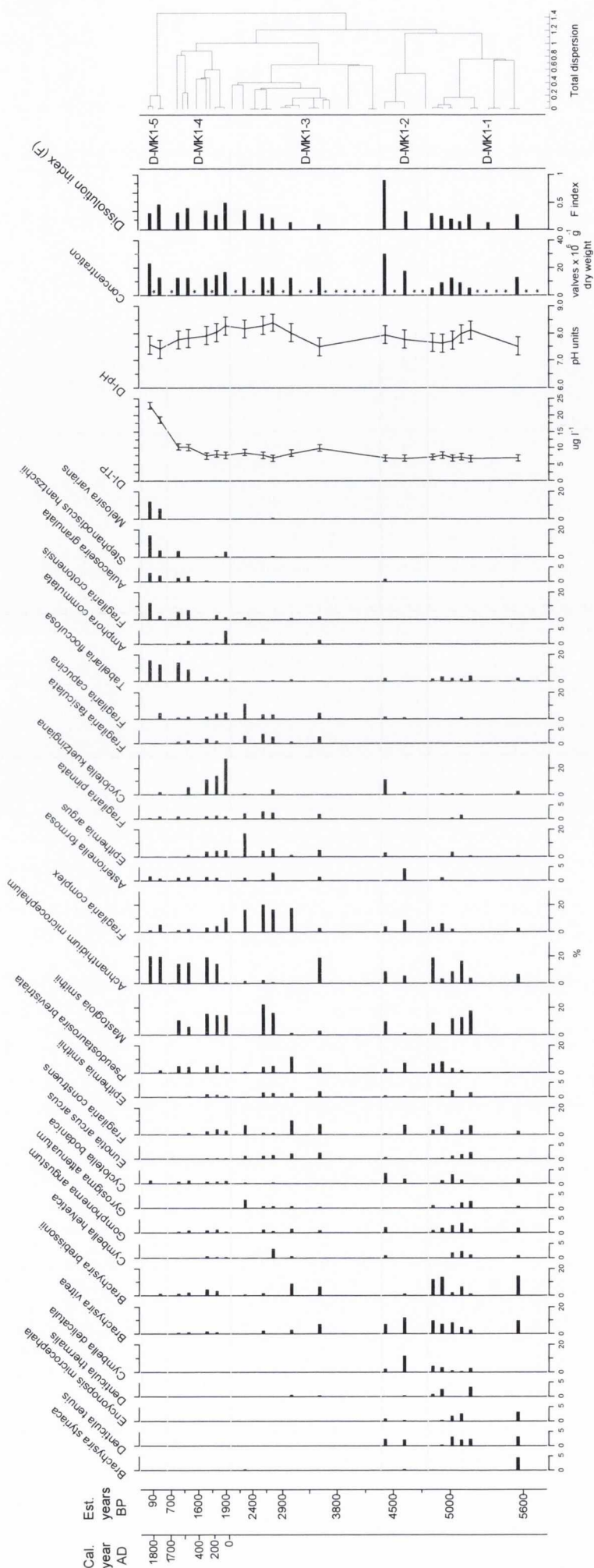
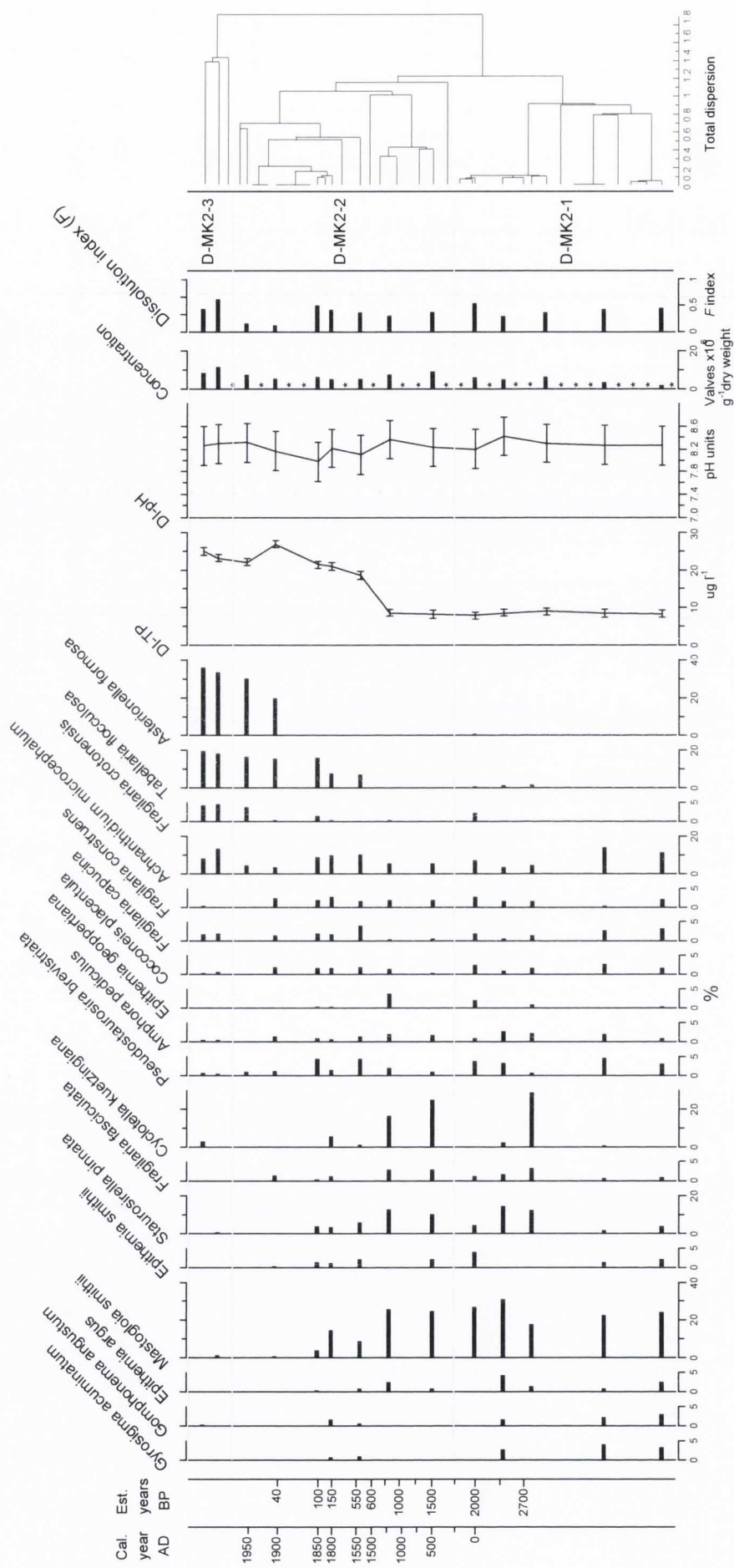


Figure 4.6 Diatom stratigraphy for the deepest point (MK-9) (a) and the Robe site (MK-4) (b) (* indicates depths with low or zero diatom concentrations). Species names are ordered chronologically, i.e. first appearance in the sediment record on the left to last appearance on the right). Errors displayed for DI-TP and DI-pH are estimated using the root mean square error of prediction (RMSEP) (see Section 3.2.1.7.1)



(b) Robe site

Figure 4.6 (continued)

D-MK1-1 (c. 5800-4800 BP)

Much of D-MK1-1 was characterised by very low or zero diatom concentrations (pre-c. 5600 BP and c. 5500-5200 BP). Where diatoms were present, the assemblages were characterised by benthic and epiphytic diatom species (e.g. *Brachysira vitrea* and *Mastogloia smithii*) indicative of oligotrophic conditions and circumneutral levels of pH (Chen *et al.*, 2008). Primary colonising species were also common, e.g. *Achnantheidium microcephalum* and *Fragilaria* species. *A. microcephalum* is a pioneering species, common after periods of disturbance (Barbiero, 2000). Planktonic species were rare in D-MK1-1.

D-MK1-2 (c. 4800-4300 BP)

In contrast to D-MK1-1, diatoms were present in substantial concentrations in all levels of this zone, which was characterised by declines in the abundances of some benthic/epiphytic species. *Aulacoseira granulata* first appeared in D-MK1-2, though with low abundances. *A. granulata* can be an indicator of mesotrophic to eutrophic conditions, but also thrives in low light conditions (Forrest *et al.*, 2002).

D-MK1-3 (c. 4300-2100 BP)

Abundances of *A. microcephalum* and *Brachysira* species were reduced towards the top of this zone, while levels of *Epithemia* and *Fragilaria* species and taxa generally associated with high nutrient concentrations increased. As with D-MK1-1, D-MK1-3 was characterised by abrupt fluctuations in diatom concentrations, with zero or very low levels during the periods c. 4100-3000 BP, c. 2800-2500 BP and c. 2300-2100 BP.

D-MK1-4 (c. 1650-500 BP)

Abundances of the planktonic taxa *F. crotonensis* and *Tabellaria flocculosa* increased, while those of *Cyclotella kuetzingiana* declined. *Stephanodiscus hantzschii*, a planktonic species that can indicate relatively high nutrient concentrations or increasing lake water depth (Brugam *et al.*, 1998), was present but with low abundances. Low or zero diatom concentrations were again evident during the periods c. 1400-1200 BP and c. 600-500 BP.

D-MK1-5 (c. 500 BP-2007 AD)

Several benthic species, including *M. smithii*, disappeared in D-MK1-5 while planktonic species increased and dominated the assemblages. Diatom concentrations were low during the period c. 1880-1920 AD.

The dissolution index, *F*, varied considerably throughout MK-9, with high values occurring near samples with zero or low diatom concentrations. Over 76 % of fossil diatom species identified in the sediment core occurred in the training dataset. Reconstructed DI-TP for the deepest point suggested that oligotrophic conditions prevailed throughout most of the mid to late Holocene record. However, from c. 400 BP, DI-TP concentrations reached the oligo-mesotrophic boundary. DI-pH values, which varied in the range 7.4-8.4, suggested alkaline conditions throughout the period covered by the core. The record for the last c. 400 years comprised only two diatom-rich (or non-zero *F*) samples.

Detrended Correspondence Analysis (DCA) analysis of the diatom data for the deepest point (Appendix S) indicated that most of the variation (c. 45 %) was accounted for by DCA Axis 1. The main sources of variation that contributed to DCA Axis 1 were levels of planktonic diatoms (e.g. *A. granulata*, *Melosira varians*, *S. hantzschii* and *T. flocculosa*), *A. microcephalum*, which increased from c. 2000 BP onwards, and the benthic diatom *M. smithii*, which were reduced from c. 700 BP. DI-TP values were also positively correlated with DCA Axis 1 and 2 (which accounted for c. 23 % of the total variation) scores, whereas DI-pH values were positively correlated with DCA Axis 3 (which accounted for c. 10 % of the total variation).

Three diatom assemblage zones were identified using the broken-stick model for MK-4:

D-MK2-1 (pre-c. 2700-1700 BP)

Benthic diatoms *Staurosirella pinnata* and *M. smithii* were common in those levels containing diatoms. Abundances of the planktonic taxon *C. kuetzingiana* peaked at c. 1900 BP. Unlike the temporally equivalent zones (the lower part of D-MK1-4 and lower zones) of the sediment record from the deepest point, diatom taxa with a preference for

relatively high nutrient levels were rare. Diatom concentrations fluctuated widely, however; there were two periods (prior to c. 2700 BP and c. 2700-1900 BP) of low or zero diatom abundances.

D-MK2-2 (c. 1700 BP to c. 1973 AD)

Where abundant, diatom assemblages were characterised by *M. smithii* and *C. kuetzingiana* between c. 1700-600 BP. The uppermost samples (i.e. from around the late 19th century) of D-MK2-2 were characterised by *T. flocculosa*, a planktonic species with a relatively high TP optimum. This zone also contained several horizons with low or zero diatom concentrations, dated c. 1700-1500 BP, c. 1300-1100 BP, c. 900-500 BP, c. 1780-1850 AD, c. 1880-1890 AD, c. 1910-1930 AD and c. 1960-1970 AD.

D-MK2-3 (c. 1973-2007 AD)

Abundances of the planktonic taxa *Asterionella formosa*, *F. crotonensis* and *T. flocculosa*, with a preference for relatively high nutrient levels, increased in D-MK2-3. The latter change from an assemblage dominated by benthic taxa and *C. kuetzingiana* appears to have occurred later than in the sediment core from the deepest point. However, the likelihood is that such variations are due to uncertainty associated with the sediment dating and the low SARs at the deepest point and that the change was fairly synchronous across the lake. There were two horizons (dated c. 1980-1985 AD and c. 1991-1998 AD) in which diatom concentrations are very low or near zero.

The dissolution index, *F*, was relatively high throughout the period covered by the sediment core. Over 76% of fossil diatom species identified in MK-4 occurred in the training dataset. DI-TP indicated the persistence of oligotrophic conditions until the relatively recent past, when a switch to mesotrophic conditions was evident. DI-pH levels varied in the range 8.0-8.4, indicating alkaline conditions throughout the period represented by MK-4. Surface sediment DI-pH levels were similar to recently measured pH levels in the lake (Dalton *et al.*, 2010), while surface sediment DI-TP levels indicated that the transfer function overestimated measured TP concentrations in the lake by c. 30 %.

DCA analysis of diatom data for the Robe site (Appendix S) indicated that much of the total variation in the diatom data was represented by DCA Axis 1 (c. 54 % of the total variation) and DCA Axis 2 (c. 26 % of the total variation). The main sources of variation that contributed to both DCA Axis 1 and 2 were levels of planktonic diatom taxa with relatively high TP optima (e.g. *A. formosa*, *T. flocculosa* and *F. crotonensis*), which increased upcore and *A. microcephalum*, which were variable throughout the sediment profile. DI-TP values were positively correlated with DCA Axis 1, but were not correlated with DCA Axis 2 scores, while DI-pH values were also positively correlated with DCA Axis 1 scores. DCA Axis 3 (which accounted for c. 6 % of the total variation) was mainly represented by benthic diatom taxa.

Diatom preservation

Table 4.3 shows a comparison of the available diatom monitoring data (secondary data, based on analyses of water samples; see Section 2.2.5.3.1 for a detailed description) from the deepest point and surface sediment diatom data from MK-9, expressed as percentages. Table 4.3 indicates some differences between the observed diatom assemblage composition in the surface sediment and that expected from the measured water column data. *F. crotonensis* and *M. varians* appear to be underrepresented in the sediment, which may indicate poor preservation due to post-depositional dissolution in the water column or at the sediment-water interface. The abundances of other taxa, e.g. *Stephanodiscus/Cyclotella* sp., in the surface sediment sample are similar to those in the water column. The most extreme difference is for *A. granulata*, which appears to be overrepresented in the surface sediment sample. However, many of the *Melosira* sp. have been renamed to *Aulacoseira* sp. since the time of sampling and therefore may actually include *A. granulata*. The higher relative abundance of some diatoms, e.g. *A. granulata*, in the sediment data is most likely due to the differential loss of other taxa that are poorly preserved or not preserved at all.

Table 4.3 Comparison of the percentage composition of the measured planktonic diatom assemblage in the water column (1986 AD; T. Champ & J. King, CFB, pers. comm.) and in the surface sediment (deepest point; MK-9)

Species	<i>A. granulata</i>	<i>A. formosa</i>	<i>C. bodanica</i>	<i>C. kuetzingiana</i>	<i>S. hantzschii</i>	<i>Stephanodiscus/ Cyclotella total</i>	<i>F. crotonensis</i>	<i>M. varians</i>	<i>N. palea</i>	<i>T. flocculosa</i>
Expected %	0	22	?	?	?	47	9	4	8	8
Min %	0	0	?	?	?	0	0	0	0	
Max %	0	100	?	?	?	100	42	47	57	
Observed %	11	6	4	0	28	33	21	18	1	23
Expected: observed ratio	n/a	4.4	n/a	n/a	n/a	1.7	0.5	0.2	8	0.3

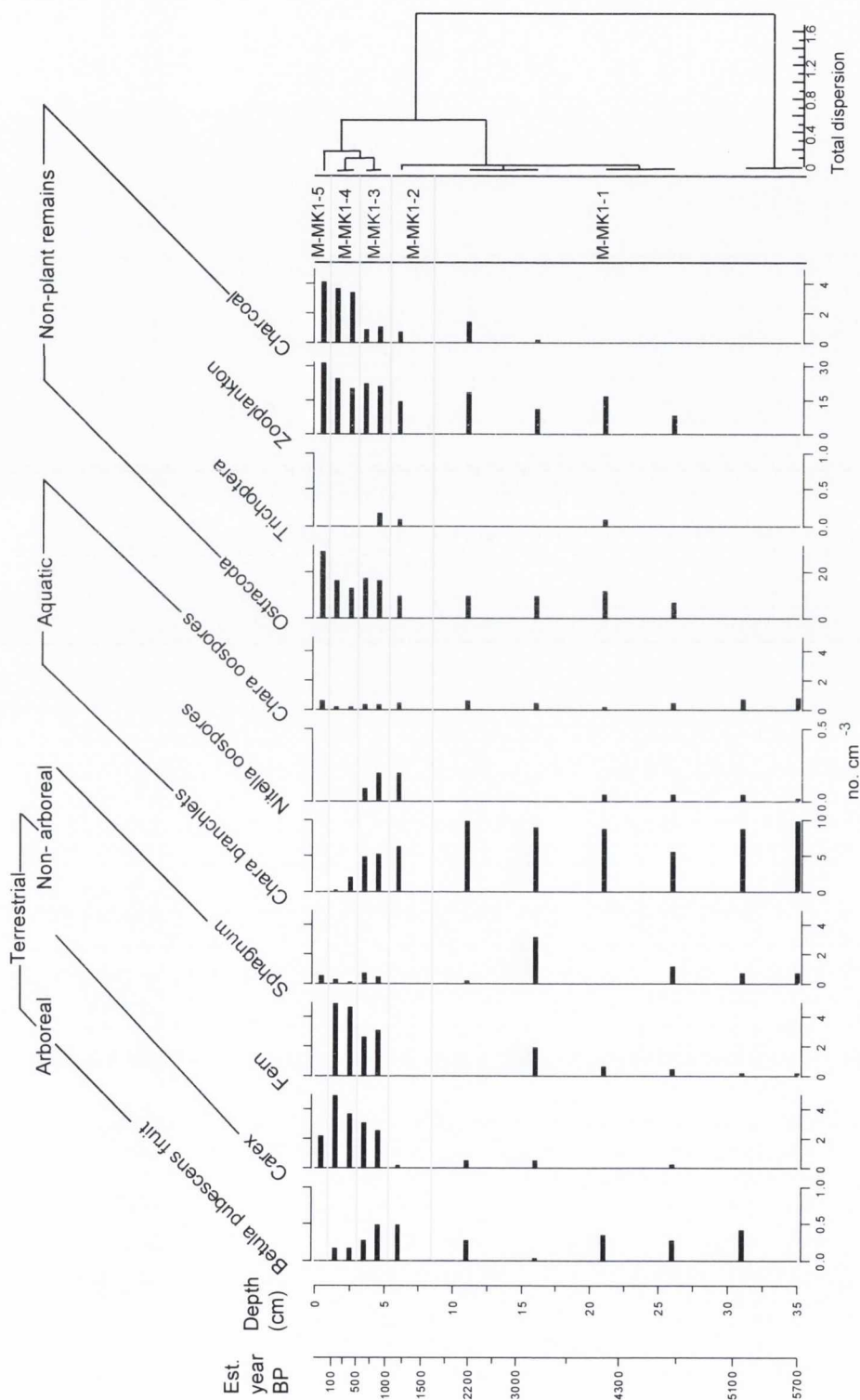
4.3.6 Macrofossil analyses

Macrofossil concentrations were also highly variable. Furthermore, samples with low to no macrofossils preserved had similar estimated ages to those with very poor diatom preservation. Where present, macrofossil assemblages largely comprised aquatic macrophyte remains ((Figure 4.7 a, b; Appendix T). Terrestrial plant remains were by comparison relatively few.

The broken-stick model identified five macrofossil assemblage zones for MK-10 (Figure 4.7 a). M-MK1-1 (c. 5700-1650 BP) was characterised by aquatic plant remains (charophytes) with some terrestrial plant remains and relatively few non-plant remains. Charophyte remains were absent and the amount of terrestrial plant material was low for most of M-MK1-2 (c. 1650-1100 BP). Charophytes reappear near the top of the zone, and there is a marked increase in *Nitella* remains. M-MK1-3 (c. 1100-600 BP) is characterised by an increase in terrestrial and non-plant remains. Charophyte remains are rare in M-MK1-4 (c. 600 BP to c. 1920 AD), while terrestrial and non-plant remains increase. In M-MK1-5 (c. 1920-2007 AD) *Chara* branchlets and *Nitella* oospores disappear, while terrestrial plant remains decrease and non-plant material increases.

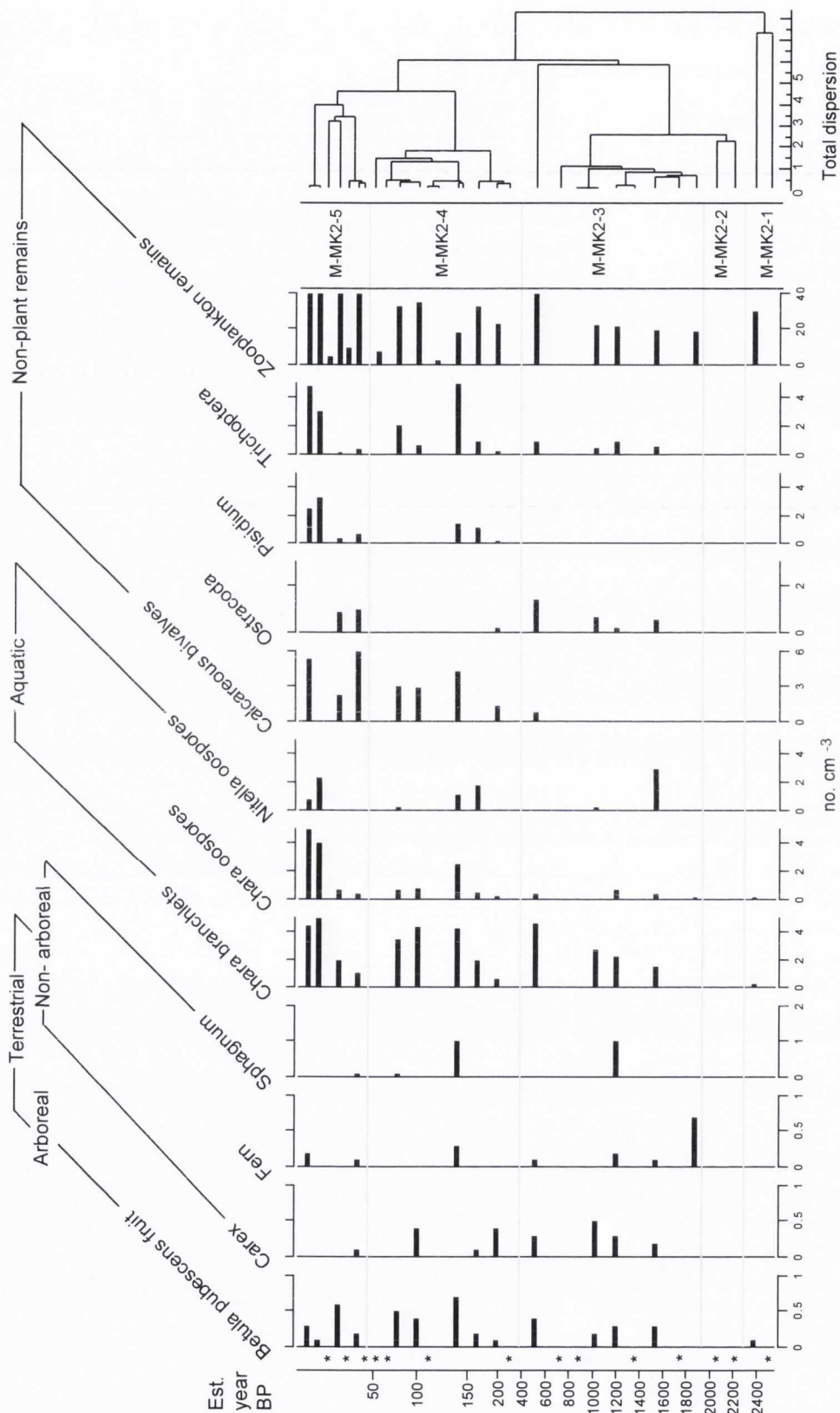
Macrofossil data for MK-5 were also grouped into 5 zones (Figure 4.7 b), based on the 'broken-stick' model. M-MK2-1 (c. 2500-2280 BP) was characterised by very low concentrations of macrofossils and consisted primarily of zooplankton remains. No macrofossils were present in M-MK2-2 (c. 2280-1940 BP). M-MK2-3 (c. 1940-390 BP) encompassed a period alternating between samples containing no macrofossils to samples with relatively high concentrations. Bivalves increased in abundance in this zone, as did oospores of *Chara* and *Nitella* and the outer cases of Trichoptera. Up-core increased abundances of non-plant remains in M-MK2-4 (c. 390 BP to c. 1975 AD) were similar to those in the preceding zone (M-MK2-3). Abundances of macrofossils varied abruptly in M-MK2-5 (post-c. 1975 AD), however, with levels of terrestrial remains generally declining and those of charophytes increasing.

In the DCA analyses of the macrofossil data from the deepest point (Appendix T), DCA Axis 1 (accounting for 79% of the variation) was represented primarily by up-core variations in *Chara* remains. DCA Axis 2 (accounting for 18% of the variation) was represented primarily by the variations in fern macrospores. *Carex* seeds and fern



a. deepest point

Figure 4.7 Macrofossil stratigraphy for the deepest point (MK-10) (a) and the Robe site (MK-5) (b) (* indicates depths with low or zero diatom concentrations). Taxa are grouped according to habitat or type



b. Robe site

Figure 4.7 (continued)

macrospores increased substantially from c. 1200 BP, while abundances of *Chara* branchlets decreased dramatically from c. 800 BP. DCA macrofossil Axis 1 (accounting for 69% of the variation) for material from the Robe coring site was represented primarily by remains of calcareous bivalves, *Chara* and trichopteran cases, which have distinct peaks at c. 500 BP, c. 1870 AD and c. 2005 AD. Macrofossil concentrations were low in the Robe sediment core, from at least c. 2700 BP to c. 1700 BP. This interval was coincident with a large peak in the C:N ratio, indicating substantial inwash of organic matter from the catchment.

4.4 Discussion

The mid-late Holocene sediment record from Lough Mask is characterised by low and non-uniform SARs and variable sediment lithology. Horizons relatively rich in autochthonous material alternated with comparatively coarse inorganic sediment and organic material of allochthonous origin. Sediment core chronologies indicated spatially heterogeneous SARs across Lough Mask. Contrary to the consensus that sediments are usually focussed in the deepest parts of lake basins (Likens & Davis, 1975; Wik & Renberg, 1991; Smol, 2008), the lowest SAR occurred in the deepest part of Lough Mask. Evidence presented in this chapter also indicates that sedimentation is likely to have been interrupted by hiatuses. However, no consistent patterns of variation between the SARs and sediment composition were evident and, therefore, isolating the hiatuses with any certainty was not possible.

Non-uniform and spatially heterogeneous lake SARs have been found in several lakes. Anderson (1989, 1990a, 1990b) demonstrated that there was no correlation between SARs and water depth in Lough Augher (Northern Ireland). Skewed sediment distributions, with the oldest sediments close to the shore protected by prevailing winds and younger sediments more widely distributed, have been linked to sediment focusing controlled by wind-driven currents in a Danish lake, Skånsø (Odgaard, 1994). The relationship between wind and sediment distribution in wind-exposed lakes has been documented elsewhere (Smith, 1975; Smith, 1979; Bloemendal, 1982; Håkanson & Jansson, 1983; Håkanson, 1997). Episodic strong-wind events have been found to resuspend and redistribute more sediment than long intervals of lower wind speeds (e.g. Carper & Bachmann, 1984; Bengtsson *et al.*, 1990; Luettich *et al.*, 1990). Similar to the findings of this chapter, Whitmore *et al.* (1996) found that quantifying the extent of

discontinuities in sediment accumulation in wind-stressed lakes prone to variable and complex sediment distribution and sediment focussing was not possible.

Lough Mask has a long fetch due to its north-east orientation in the direction of prevailing winds (K. Donnelly, EPA, pers. comm.). Little or no sediment accumulation takes place in the southeast part of the lake (K. Rogers, Western Regional Fisheries Board, pers. comm.). Together with the findings of the current research, the available evidence suggests that wind-driven sediment accumulation in Lough Mask results in a spatially heterogeneous accumulation of sediments. Given the uncertainties arising from such non-uniform sediment accumulation patterns and the low sediment dating resolution, the following interpretations of sediment-based data are made with caution.

Quasi-cyclical variations in the concentrations of diatoms and macrofossil remains are conspicuous, together with smaller magnitude variations in geochemistry (Al, K and Na concentrations). Where biological proxies are present they indicate oligotrophic conditions throughout most of the mid to late Holocene, with benthic diatoms (with low TP optima) and aquatic macrophytes (mainly charophytes), indicative of low nutrient concentrations and high water clarity, predominant. The benthic diatom assemblages are characterised by primary colonisers, including *Fragilaria* species and *A. microcephalum*, and this may reflect a high frequency of periods of disturbance or periods during which the availability of nutrients for primary productivity was reduced (Smith, 2002) in Lough Mask.

Figure 4.8 shows the extent to which the sedimentary horizons with depauperate assemblages of diatom and macrofossil remains overlap temporally. If we allow for the possible uncertainties and assumptions associated with the sediment dating models, some overlap exists between horizons from different coring sites (e.g. between c. 2800-2500 BP, c. 2300-2100 BP and c. 900-500 BP), which suggests that causal factors could have been lake-wide. Interpretation of variations in the preservation of subfossil diatoms in the lake sediment record depends on an understanding of taphonomic (including diatom death to burial) and sedimentological (including issues with the sediment dating) processes (Battarbee *et al.*, 2005). Impoverished subfossil assemblages in sediment cores can result from high SARs (Podrifske & Gajewski, 2007), dissolution or constraints on original productivity (Ryves *et al.*, 2006). There is no apparent relationship between low concentrations of biological proxies and increased SARs in the

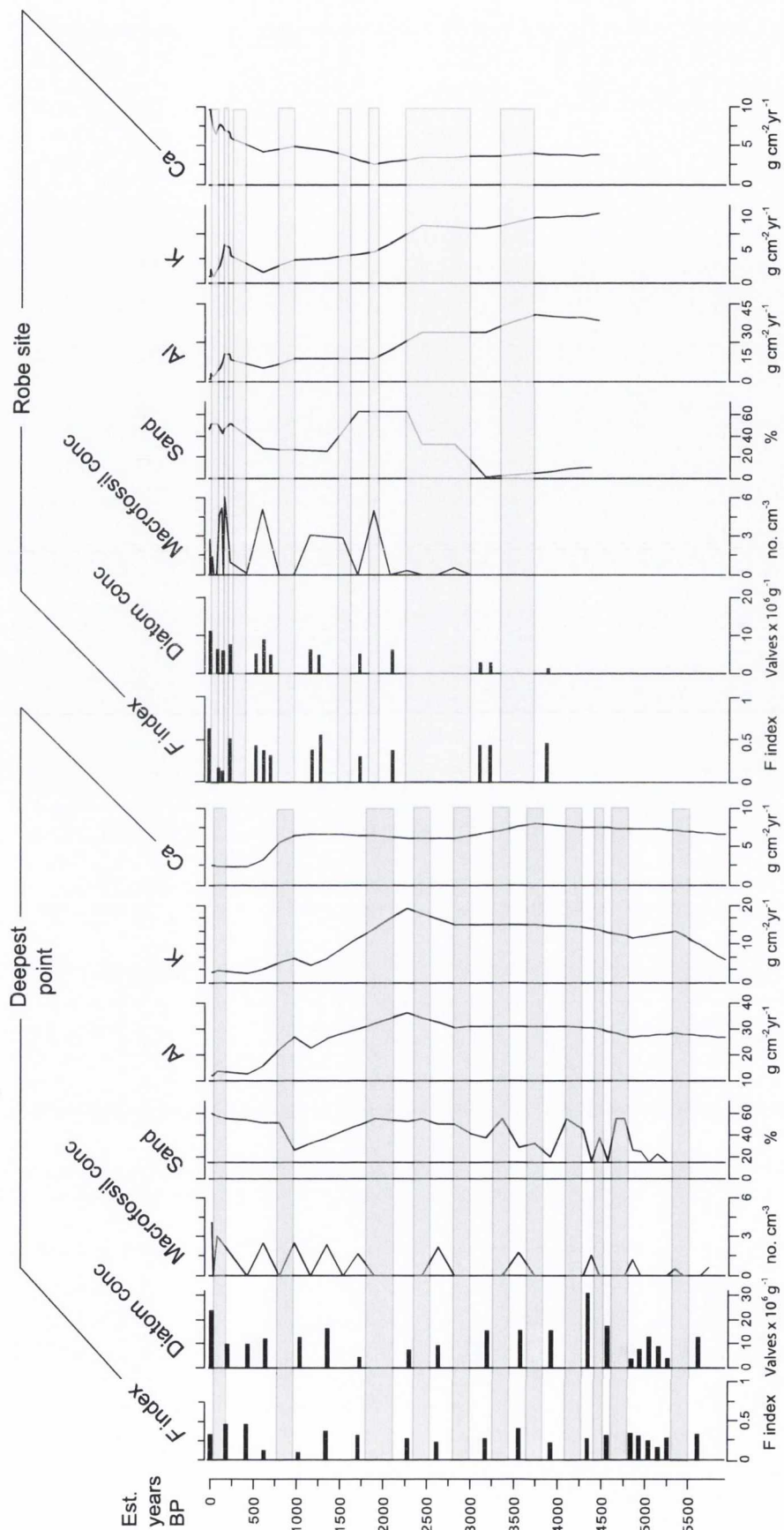


Figure 4.8 Comparison between horizons with depauperate assemblages of diatoms and macrofossils, sand influxes and selected geochemical elements. Light grey = low diatom concentrations at the Robe site, dark grey = low diatom concentrations at the deepest point

cores from Lough Mask, however, although short periods of enhanced sedimentation may be masked by relatively weak dating control in the older part of the record. Lake water Si concentrations are controlled by catchment influx and in-lake processes (such as diatom uptake, outflow and recycling from the sediments) (Battarbee *et al.*, 2005; Flower & Ryves, 2009). Influx of silicates to a lake from the catchment depends on the relative inputs of Si-enriched groundwater and Si-depleted surface water, when plankton uptake of Si during summer is relatively high and baseflow conditions dominate (Neal *et al.*, 2005).

Diatom growth in freshwater is driven primarily by the availability of dissolved Si in the water column (Lund, 1950; 1954). Diatom growth in lakes in Ireland is usually terminated by Si depletion during the spring bloom, which is often driven by elevated P concentrations (e.g. Lough Neagh; Gibson *et al.*, 2000). Constraints on original productivity to the extent that would limit diatom growth altogether, for relatively long periods, are not evident from the available phytoplankton monitoring data for Lough Mask, which indicates that annual diatom growth is supported (see Section 2.2.5.3.1 for further details). Si depletion in the water column following the spring diatom bloom is evident, however, from the phytoplankton monitoring data and McCarthy *et al.* (2001). Estimates of the accumulation of diatoms to the sediment in lakes are highly variable. Differential diatom preservation, evident from differences between the assemblage composition of the surface sediment from those of the water column in this chapter, suggests that post-depositional dissolution of diatoms and Si recycling from the sediment occurs in Lough Mask. Battarbee *et al.* (2005) found that only c. 1 % of the diatom crop are preserved in the lake sediments in Lake Baikal due to post-depositional differential dissolution, with many dissolving at the sediment-water interface, as a result of Si depletion. Studies of diatom dynamics in Lough Neagh by Jewson *et al.* (1981) showed that c. 90 % of the diatom crop from the spring bloom reach the sediment, while c. 26 % of the incoming silicate (from sedimenting diatom valves) is retained in the sediment.

Gibson *et al.* (2000) showed that diatoms in Lough Neagh require substantial silicate release from the sediment for growth. Without Si release the spring diatom population would be only one-third of that observed in the lake. Relatively high rates of dissolution in the sediment record from Lough Mask are also evident from variations in the dissolution index, F , close to horizons with low diatom concentrations, also suggesting that post-depositional dissolution of diatoms at the sediment-water interface

due to diatom-driven Si depletion in the water column is the most likely cause of depauperate horizons.

Several factors influence Si solubility, and thus diatom dissolution, in freshwater environments: high alkalinity, pH and calcite contents increase the solubility of silicates (Ryves *et al.*, 2006). Simms (2005) interpreted karstic features on the eastern shores of Lough Mask in terms of climate-driven alterations between calcite dissolution and precipitation. However, there is no evidence for low pH extremes in Lough Mask from available contemporary monitoring data, which indicates that the open waters are relatively well-mixed (see Section 2.2.5.2). The main drivers of Si availability in Lough Neagh are within-lake processes rather than catchment inputs, in which Si concentrations decrease at the beginning of the year as a result of diatom growth and from July onwards Si is released from the sediment (Gibson *et al.*, 2000). Temperature has been found to be the only factor significantly related to Si release from the sediment in Lough Neagh (Gibson *et al.*, 2000). However, the influence of factors such as benthic animal populations (e.g. chironomids) in Si recycling is not fully understood (Gibson *et al.*, 2000). Diatom loss from the sediment can also occur as a result of lake outflow, parasitism and grazing. However, these factors have been found to be minimal in similar nearby lakes (Lund, 1954; Jewson *et al.*, 1981).

There are no Si concentration data for Lough Mask upon which to base further investigation into the effects of Si recycling from the sediment. However, available phytoplankton monitoring data (see Section 2.2.5.3.1) indicate a seasonal succession of diatoms that is typical of seasonal Si depletion (Tilham *et al.*, 1982; Hecky & Kilham, 1988). Moreover, the comparison between the percentage composition of the planktonic diatom assemblage in the water column (1986 AD) and the surface sediment at the deepest point suggested that differential diatom dissolution takes place in Lough Mask, with some more delicate taxa being underrepresented in the sediment and, as a result, other taxa being overrepresented. However, the comparison between monitoring and sediment-based data is also subject to error. The differences between the measured and sediment datasets could also be linked to a mismatch between the period of phytoplankton sampling and the time period represented by the surface sediment sample or sediment focussing.

Changes in the composition of living diatom assemblages due to climate change are well known (e.g. Battarbee *et al.*, 2002; Battarbee *et al.*, 2005). Moreover, changes in subfossil diatom assemblages in lake sediments have been linked to climatic variations, including changes in temperature (Smith, 2002), ice cover (Smol *et al.*, 2005) and precipitation (Reed, 1998; Russell & Johnson, 2005). Relatively little is known about the taphonomic effects of climate variability, however. Low diatom concentrations have been recorded in many Arctic lake sediment cores (e.g. Smith (2002)). Furthermore, low diatom concentrations in sediments extracted from lakes in semi-arid regions have been linked to climatically-driven variations in Si inputs (Reed, 1998; Russell & Johnson, 2005). In climatically more humid parts of the world, however, a high frequency of sedimentary horizons with depauperate assemblages of biological proxies is probably more often than not seen as a good reason to abandon further study at that site and sites like it (Podrifska & Gajewskia, 2007).

Allowing for the assumptions and uncertainties associated with the sediment dating model, the timing of periods of low diatom preservation in the sediment cores from Lough Mask is in good agreement with those of oscillations in precipitation levels evident in other mid to late Holocene sediment records from Ireland and northwest Europe. The three earliest intervals recorded (pre-c. 5600 BP, c. 5500-5200 BP and c. 4700-4500 BP) coincide with the timing of increased lake levels, and wetter climatic conditions, evident in sediment records from An Loch Mór, a small lake located on the Aran Islands on the west coast of Ireland (Holmes *et al.*, 2007). $\delta^{18}\text{O}$ changes in a c. 3500 year record from the Crag stalagmite, western Ireland (McDermott *et al.*, 1999), and a c. 1000 year sediment record from Lough-na-Shade, Northern Ireland (Holmes *et al.*, 2010), indicate episodes of increased wetness c. 3455 BP, c. 2600 BP, c. 1630 BP, c. 1095 BP and c. 540 BP, all of which overlap with the intervals of low diatom and macrofossil concentrations in sediments from Lough Mask. These episodes are also in agreement with the timing of increased surface wetness in Scottish bog profiles (Chambers *et al.*, 1997), with the exception of the c. 1600 BP event that occurs c. 300 years earlier in Lough Mask. The Lough Mask data also correspond with the findings of Chambers *et al.* (2010) who found evidence of relatively wet conditions, in sediment records from bogs, centred upon c. 4200 BP, c. 2800 BP and the period c. 1200-200 BP.

Though there are many coherent climatic patterns evident in the Holocene at a regional scale, climate records can vary geographically (Chambers *et al.*, 2010). This

variability is likely to reflect local factors at individual sites (e.g. catchment conditions, human impact or vegetation succession), variability in the strength and nature of global climate forcing factors and the uncertainty associated with sediment dating. Two well-established coherent signals of climate change (Charman, 2010) are replicated in the Lough Mask sediment record, the c. 2700-2800 BP (evident in both the deepest point and Robe site records) and c. 550 BP (evident in the Robe site record) events. The change to increased climate wetness at c. 2700-2800 BP, evident in both of the Lough Mask coring sites, is one of a series of major changes in bog profiles (Swindles *et al.*, 2007; Chambers *et al.*, 2010) and higher lake levels (Magny *et al.*, 2009) in northwest and west-central Europe.

The most coherent shifts to wetter climatic conditions during the Holocene, evident from terrestrial sediment records from Britain and Ireland, commenced at c. 3600 BP, c. 2760 BP and c. 1600 BP (Charman *et al.*, 2006) and also overlap with periods of low concentrations of remains of diatoms and macrofossils in the sediment record in Lough Mask. However, there are wetter phases evident in other sediment records that do not seem to be recorded in the sediments analysed from Lough Mask. Out of eight periods of change to wetter conditions identified by Barber *et al.* (2003), in sediment profiles from raised bogs in Britain and Ireland, one (c. 1000 BP) is not evident in Lough Mask while one (c. 2250 BP) is only evident at the Robe site. Charman *et al.* (2006) also note smaller magnitude changes to wetter conditions at c. 2050 BP and c. 860 BP, events that are not evident in the Lough Mask sediment record. These variations in the sediment record from Lough Mask most likely due to the relatively low resolution of the sedimentary record, breaks in sedimentation (caused by climatic or hydrological changes), uncertainty associated with macrofossil records from relatively deep sediment coring sites or errors in the age-depth models or perhaps a different driver of poor subfossil preservation. The two most recent periods, c. 1980-1985 AD and c. 1991-1998 AD, with low micro- and macro-fossil concentrations, evident at the Robe site, coincide with relatively high mean annual precipitation (based on data obtained from Met Éireann; see Section 2.2.3).

The mechanisms for the link between variations in the preservation of diatoms and precipitation levels are unclear, particularly as low diatom preservation is usually linked to low Si inputs from the catchment and, therefore, relatively drier climate conditions (e.g. Nöges *et al.*, 2008). One possible mechanism is variations in Si influx as

a function of flow type, with higher concentrations occurring during groundwater-dominated and low flow conditions, and lower concentrations occurring at high flows or surface water-dominated conditions (Neal *et al.*, 2005). This pattern of variation in Si concentrations is evident in streams across the UK, including those in the north of Ireland (Neal *et al.*, 2005). There are two main reasons for these patterns. The first relates to the relative inputs of groundwater, which are in contact with and weathering inorganic components (e.g. aluminosilicates) of soil and bedrock. Therefore, during relatively drier climate periods, when streamflow primarily originates from groundwater, Si concentrations in the water column are relatively high. Surface water during high flow conditions are mainly derived from the acidic and organic rich soil zone, where acidic conditions prevail and there is very limited time and inorganic material for weathering. Therefore, during relatively wet climatic periods Si concentrations would be expected to be relatively low. The second reason relates to biological uptake of Si, primarily by diatoms, which is greatest during the spring and summer, also the groundwater-dominated period of flow. Si levels can be severely reduced during drier climate periods (Neal *et al.*, 2005).

Peaks in all major elements occur at c. 1800 BP. There can be several reasons for peaks in sediment Fe and Mn levels and therefore their profiles should be interpreted with caution. Variations in lake sediment Fe and Mn profiles often reflect redox changes in the sediment with depth (Engstrom & Wright, 1984). The sediment Fe:Mn ratios in the deepest point and Robe site sediment cores were negatively correlated with Fe concentrations and, therefore, changes in the redox conditions in the lake water column are most likely responsible for the variations (Mackereth, 1966). Some of the horizons with depauperate assemblages of biological proxies at both coring sites are also characterised by coarser sediment (higher sand content) and relatively higher concentrations of mineral elements, notably Al, Ca and K. Coarser sediment deposits in lakes often correspond with highstands and wetter climatic conditions (Magny, 2007). Furthermore, increased concentrations of Al, Ca and K in sediments can represent the accumulation of minerogenic material eroded from the catchment (Nesje *et al.*, 2007).

The reduced transparency of lake water as a result of higher sediment loads, following wetter climate conditions and catchment disturbance, may also explain a substantial reduction in the concentration of *Nitella* oospores between c. 2000-600 BP. *Nitella* is very sensitive to water quality (particularly water clarity, pH and nutrient

content) (Krause & King, 1994). Catchment disturbance would also explain the high proportion of allochthonous-sourced organic matter at the Robe site at this time and may account for moderate nutrient enrichment (the onset of mesotrophic conditions) and reduction in charophyte remains evident at the deepest point by c. 400 BP. However, this upper part of the sediment record is poorly resolved and preservation of diatoms and macrofossils is variable. Therefore moderate nutrient enrichment evident from the switch from a *C. kuetzingiana* dominated assemblage to one characterised by *F. crotonensis*, *T. flocculosa* and *A. formosa* is likely to be synchronous with that evident at the Robe site, with the variation in timing owing to dating uncertainties and the slow rate of sediment accumulation in the sediment core from the deepest point. Early eutrophication has, however, also been detected in lake sediment records from elsewhere in Ireland (Taylor *et al.*, 2006; Dalton *et al.*, 2009). Eutrophication was evident by the early 19th century in sediments from nearby Lough Carra (Donohue *et al.*, 2010). Although rapid and widespread human depopulation took place following the Great Famine from the mid-19th century onwards, particularly in the west of Ireland (Ó Gráda, 1995), major human-induced disturbance is evident in the Lough Mask catchment in the form of ADS (Coxon & Drew, 2000), which undoubtedly contributed to changes in the physical properties and biological remains in the relatively recent sediment record.

The interpretations of the current research are subject to uncertainty associated with the depauperate horizons in the diatom and macrofossil records and possible breaks in sedimentation, which may or may not be linked to interactions between climate and catchment conditions. However, comparisons with regional palaeoenvironmental data showed that, though complex, the sediment-based data are likely to provide a valuable record of long-term environmental change. Moreover, the findings present some new and preliminary insights into the potential links between the absence of diatom remains in sediment records from lakes in temperate locations, and climate conditions. These links are generally poorly-understood (Battarbee *et al.*, 2005; Mackay *et al.*, 2006; Podrilska & Gajewski, 2007).

4.5 Conclusions

This study aimed to investigate the relationship between variations in the preservation of sediment biological proxies and Holocene environmental change in a climatically sensitive large lake in the west of Ireland. The results presented in this chapter indicate

that variations in the presence of siliceous and calcareous micro- and macrofossils, sediment lithology and geochemistry may be linked to oscillations in climate conditions, from relatively wet to dry conditions and vice versa. However, the latter is subject to uncertainty associated with non-uniform SAR and post-depositional dissolution of subfossils. The results of this chapter also highlight potentially complex aquatic effects of interactions between different drivers of ecological and sedimentological changes, including past variations in catchment conditions, climate and water chemistry during the middle to late Holocene. Moreover, the results are consistent with previous findings of the site-specific nature of Holocene climate variability, and have major implications for the timing of aquatic ecological responses to environmental change, the effects of which may well be delayed or obscured by natural ecological variability.

As a result, the findings complicate the interpretation of palaeolimnological data and their use in aquatic environmental management, including the establishment of baseline/reference conditions for relatively complex lakes, and the simulation of future changes in aquatic ecological pressures and the impacts of such pressures.

Chapter 5

Evidence of climate-enhanced eutrophication in a west of Ireland lake

5.1 Abstract

Little is known about the relative roles of climate and humans in driving aquatic trophic changes and how these roles have varied over time. Furthermore, distinguishing between the effects of climatic change and human activity can be difficult because their impacts may be similar. Moreover, climate change and human activity may act in concert; for example, warming may enhance the effects of nutrient enrichment. Palaeolimnology together with historical data can help segregate the different causes of aquatic variability and can be used to determine the extent of directional change over natural variability. A combination of historical, dynamic modelling and multiproxy palaeolimnological data were used to examine climate and human-induced trophic variability in Lough Mask, Co. Mayo, in the west of Ireland over the last c. 140 years. The results indicate that prior to c. 1970 AD trophic variability was linked to variations in climate, in particular winter precipitation levels and the NAO, and human population. Nutrient enrichment effects, though evident from c. 1950 AD, were more pronounced from c. 1970 AD, with cultural eutrophication seemingly linked to elevated summer temperatures and enhanced thermal stratification, and increased catchment P loading as a result of agricultural intensification, according to the CCA results. Partial CCA analysis showed that climate variability, i.e. warming and associated enhanced thermal stratification, was the main driver of eutrophication post-c. 1970 AD, followed by agricultural intensification. The combined effects of climate and agricultural intensification were also evident from the partial CCA analysis. The important influence of climate variability on aquatic trophic conditions, particularly warming in recent years, suggests that future climate changes are likely to interfere with the response of water bodies to measures aimed at alleviating cultural eutrophication pressures. Plans developed to meet the demands of the EU WFD (2000/60/EC) are thus likely to have to accommodate both direct and indirect aquatic impacts of future climate changes.

5.2 Introduction

Eutrophication and climate change are important factors influencing lake ecosystem structure and functioning (Carvalho & Kirika, 2003; Hering *et al.*, 2010; Moss *et al.*, 2011). Eutrophication, resulting from nutrient enrichment, is currently a major water quality problem (Smith & Schindler, 2009; Donohue *et al.*, 2010; Dokulil & Teubner, 2011) and is

the principal pressure on water quality in Ireland (Jennings *et al.*, 2003; McGarrigle *et al.*, 2010). Increased external P loading from anthropogenic activity, or cultural eutrophication, is the primary cause of nutrient enrichment in freshwater ecosystems (Schindler *et al.*, 2008; Donohue *et al.*, 2010), with diffuse loading from agricultural sources a major contributor (Jennings *et al.*, 2003; Kronvang *et al.*, 2009), in addition to loading from municipal and industrial (Smith *et al.*, 2006; Dalton *et al.*, 2009) and domestic point sources (Jordan *et al.*, 2012).

Although aquatic responses to nutrient enrichment have been widely studied, far less attention has been paid to the aquatic impacts of recent climate variability (Scheffer *et al.*, 2001a; Jeppesen *et al.*, 2010). Climate variability is a fundamental driver of in-lake physical, chemical and biological changes (Battarbee, 2000) and, therefore, is expected to influence aquatic responses to processes such as eutrophication. For example, the NAO, a decadal phenomenon related to variations in barometric pressure in the North Atlantic Ocean (Hurrell & Van Loon, 1997), determines the winter climate variability of regions bordering the North Atlantic, including western Europe (Diefendorf *et al.*, 2006). In particular the NAO influences winter rainfall and temperature levels. This influence is strongest on the western fringe of Europe (Blenckner *et al.*, 2007), and is also apparent to a lesser extent in spring and summer (Jennings *et al.*, 2000). As nutrient loads from diffuse pollution sources are strongly linked to rainfall levels (Greene *et al.*, 2011), NAO variability is expected to influence eutrophication pressures in regions bordering the North Atlantic. Despite this, the degree to which NAO influences aquatic trophic variability remains largely unknown (Jennings *et al.*, 2000; Blenckner *et al.*, 2007). Other climatic phenomena, such as the Mediterranean Oscillation (MO) and the east Atlantic–west Russia teleconnection pattern (EA-WR) are known to influence precipitation patterns over Europe, on timescales similar to that of the NAO (Krichak & Alpert, 2005; Dokulil & Herzig, 2009). However, their effects on climate and lacustrine trophic variability are also poorly understood.

Changes in water temperature are likely to influence trophic status (Jeppesen *et al.*, 2010). The effects of relatively recent climate change in aquatic ecosystems at high latitude, where the influence of anthropogenic activities is often low (Livingstone *et al.*, 2005; Drebler *et al.*, 2011), are well documented. Aquatic ecosystems in the Arctic are regarded as relatively sensitive to climate impacts (Smol & Douglas, 2007), and increased nutrient

loading and enhanced primary productivity have been linked to warming and elevated precipitation during the 20th century (Jiang *et al.*, 2011). In temperate regions, lakes have undergone substantial changes as a direct result of human activity, such as those due to nutrient enrichment. Deciphering the effects of climate change from a complex of other potential pressures can be difficult (Dreblor *et al.*, 2011). Moreover, the effects of direct human- and climate-induced variability in ecological conditions are often similar (Smol *et al.*, 2005; Jeppesen *et al.*, 2010; Bennion *et al.*, 2011a; Hadjikakou *et al.*, 2011; Battarbee *et al.*, in press). For example, the effects of climate warming has been found to mimic those of cultural eutrophication (Jeppesen *et al.*, 2010; Hamilton & Landman, 2011). Furthermore, co-occurrence of increased temperatures and nutrient availability could potentially have synergistic effects.

The extent of cultural eutrophication during recent decades has led to the establishment of legislation aimed at restoring and maintaining water quality (Bertahas *et al.*, 2006). One example of such a legislative response, at international level, is the EU WFD (2000/60/EC) (European Parliament and Council 2000), which requires all freshwater bodies in EU member states to equate at least to good water quality status, showing little or no human impact, by 2015 (Kirilova *et al.*, 2009). EU Directive (91/676/EEC), commonly known as the Nitrates Directive (Howarth, 2006), also plays a key role in the delivery of water quality improvements required by the WFD. Climate change effects are not explicitly included within the remit of the WFD. However, how climate change interacts with more direct human impacts, such as cultural eutrophication, and modifies the recovery of water bodies following the implementation of measures aimed at easing pollution are important but as yet largely under-studied considerations (Carvalho & Kirika, 2003; Blenckner *et al.*, 2007).

Evidence of past variability in the drivers of aquatic ecosystem changes and their effects can be preserved in lake sediments. Analysis of this evidence, using palaeolimnological and statistical methods, provides a basis for assessing and distinguishing the effects of human and climatic drivers of aquatic ecological variability in the past (Battarbee, 2000; Smol, 2010; Bennion *et al.*, 2011a). However, the extent to which climatic variations may be recorded in lake sediment proxy data can be unclear (Battarbee *et al.*, 2002; Battarbee *et al.*, in press). Hindcast modelling, using historical climate and census

data, provides additional evidence for these reconstructions and a basis for future simulations under different catchment and aquatic management scenarios. Knowledge of past variability, particularly the relative influence of the different drivers of variation, can contribute to understanding how aquatic ecosystems could potentially behave in response to future environmental changes. The aim of this chapter is to use a multiproxy palaeolimnological approach, together with related historical and modelled catchment data, to attempt to distinguish the relative influence of climatic and human drivers of trophic variability in Lough Mask and discuss the findings in the context of the WFD.

A novel multidisciplinary approach, combining sediment-based reconstructions of lake trophic conditions with historical and modelled climate and catchment pressure data, was used to separate out the potential climate and human drivers of past trophic variability. Sediment-based palaeolimnological methods, using physical, geochemical and biological information archived in lake sediments, enable past aquatic ecological conditions (including baseline - pre-significant human impact - or reference conditions) to be reconstructed over timescales beyond that of available monitoring programs (Smol, 2010). Material from three sediment cores, MK-11, MK-12 and MK-13 (see Table 3.1) collected from the southwest coring site in Lough Mask (see Figure 2.2) was used to address the aim outlined above. Details of the palaeolimnological, dynamic modelling and data analysis methods used in the research are described in Chapter 3.

5.3 Results

5.3.1 Sediment chronology

All 10 samples analysed in MK-11 for ^{210}Pb were above background levels, indicating sediment ages for the core were within the last c. 200 years (Table 5.1). As background level of ^{210}Pb were not reached in the core, a background of 1.62 DPM g^{-1} was chosen based on the background activity determined by the ^{226}Ra analysis. The ^{137}Cs profile was well above background, with a surface activity of c. 14 DPM g^{-1} and increasing to maximum of c. 41.6 DPM g^{-1} at 10-11 cm. The ^{137}Cs activity then declined gradually with depth. The estimated date for the basal sample (38 cm) was c. 1870 AD. The activity profile did not cover a long enough period to apply the CRS model. Activity profiles indicated that the

SAR was relatively constant below 13 cm (Appendix R), allowing the linear regression model to be applied to estimate SAR ($y = 0.32 x - 0.64$). SAR increased substantially over the period represented by the sediment core, from $0.054 \text{ g cm}^{-1} \text{ yr}^{-1}$ at c. 1870 AD to $0.074 \text{ g cm}^{-1} \text{ yr}^{-1}$ from c. 2000 AD.

Table 5.1 Estimated rates of sediment accumulation (SAR) and ages of sediment samples from MK-11 based on radiometric (^{210}Pb and ^{137}Cs) analysis (see Appendix R for raw data)

Core (sample depth, cm)	Linear regression estimated age (years)	SAR ($\text{g cm}^{-2} \text{ yr}^{-1}$)
MK-11 (0-0.5)	4.8	0.07
MK-11 (1.5-2)	19.0	0.07
MK-11 (7-8)	31.4	0.07
MK-11 (10-11)	42.1	0.07
MK-11 (13-14)	51.0	0.07
MK-11 (16-17)	62.1	0.07
MK-11 (19-20)	69.9	0.06
MK-11 (22-23)	79.3	0.06
MK-11 (25-26)	90.5	0.06
MK-11 (28-29)	101.0	0.06
MK-11 (31-32)	112.0	0.06
MK-11 (34-35)	124.1	0.06
MK-11 (37-38)	136.3	0.05

5.3.2 Sediment stratigraphy, LOI and stable isotopes

Sediments from the southwest coring site comprised organic-rich silt with abundant plant macrofossil material (Figure 5.1). LOI values varied in the range 25-40 % for the three sediment cores (Figure 5.1). Upcore variations in lithostratigraphy, LOI and carbonate values were relatively stable. Levels of $\delta^{15}\text{N}$ in MK-12 (Figure 5.1) were consistently $> 2.5\text{‰}$ but less than the threshold for aquatic plants (4.9‰), indicating organic matter sourced from a mixture of terrestrial and aquatic plants (Meyers, 1994). $\delta^{13}\text{C}$ values were in

the range -27 to -29‰ indicating a mainly terrestrial source for organic material. C:N ratios were relatively high (> 30) throughout the sediment core (Figure 5.1), particularly prior to c. 1950 AD, indicating that organic matter accumulating in sediments originated almost entirely from terrestrial sources. The C:N ratio decreased post-c. 1950 AD falling to 23.2 in c. 2006 AD, reflecting an increased influence of algal sources of organic matter in the lake.

5.3.3 Sediment geochemistry

Up-core variations in geochemical concentration and accumulation rate data (Figure 5.2) were grouped into three zones: G-MK3-1 (c. 1870-1948 AD); G-MK3-2 (c. 1948-1978 AD) and G-MK3-3 (post-c.1978 AD). Low and stable concentrations and accumulation rate of chemical elements were evident for most of G-MK3-1. Al, K and Na concentrations display relatively stable profiles, with some small increases at c. 1880 AD and c. 1930 AD, and concentrations were relatively high throughout G-MK3-2. This zone was also characterised by increases in concentrations of TP and Mn (from c. 1965 AD), while further increases were also evident in G-MK3-3, peaking at the top of the core. The Fe:Mn ratio was negatively correlated with Fe concentrations ($r^2 = -0.7$; $p < 0.05$; $v = 22$) indicating that variations in the redox conditions at the sediment-water interface are most likely responsible for the variations in these elements, rather than changes in catchment supply (or redox conditions in catchment soils). The Fe:P ratio also declined substantially over the last 100 years, to a point where internal P loading is possible.

5.3.4 Diatom analysis

Up-core variations in diatom abundances in MK-12 are summarised in Figure 5.3. Twenty nine of the 43 sediment levels analysed in MK-12 were relatively depauperate in diatom taxa, but those taxa that were encountered were present in relatively high concentrations (Appendix S). Three diatom assemblage zones, representing three different overall states of lake water quality, were identified and are described below. All 3 zones included abrupt fluctuations in diatom concentrations, with 13 samples with zero or very low levels over the period represented by the sediment core.

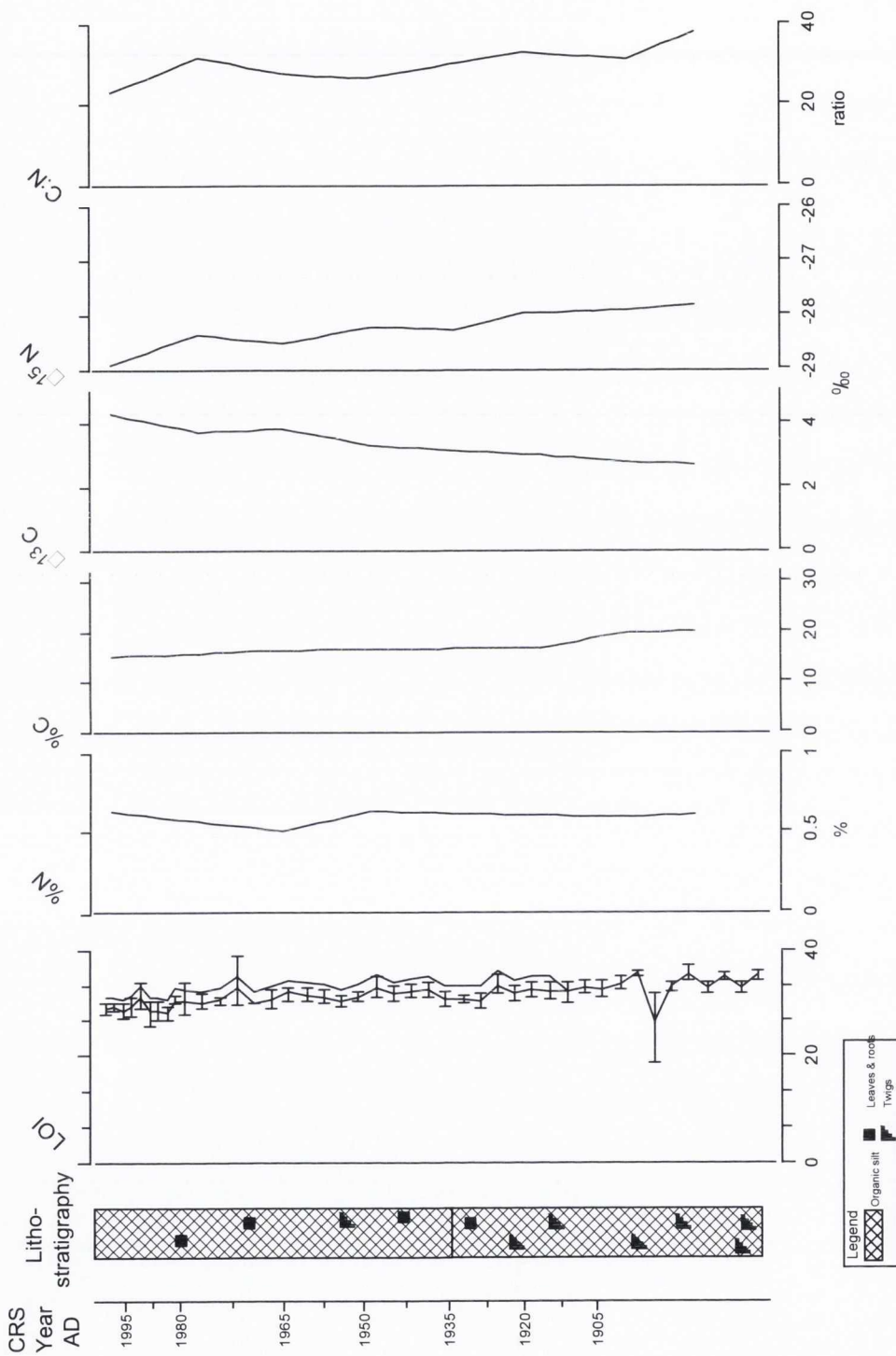


Figure 5.1 Stratigraphic diagram showing upcore variations in lithostratigraphy (MK-12), LOI (all cores), carbonate (MK-12) and stable isotope analysis ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ content, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ ratios of C:N) (MK-12). Lithostratigraphic analysis was carried out following the Troels-Smith (1955) method

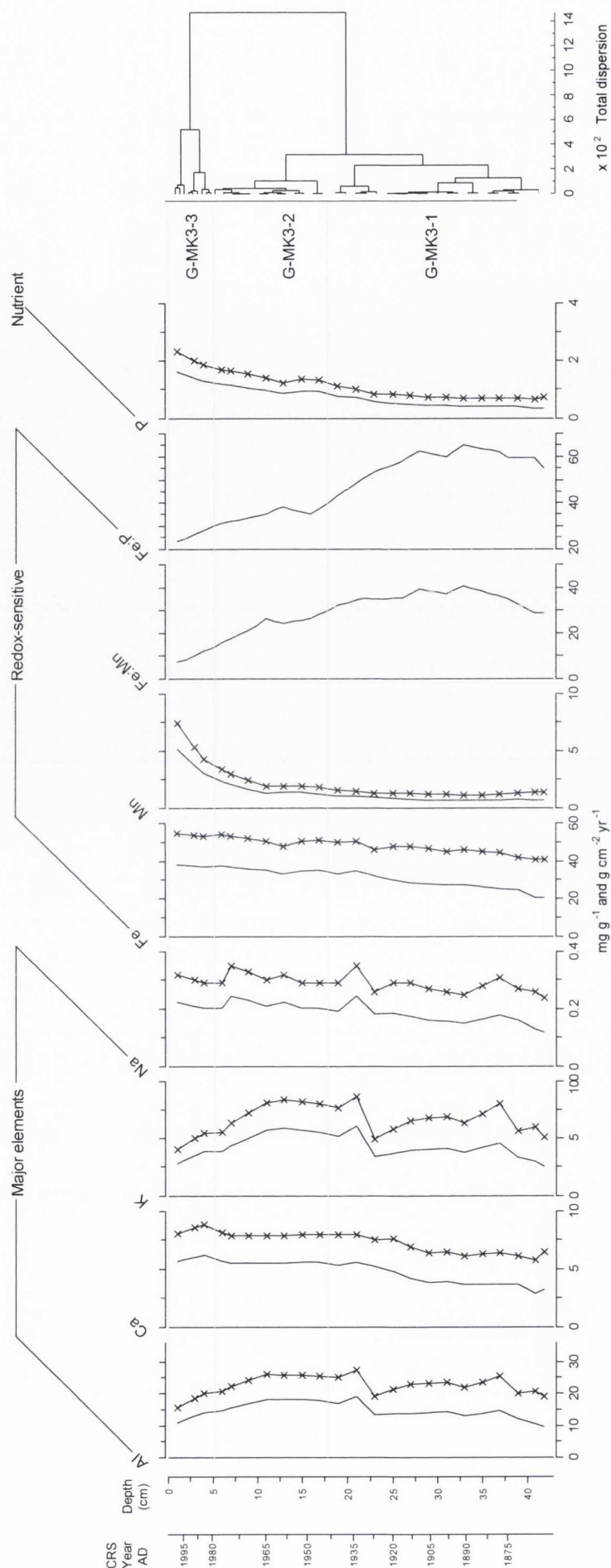


Figure 5.2 Up-core variations in concentration of geochemical elements in the southwest site (MK-12)

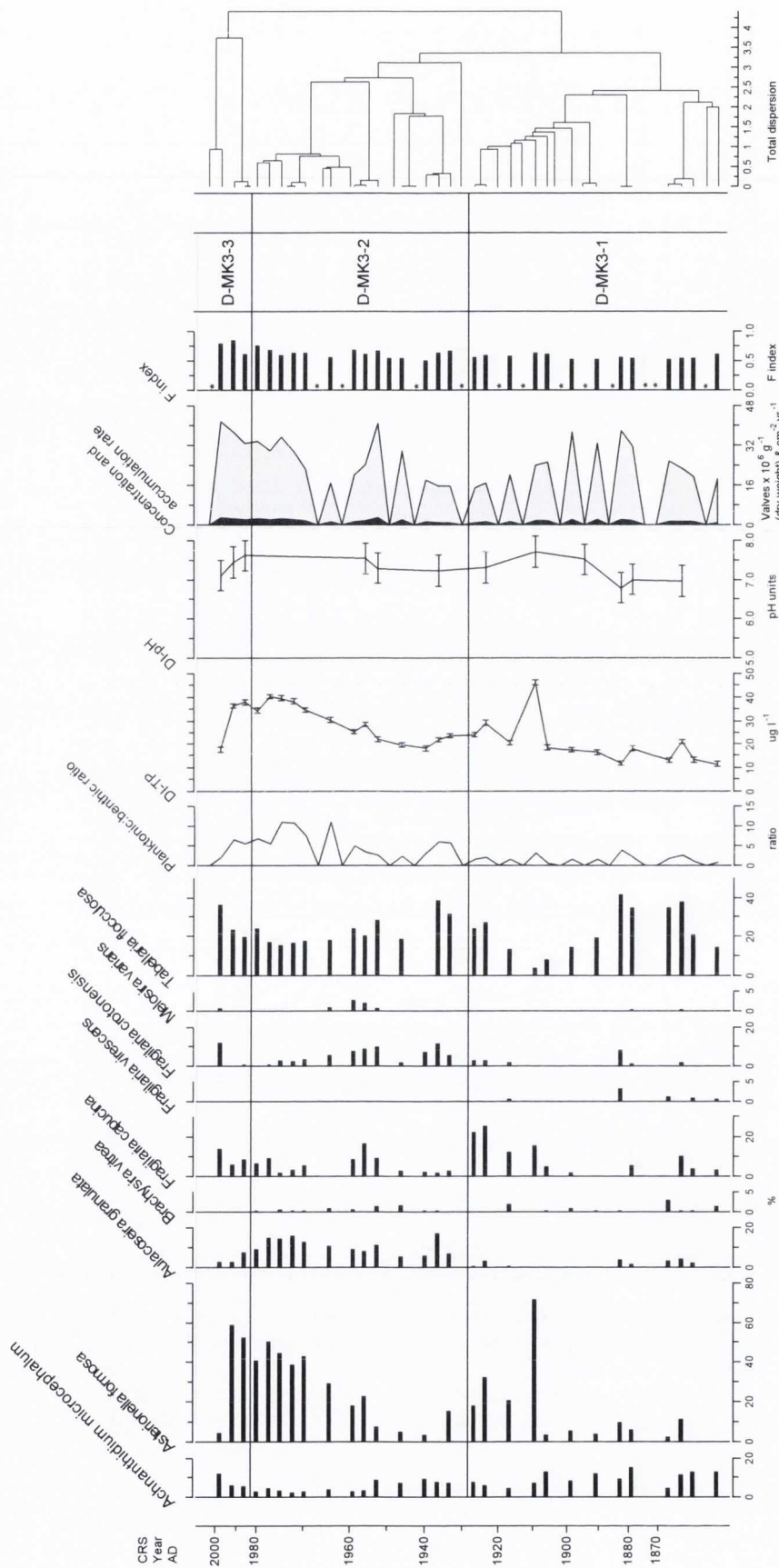


Figure 5.3 Diatom stratigraphy for the southwest site (MK-12) showing diatom abundance (for taxa which comprised >2% abundance), the ratio of planktonic to benthic diatoms, diatom-inferred TP (DI-TP), diatom-inferred pH (DI-pH), diatom concentrations (black) and accumulation rates (grey), and the *F* index (* indicates depths with low or zero diatom concentrations). Species names are ordered alphabetically. Errors displayed for DI-TP and DI-pH are estimated using the root mean square error of prediction (RMSEP) (see Section 3.2.1.7.1)

D-MK3-1 (c. 1870-1930 AD)

Diatom assemblages in this zone were characterised by *T. flocculosa*, a planktonic species (Kelly, 2000) with a moderate TP and relatively low pH optima (Appendix O) and *A. microcephalum*, a pioneering species (Barbiero, 2000). *A. granulata*, an indicator of moderate to high TP optima (Appendix O) and high turbidity, was present in moderate abundances. Benthic species were rare in this zone. Post c. 1900 AD, species with relatively high TP and neutral pH optima (Appendix O), including *A. formosa* and *Fragilaria capucina*, were also common. DI-TP levels indicated mesotrophic conditions, until c. 1910 AD when DI-TP levels peaked (c. 46 $\mu\text{g l}^{-1}$) and reached eutrophic conditions. DI-pH levels fluctuated between 6.8-7.7 pH units throughout the zone, suggesting slightly acidic to alkaline water conditions. The ratio of planktonic to benthic diatom taxa was relatively low throughout the zone.

D-MK3-2 (c. 1930-1982 AD)

D-MK3-2 was also characterised by relatively high abundances of *T. flocculosa*. However, abundances of this species were reduced post c. 1940 AD. The planktonic taxa *A. granulata* and *F. crotonensis*, which have relatively high TP optima (Appendix O), became more abundant indicating elevated trophic conditions in this zone. From c. 1970 AD, D-MK3-2 was characterised primarily by *A. formosa*, while abundances of *A. microcephalum* were reduced. The reconstructed DI-TP levels indicated eutrophic conditions until c. 1940 AD, when concentrations again fell to mesotrophic levels. Mesotrophic conditions persisted in the lake until c. 1960 AD when eutrophic levels appear to have been established. DI-pH levels were generally higher than those evident in D-MK3-1, falling in the pH range 7.2-7.7 pH and suggestive of slightly alkaline conditions. The ratio of planktonic to benthic diatoms taxa increased in this zone, particularly between c. 1960-1980 AD.

D-MK3-3 (c. 1982-2007 AD)

D-MK3-3 was characterised by the presence of *A. formosa* prior to c. 1995 AD, after which abundances declined along with other planktonic species. In contrast, abundances of *T. flocculosa* and *Fragilaria* taxa increased post-c. 1995 AD, while abundances of *A.*

microcephalum increased post c. 2000 AD. Eutrophic conditions, evident from reconstructed DI-TP values, persisted during this period until c. 2000 AD, when a reduction to mesotrophic levels occurred. DI-pH levels were similar to those evident during D-MK3-2, and fluctuated between 7.1-7.6. Although there are no contemporary measurements of TP and pH for the southwest part of the lake, monitoring data for the deepest part of the lake indicate pH values in the range c. 7.4-8.5 (mean = c. 8.2), slightly higher than DI-pH values, and TP concentrations in the range c. 7-22 $\mu\text{g l}^{-1}$ (mean = c. 12 $\mu\text{g l}^{-1}$) between 2000-2003 AD (Section 2.2.5.2). Monitoring data for TP from the deepest part of the lake are therefore consistent with DI-TP values for the surface sediment from the southwest site. The ratio of planktonic to benthic diatom taxa was relatively high in this zone, but was reduced from c. 2000 AD. The dissolution index (*F*), which was in the range 0.5-0.9, indicated that preservation of diatom frustules was relatively good in those samples containing diatoms.

5.3.5 Macrofossil analysis

Concentrations of aquatic macrophyte remains (including *Chara* and *Nitella*) were variable and followed a quasi-cyclical pattern ranging from low to relatively high concentrations, with timings of low concentrations closely comparable (e.g. c. 1930 AD, 1955 AD and c. 1975 AD) with those observed in the diatom data. Terrestrial macrophyte remains were conspicuous components of sediments throughout the core, but were mostly fragmented, decomposed and unidentifiable to meaningful taxonomic levels. Three zones were identified in the macrofossil data for MK-13 (Figure 5.4). Terrestrial plant remains were abundant in M-MK3-1 (c. 1870-1920 AD), while aquatic plant remains were absent. M-MK3-2 (c. 1920-1970 AD) is characterised by a reduction in some terrestrial plant taxa remains and an increase in both aquatic plants and non-plant remains. The main aquatic macrofossils were charophyte remains and *Nitella* oospores. Charophytes, in particular *Nitella*, are indicators of high water clarity and low nutrient levels. M-MK3-3 (c. 1970-2007 AD) was characterised by a reduction in some terrestrial plant taxa and an increase in aquatic plants (charophytes) in the uppermost sediment samples.

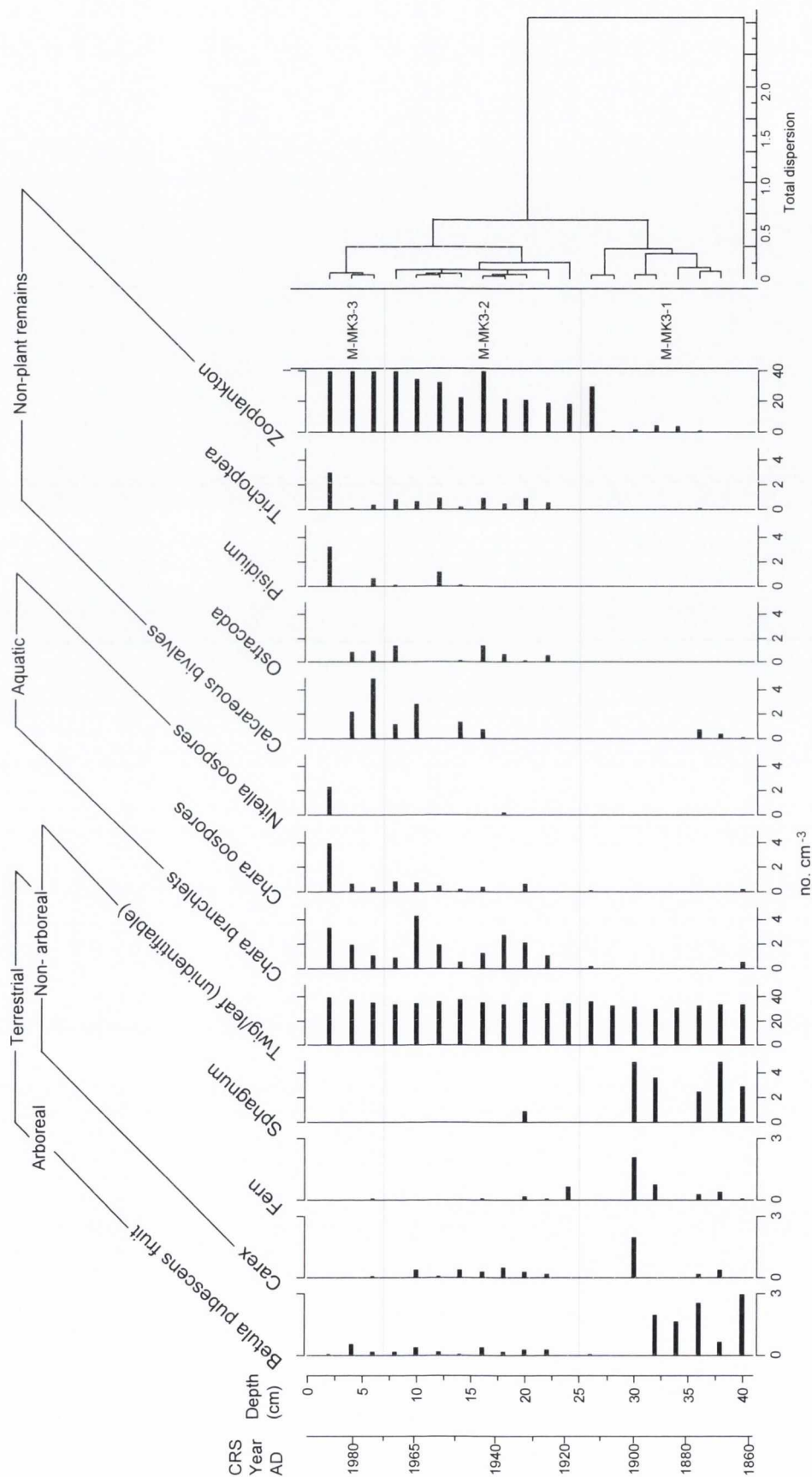


Figure 5.4 Macrofossil stratigraphy for the southwest (MK-13). Taxa are grouped according to habitat or type

5.3.6 Historical and hindcast modelling data

Major reductions, from 35.4 per km² in 1900 AD to 19.1 per km² in 1970 AD, have characterised human population densities in the Lough Mask catchment during the 20th century (Figure 5.5; Appendix E). In contrast, cattle and sheep numbers increased from the early 1900s, and particularly after 1950 AD (Figure 5.5; Appendix E). Despite these variations in human and livestock numbers, land use patterns (see Section 2.2.4.2) have not changed significantly during the same period. There was a significant ($r^2 = 0.75$; $p < 0.01$; $v = 90$) trend of increasing annual mean air temperatures from 1960-2006 AD. However, no overall significant trend was evident in annual precipitation data. Modelled catchment nutrient loads also increased significantly ($r^2 = 0.75$; $p < 0.01$; $v = 90$) over the period, and particularly from the 1970s (Figure 5.5), with the increased loads mainly sourced in the eastern subcatchments (Robe and Carra; Appendix U). Modelled in-lake water temperatures revealed strengthened thermal stratification in Lough Mask from the mid-1960s, and significant trends of increasing surface ($r^2 = 0.62$; $p < 0.05$; $v = 40$) and deep water temperatures ($r^2 = 0.69$; $p < 0.05$; $v = 40$) over the simulation period.

5.3.7 Ordination

CCA analyses enabled the relative roles of climatic variability and human pressures in influencing ecological variability in Lough Mask to be established. The results of three separate CCA analyses, where the individual palaeolimnological datasets (geochemistry, diatoms and macrofossils) were used as response variables and the historical and hindcast modelling variables (Section 5.3.6) were used as independent variables, are described below.

5.3.7.1 Geochemistry

Two broad groupings of independent variables responsible for variations in the geochemistry dataset were apparent from the CCA analysis: those associated with agriculturally-driven nutrient enrichment, and climate conditions (including variables that influence in-lake stability). Approximately 84% of the variance in the sediment geochemistry dataset was explained by the independent variable dataset. The first four CCA axes were statistically significant ($p < 0.005$) in explaining the variance in the geochemistry

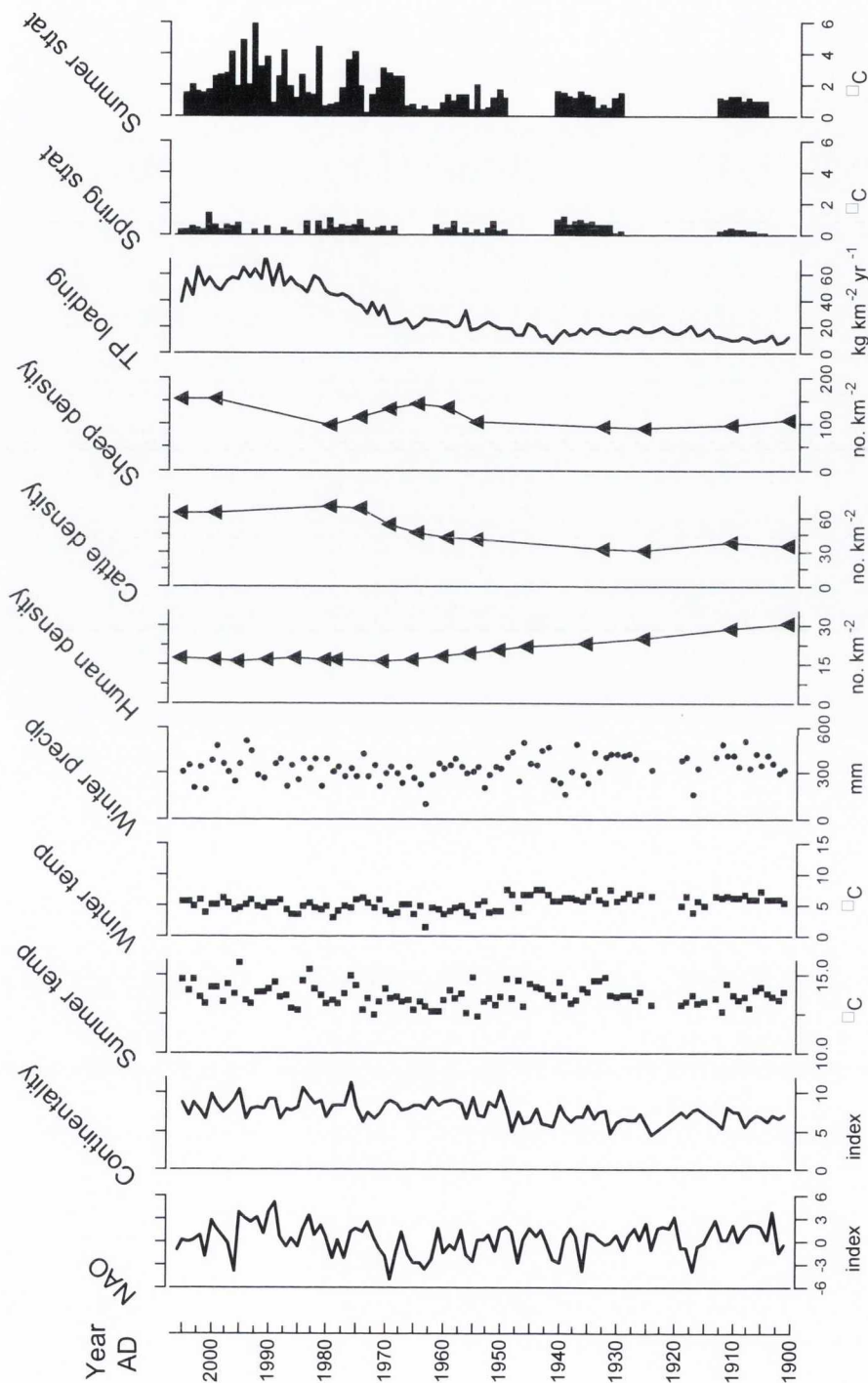


Figure 5.5 Climate and catchment pressure data (human population, cattle population, sheep population, modelled annual catchment TP loads, summer mean air temperature, winter mean precipitation, winter mean air temperature, spring mean thermal stratification, summer mean thermal stratification, continentality index and NAO index). See Section 2.2.3, 2.2.4 and 3.2.2 for details of data collation and modelling methods

data, while the first two axes accounted for the majority of the total variance (c. 78 %). CCA Axis 1 was positively correlated with cattle numbers, sheep numbers, catchment TP loads and, to a lesser extent, winter temperature and continentality, and negatively correlated with human population (Figure 5.6 a). Thermal stratification during spring and summer was also positively correlated with CCA Axis 1. CCA Axis 2 was only positively correlated with winter temperatures and negatively correlated with human population, summer temperatures, winter precipitation and summer thermal stratification (Figure 5.6 a).

The sediment samples dated pre-c. 1970 AD, which are located primarily in the lower left quadrant of the ordination plots (Figure 5.6 a), are characterised by low sediment TP and Mn concentrations and high sediment Fe:Mn and Fe:P ratios. The pre-c. 1970 AD samples were correlated negatively with CCA Axis 1 (which explained 66%, $p < 0.05$, of the total variation in the dataset) and with CCA Axis 2 (accounting for 12%, $p < 0.05$, of the total variation in the dataset). The sediment samples dated post-c. 1970 AD (located mainly in the lower right quadrant of the ordination plots) had high sediment TP and Mn concentrations and low sediment Fe:Mn and Fe:P ratios. Most of the samples correlated positively with CCA Axis 1 and correlated negatively with CCA Axis 2.

5.3.7.2 Diatoms

Similarly, two broad groupings of independent variables that influenced variations in the sediment diatom data were evident from the CCA analysis (Figure 5.6 b); those associated with agriculturally-driven nutrient enrichment and those associated with climate conditions. Approximately 51% of the total variance in the diatom dataset was explained by the independent variable dataset. Only CCA Axis 1, which accounted for c. 22 % of the total variance in the diatom data, was statistically significant ($p < 0.05$) in explaining the variance in the diatom dataset. CCA Axis 1 was negatively correlated with summer thermal stratification, cattle population and the NAO, and, to a lesser extent, catchment TP loads and summer temperatures, and was only weakly positively correlated with human population (Figure 5.6 b). Sediment samples dated pre-c. 1970 AD, which had relatively high proportions of benthic diatom species (e.g. *Fragilaria* sp., *B. vitrea* and *A. microcephalum*) and pioneering taxa, with relatively low DI-TP values, were located mainly in the upper and lower right quadrants of the ordination plot (Figure 5.6 b). Most of the pre-c. 1970 AD

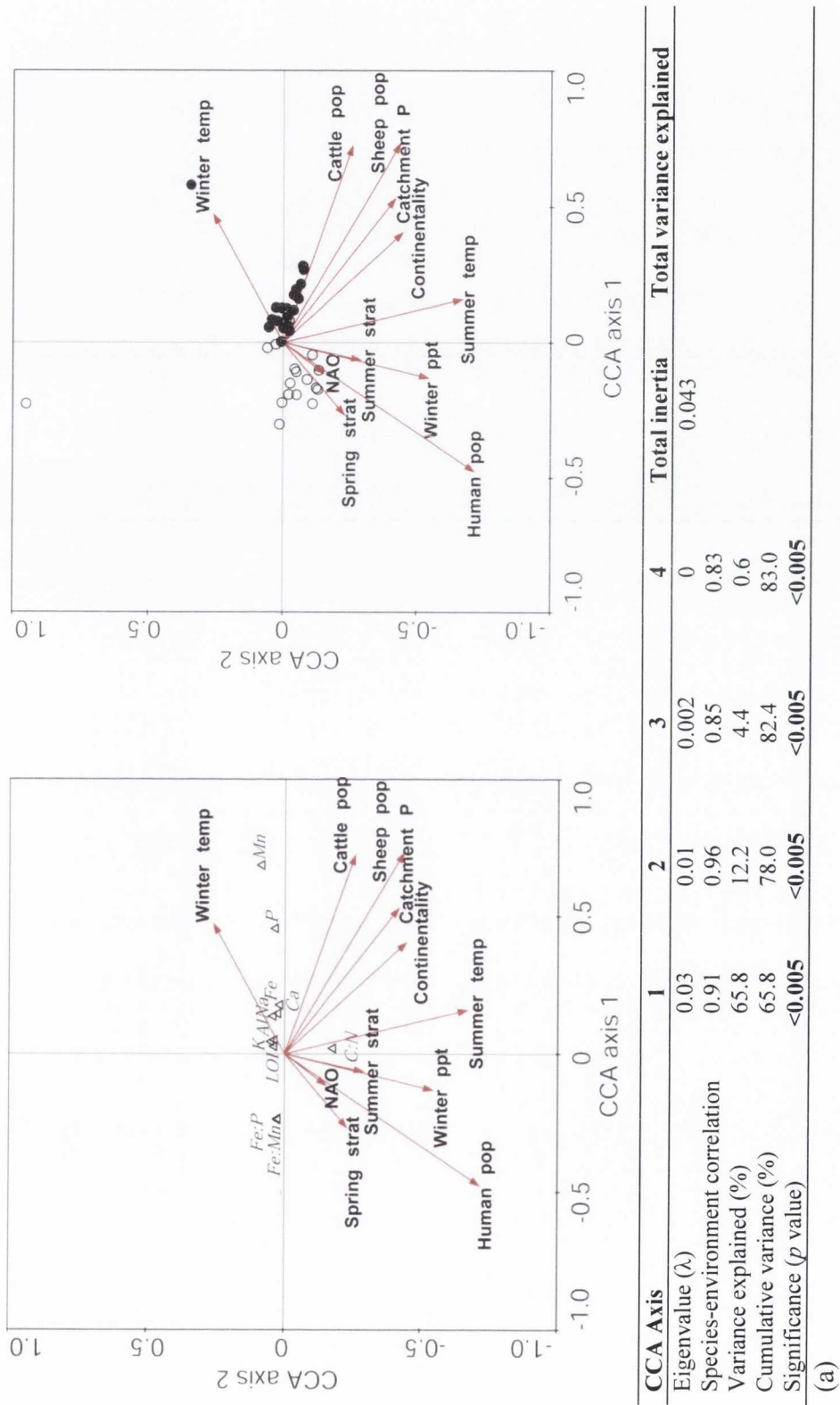


Figure 5.6 CCA diagrams (species and samples biplots) and results for: geochemistry data (a), diatom data (b) and macrofossil data (c). Filled circles = post-c. 1970 AD samples; open circles = pre-c. 1970 AD samples; open triangles = sediment proxies (response variables), arrows = independent variables

CCA Axis	1	2	3	4	Total inertia	Total variance explained
Eigenvalue (λ)	0.10	0.05	0.03	0.02	0.45	
Species-environment correlation	0.83	0.74	0.61	0.32		
Variance explained (%)	22.3	11.7	6.5	5		
Cumulative variance (%)	22.3	34.0	40.5	45.5		
Significance (<i>p</i> value)	<0.05	>0.05	>0.05	>0.05		

(b)

Figure 5.6 (continued)

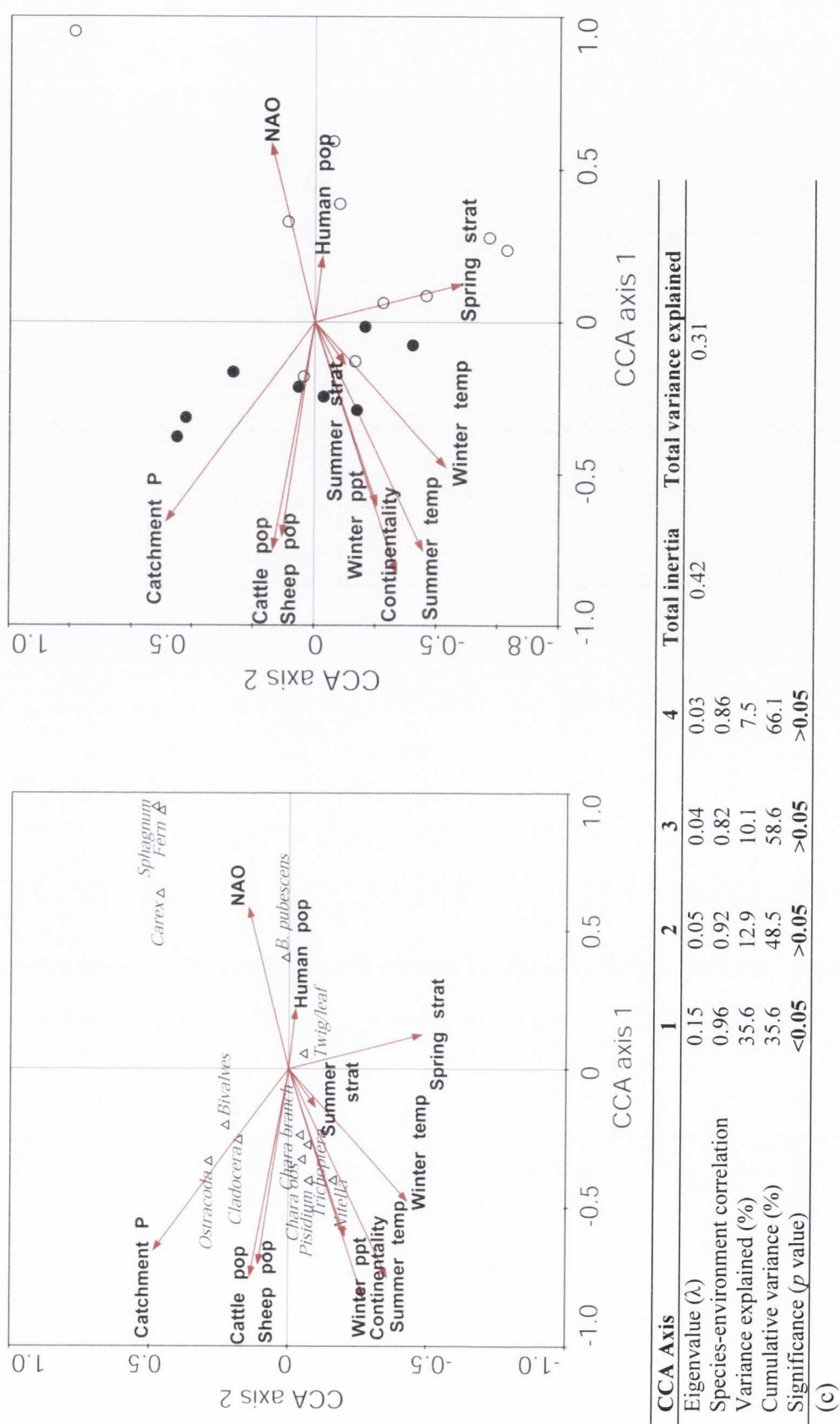


Figure 5.6 (continued)

samples were correlated positively with CCA Axis 1. The sediment samples dated post-c. 1970 AD (located mainly in upper and lower left quadrants of the ordination plot) had relatively high proportions of planktonic diatom taxa (e.g. *A. granulata*, *M. varians* and *C. kuetzingiana planetophora*) and relatively high DI-TP values. Most of these samples correlated negatively with CCA Axis 1.

5.3.7.3 Macrofossils

The CCA analysis of sediment macrofossil response data also indicated two broad groupings of independent variables that drove variations in the sediment macrofossil data (Figure 5.6 c); those associated with agriculturally-driven nutrient enrichment and climate conditions. Approximately 74 % of the variance in the sediment macrofossil dataset was explained by the independent variable dataset. Only CCA Axis 1 was statistically significant ($p < 0.05$) in explaining the variance in the macrofossil data, and accounted for c. 36 % of the total variance. CCA Axis 1 was positively correlated with the NAO and human population and negatively correlated with continentality, summer temperatures, cattle numbers, sheep numbers, catchment TP loads and, to a lesser extent, winter precipitation (Figure 5.6 c). Sediment samples located mainly in the upper and lower right quadrants of the ordination plot were dated pre-c. 1970 AD and had relatively high proportions of terrestrial plant remains and relatively low proportions of aquatic macrofossils. Most of the samples dated to pre-c. 1970 AD were correlated positively with CCA Axis 1. The sediment samples dated post-c. 1970 AD (located mainly in upper and lower left quadrants of the ordination plot) had relatively high proportions of aquatic macrofossils and relatively low amounts of terrestrial plant remains. Most of these samples correlated negatively with CCA Axis 1. Samples with relatively high proportions of calcareous macrofossils *Chara* and *Nitella* (which plot in the lower right quadrant of the diagram) were positively correlated with variables associated with climate.

5.3.7.4 Partial CCA of diatom responses

Partial CCA analysis of the diatom response dataset was performed using the two separate groups of independent variables, apparent from the individual CCA analyses; those associated with agriculturally-driven nutrient enrichment and those associated with climate

conditions. Results of partial CCA indicated to what extent these two groups of variables explained unique aspects of diatom species composition, and how much of the variance was explained by a combination of agriculture and climate variables (Figure 5.7 a, b). The variance was partitioned into the following components:

- variance uniquely described by climate variables (but not explained by those linked with agriculture) = 31 %
- variance uniquely described by the agriculture variable (but not by the those describing climate conditions) = 11 %
- variance jointly described by both climate and agriculture = 8 %
- variance that was unexplained = 49 %

5.4 Discussion

The results presented in this chapter indicate that the relative importance of drivers of trophic variability at Lough Mask have changed substantially since the late 19th century. Results of the CCA analysis suggests that winter precipitation levels, the NAO and human population were the most important factors influencing trophic conditions in the lake prior to c. 1970 AD. Nutrient enrichment effects were more pronounced from c. 1970 AD, with cultural eutrophication seemingly linked to elevated summer temperatures and enhanced thermal stratification, and increased catchment P loading as a result of agricultural intensification. Results of partial CCA analysis indicate that approximately one-third of the total variance in the diatom data could be explained by climate variables, while an additional 11 % was accounted for by agricultural intensification alone, and 8 % by climate and agricultural intensification combined.

The results indicate a link between precipitation-driven trophic variability and the NAO. Prior to c. 1970 AD, abundant diatom taxa indicative of high water turbidity, such as *A. granulata*, terrestrial plant remains and indicators of inputs of terrestrial organic matter reflect relatively high runoff from the catchment land surface compared with groundwater. High rates of runoff are most likely to occur during the autumn and winter months, when precipitation levels are at their highest, and may be enhanced by more negative NAO index values at these times. The dependency of NAO variability on long-term climatic trends is

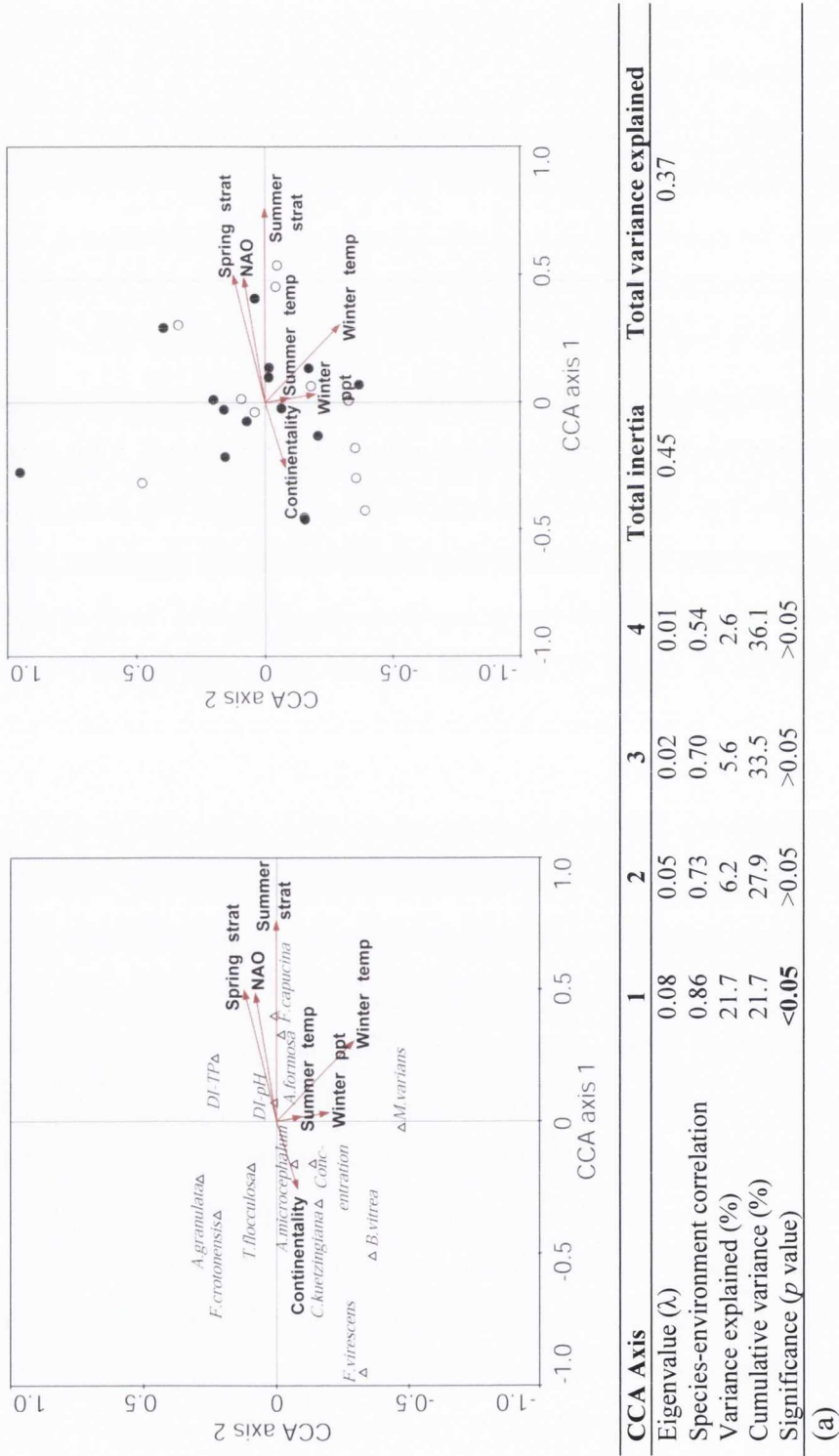


Figure 5.7 Partial CCA diagrams (species and samples biplots) and results for: diatom data with independent climate variables (a), which account for c. 37 % of the total variance and diatom data with independent agriculture variables (b), which account for c. 18 % of the total variance. Open circles = pre-c. 1970 AD samples; filled circles = post-c. 1970 AD; open triangles = sediment proxies (response variables); arrows = independent variables

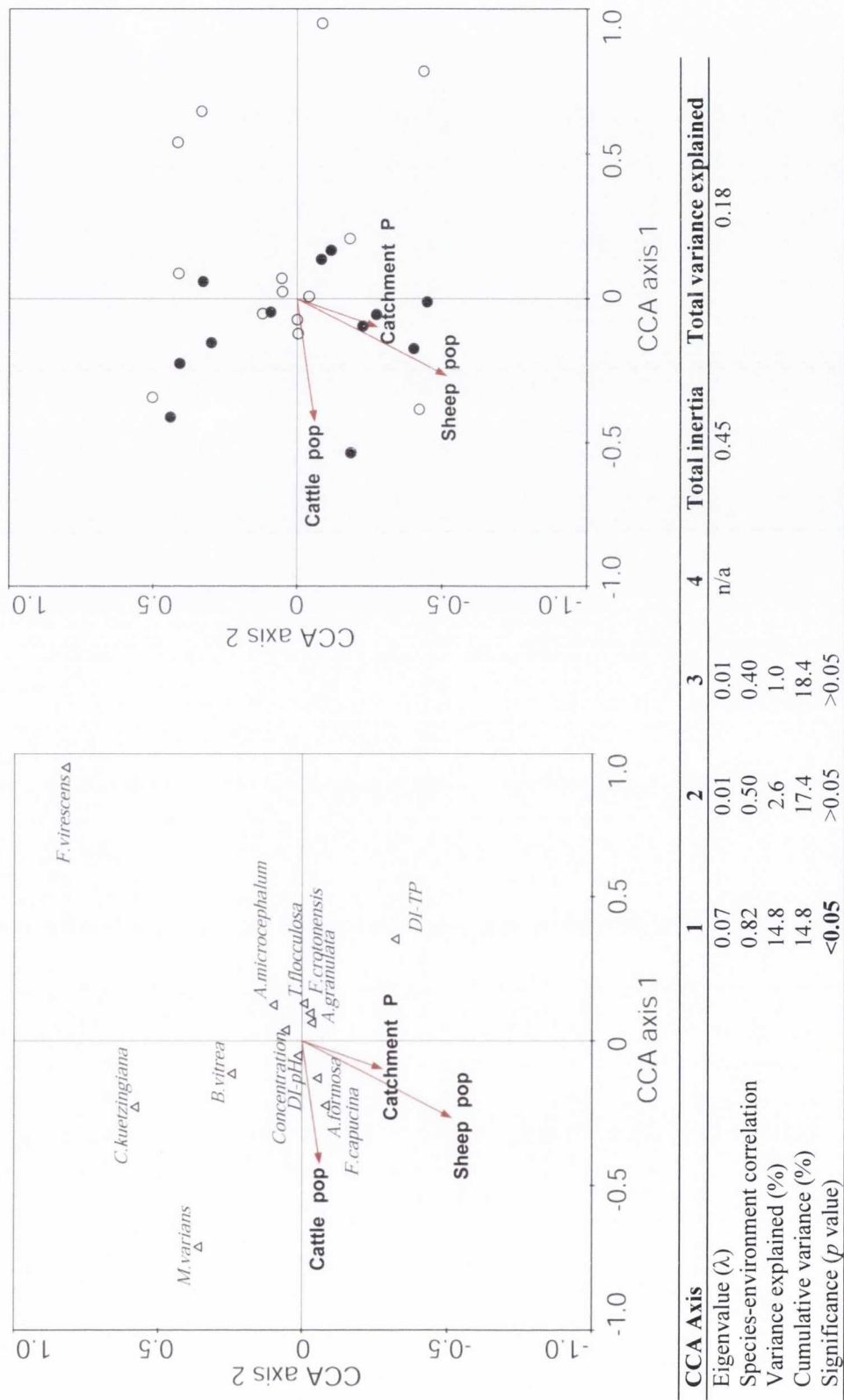


Figure 5.7 (continued)

relatively well established (Butler *et al.*, 1999; Diefendorf *et al.*, 2006; George *et al.*, 2010). Relationships between the NAO and aquatic conditions, particularly primary productivity, are more variable and less well understood (Jennings & Allott, 2006; Nöges *et al.*, 2010). Several studies in Europe have reported relationships between the NAO and spring phytoplankton phenology, with spring blooms occurring earlier in years with high NAO index values (e.g. Weyhenmeyer *et al.*, 1999; Gerten & Adrian, 2000). Analysis of data from lakes across Europe by Blenckner *et al.* (2007), however, showed that phytoplankton biomass was unrelated to the NAO, with the exception of a positive relationship to cyanophyte biomass in summer. In Ireland, Jennings *et al.* (2000) found an inverse relationship between the NAO and winter chlorophyll levels in Lough Leane, in southwest Ireland, although the mechanism for the relationship was unclear. Results of the CCA analysis of the Lough Mask data suggest that the NAO was positively correlated with abundances of diatom species with relatively high TP and neutral pH optima, and this relationship was strengthened post-c. 1970 AD. The NAO was negatively correlated with the abundances of species indicative of moderate TP and lower pH optima, and this relationship was weaker post-c. 1970 AD.

The influence of climate variability on the post-depositional fate of sediment geochemical elements may also be evident from the CCA analysis. Increased sediment TP and Mn concentrations post-c. 1970 AD appear to have resulted from changes in redox conditions at the sediment-water interface, which may be linked to enhanced summer thermal stratification and associated variations in water column stability (Engstrom & Wright, 1984). However, elevated sediment TP concentrations were, to a lesser extent, also linked to increased catchment P loading from agricultural sources.

The evidence presented in this chapter suggests eutrophication effects during the 20th century at Lough Mask are linked to climate warming and strengthened thermal stratification primarily, and agricultural intensification. The evidence presented are in agreement with the findings of, for example, Mooij *et al.* (2005), Hamilton *et al.* (2010) and Hobæk *et al.* (2012). Moreover, the influence of climate change on in-lake ecological dynamics appears to be even greater than that of late 20th century agricultural intensification. Relatively high abundances of planktonic diatoms are linked to enhanced thermal stratification in the lake post-c. 1970 AD. Eutrophication over the last 30-40 years

associated with strengthening of thermal stratification, linked to elevated summer temperatures, surface water temperatures and the NAO is also evident in lakes in temperate regions (Winder & Schindler, 2004). Similar findings, based on ordination analyses of diatom responses to potential nutrient and climate drivers by Hobæk *et al.* (2012), were evident for Lake Mjøsa, a large and deep lake in south-eastern Norway. Warmer conditions favour the development of planktonic diatom species, such as *Cyclotella*, through enhanced growing condition or changes in habitat availability (Battarbee *et al.*, 2002). Changes in the timing and intensity of thermal stratification may improve growing conditions for primary producers or disrupt the grazing of phytoplankton by other organisms, such as zooplankton (George & Harris, 1985; Winder & Schindler, 2004), thereby enhancing eutrophication effects. The strengthening of thermal stratification in other European lakes has been linked to variations in the NAO (George, 2000) and phenological shifts in diatom species composition. The advancement of spring blooms of diatoms, evident from a long-term dataset from the UK since 1955, have also been linked to lagged winter climate conditions and variations in the NAO (Thackery *et al.*, 2008). However, climate variability can influence lakes differently. For example, in lakes that display two distinct productive periods, climatic fluctuations in spring or autumn can influence in-lake trophic conditions (Catalan *et al.*, 2002).

Evidence for a link between climate warming and continentality in dictating trophic conditions post-c. 1970 AD may also highlight the role of other climatic phenomena, such as the MO or the EA-WR, both of which are known to influence weather patterns over Europe. Salmaso (2012) suggests that the MO and EA-WR teleconnection patterns play an important role in the development of primary producers in Lake Garda (northern Italy) because of their influence on lake water temperatures, circulation patterns and nutrient recycling. However, the roles of the MO and the EA-WR in lake ecological variability are not well documented. In temperate regions, increased nutrient enrichment effects as a result of climate warming in several lakes have been observed during the latter half of the 20th century (e.g. Marshall & Randhir, 2008; Dalton *et al.*, 2010; Moss *et al.*, 2012), and predicted for future climate warming scenarios (Jennings *et al.*, 2009). Increased primary productivity, as a result of warming and nutrient enrichment, is evident in lakes in northern and western Europe (e.g. Blenckner & Hillebrand, 2002; George *et al.*, 2004; Mooij *et al.*, 2005). However, the extent of such effects have also been found to be varied and site-specific (Battarbee *et al.*,

2002). Future warming, a component of directional climate change, is projected to further increase productivity in the region (Blenckner *et al.*, 2010; Trolle *et al.*, 2011). Climate-driven eutrophication is evident much earlier in lakes at high latitude than in those located at low latitudes (Smol & Douglas, 2007; Kirilova *et al.*, 2009; Jiang *et al.*, 2011), where the influence of human pressures is relatively low compared with Lough Mask.

Cultural eutrophication, linked to agricultural intensification, commenced much earlier than documented in the literature for Lough Mask (e.g. McGarrigle & Champ, 1999; McCarthy *et al.*, 2001; Toner *et al.*, 2005). In addition, according to the partial CCA, the relative contribution of agriculture to nutrient enrichment effects in Lough Mask is less than previously thought. The link between the intensification of agriculture and eutrophication during the mid-late 20th century in Lough Mask is, however, concurrent with regional trends, and evidence from other lakes in Ireland, e.g. Lough Erne (Battarbee, 1986; Zhou *et al.*, 2000), Crans Lough (Dalton *et al.*, 2009) and Lough Leane (Dalton *et al.*, 2010). Major increases in aquatic nutrient loading from c. 1945 AD, driven primarily by intensive agriculture, are also evident in lake sediment cores across the wider European region (Keatley *et al.*, 2011). The combined effects of agriculture and climate variability on nutrient enrichment and elevated trophic conditions in the lake were also evident from the partial CCA. Moreover, winter precipitation levels were positively correlated with variables associated with agricultural intensification, in support of the general consensus that higher rainfall results in increased nutrient concentrations and primary productivity, as a result of enhanced runoff and increased nutrient loading from diffuse sources (Mooij *et al.*, 2005; Christofferson *et al.*, 2006; Greene *et al.*, 2011).

There are a number of potential sources of uncertainty in the results presented in the current chapter, which have important implications for the validity of interpretations of the results. As the CCA analysis involved a comparison of instrumental/documentary records and sediment data the results are inevitably complicated by differences in the nature of these datasets. The results of the CCA depend on there being a one to one correspondence between calendar and radiometric dates, which is unlikely. The extent to which variations in the sediment record can be determined depends on the quality of sediment record, the rate of sediment accumulation, the sensitivity of sediment proxy methods and a thorough understanding of the aquatic ecological pressure-response relationships (Battarbee *et al.*,

2002). Diatoms, for example, may be an indicator of a number of different climatic or human-induced changes, including direct temperature effects, nutrient loading, stratification and mixing or water quality changes, and diatom responses to climate change can vary from site to site. Uncertainty is further complicated by the interpolation of sediment sample dates and sediment proxy data. Other factors that were not accounted for in the statistical analysis due to a lack of information could also influence the outcome of the analysis (Battarbee *et al.*, 2002), such as Si release from bottom sediments or hydromorphological modifications in the catchment (e.g. ADS). Si release from the sediment, following depletion in the water column as a result of the spring bloom of diatoms, can have a major influence on the size of the diatom population the following spring (Jewson *et al.*, 1981). The possibility of delayed ecological responses to variations in climate conditions and human pressures are difficult to assess when dealing with datasets that are relatively large and comprise a wide range of variables, such as those in the current research, and can be expected to be influenced by climate variability in many different ways both directly and indirectly (Battarbee *et al.*, 2002).

According to the partial CCA results, climate was more influential than agricultural intensification in dictating eutrophication effects in Lough Mask during the latter part of the 20th century, while almost half of the variance in the sediment diatom data was not explained by climate variability or human activity. However, there are several issues regarding CCA analysis and variance partitioning, in general, that require caution when interpreting the results such techniques (Borcard *et al.*, 1992; Økland & Eilertsen, 1994; Birks, 1996; Ohmann & Spies, 1998). As there were more climate variables incorporated in the analysis than those associated with human activity the suggestion of greater importance of climate over agricultural intensification may be an artefact of variable number (Økland, 1999). Furthermore, although CCA is generally not seriously affected by the ‘arch effect’ (Palmer, 1993), a mathematical artefact whereby the second axis is a quadratic distortion of the first axis, it can be present and not apparent because the analysis is constrained by environmental variables (Økland, 1999). The arch itself can also have variance, and in many cases is part of the unexplained variance, and is practically impossible to factor out (Økland, 1999). In addition, multiple comparison statistical tests including ordinations can create statistically significant relationships (Millard & Neerchal, 2001).

The findings presented in this chapter have important implications for the implementation and success of the WFD and associated water quality policy. The findings suggest a greater role of directional climate change in influencing lake trophic conditions than previously thought, and therefore the potential effects of climate change will have to be incorporated into catchment management plans. Furthermore, the possibility of interaction effects of multiple pressures acting in combination are also suggested in the current research and therefore will also need to be addressed in catchment management plans. Moreover, climate variability is likely to be an important, geographically-specific determining factor in the success of future catchment management plans.

5.5 Conclusion

The benefits of a multidisciplinary approach and long-term records of ecological conditions for deciphering the relative importance of human and climatic drivers of trophic variability are demonstrated in this chapter. Allowing for the uncertainty involved in the data comparisons and the statistical analysis detailed above, the results suggest that conditions in Lough Mask, as an example of a lake on the Atlantic margins of Europe, are particularly sensitive to variations in climate conditions associated with the NAO and warming, and that the latter played an important role in dictating in-lake conditions prior to c. 1970 AD. Eutrophication was driven by a combination of warming-induced thermal stratification, the NAO and agricultural nutrient loading in the latter half of the 20th century. Ultimately, this chapter demonstrates that the impacts of climate variability on lake ecological conditions may be greater than previously thought. Therefore, the influence of climate variability, acting alone and in combination with other catchment pressures, is likely to be an important, geographically-specific determining factor in the future success of WFD implementation and will have to be accounted for in catchment management plans.

Chapter 6

**Reconstructing long-term trophic histories for lakes using
two independent approaches: application of dynamic
modelling and palaeolimnology to Lough Mask**

6.1 Abstract

An understanding of the extent to which natural variability has been and is being exceeded by the effects of human activity can make an important contribution to the effective management of impacted water bodies, including their restoration. Frequently, however, the required monitoring data are not available, particularly for the period prior to human impact, or are of insufficient quality. Two methodological approaches that can help address this problem are often proposed, both of which involve the reconstruction of past variations in water quality and associated ecological conditions through indirect means: dynamic hindcast modelling and palaeolimnological analyses. Both proposed solutions are not without their own problems, however. In this chapter, a combination of dynamically-linked models (a catchment model and an in-lake ecological response model) and palaeolimnological techniques (including sediment-based DI-TP), were used to reconstruct TP concentrations and measures of primary productivity (total chlorophyll *a*) in Lough Mask for the period 1905-2006 AD. Although results from both approaches indicated similar patterns of nutrient enrichment in the lake during the 20th century, sediment-based DI-TP values consistently overestimated available monitored TP data and were higher than hindcast modelled in-lake TP concentrations. Both approaches indicated oligotrophic to mesotrophic conditions in Lough Mask prior to c. 1950 AD. Elevated trophic conditions (in the range mesotrophic-eutrophic) were evident from c. 1970 AD. Modelling results indicated that increased diffuse P loading from agricultural sources was the main driver of increased nutrient loading to the lake from c. 1970 AD. However, eutrophication evident from c. 1970 AD was also linked with climatic warming, and associated strengthened thermal stratification. Results generated by the two approaches suggest that pre-1950 AD trophic conditions could be used as a reference baseline, representing conditions prior to major impacts from agricultural intensification, for defining current water quality management targets.

6.2 Introduction

Anthropogenic pressures, such as water abstraction, pollution and sedimentation, have altered the natural variability in aquatic ecosystems, in particular over the last c. 200 years (Zalasiewicz *et al.*, 2008). The effects of anthropogenic activity on these ecosystems include the acceleration of conditions that would have occurred naturally over a longer

period of time (Ahn *et al.*, 2006), e.g. eutrophication. Eutrophication, the aquatic effects of enrichment by nutrients, is currently a major water quality issue in Ireland (Jennings *et al.*, 2003; Donohue *et al.*, 2010; McGarrigle *et al.*, 2010). Excessive P loading from human activity is the main driver of eutrophication in freshwater ecosystems (Schindler *et al.*, 2008). Diffuse P loading from agricultural activity is one of the main sources of nutrient enrichment in Ireland (Jennings *et al.*, 2003) and elsewhere (Kronvang *et al.*, 2009). Point sources of P, from municipal and industrial waste, can also be important contributors to eutrophication (Smith *et al.*, 2006; Dalton *et al.*, 2009), particularly during low flows (Greene *et al.*, 2011; Macintosh *et al.*, 2011). The response of lakes to pressures, such as nutrient loading, can be site-specific and depends on lake type (determined by factors such as altitude, alkalinity and depth) (Lyche-Solheim *et al.*, 2008) and geographical location (Jeppesen *et al.*, 2010). Furthermore, interactions between more than one pressure, such as climate change and anthropogenic nutrient loading, can exacerbate eutrophication impacts (Jeppesen *et al.*, 2005; Battarbee *et al.*, 2008).

Improving, maintaining and restoring good ecological water quality by 2015 is a key aim of the EU WFD (2000/66/EC) (Anon, 2005). Among the requirements of the WFD are the definition of reference or baseline conditions for all water bodies, representing ecological conditions prior to significant human impact, and the establishment of appropriate water quality targets for restoration of polluted water bodies to defined baseline conditions (Kelly-Quinn *et al.*, 2009). Of critical importance to meeting these requirements is an understanding of aquatic ecological pressure-response relationships (Heiskanen & Solimini, 2005; Irvine *et al.*, 2005). However, long-term aquatic ecological monitoring datasets, which are clearly vital here, are often absent. As a consequence, links between pressures and ecological responses in lakes can be difficult to decipher (Bennion & Battarbee, 2007). In Ireland, for example, little is known about trophic conditions in lakes prior to the commencement of monitoring in the 1970s (Jennings *et al.*, 2008), although information on potential drivers of changes in lake water quality, such as population, climate and land use change data, are often available at relatively high resolution (see Chapter 2).

Dynamic modelling can provide a powerful means of examining ecological pressure-response relationships, by providing a means through which datasets from monitoring surveys can be supplemented and extended, and a basis for unravelling the relative effects of

different pressures (Anon, 2005; Irvine *et al.*, 2005; Jennings *et al.*, 2008). Palaeolimnology, involving sediment-based proxies of environmental conditions, can also help elucidate ecological pressures-response relationships in lakes (Smol, 2008; Dalton *et al.*, 2009, 2010). Diatoms can be used as a sediment-based proxy of aquatic ecological conditions (Battarbee *et al.*, 2001) and to infer past levels of epilimnic TP (DI-TP) using the transfer function approach (Chen *et al.*, 2008). Palaeolimnology and dynamic modelling have been suggested as potential means of reconstructing past in-lake conditions (Jennings *et al.*, 2008; Dalton *et al.*, 2010) and addressing WFD-related information gaps (Irvine *et al.*, 2005). Moreover, a better understanding of pressure-response relationships can be achieved by employing more than one approach to reconstructing long-term records (Jeppesen *et al.*, 2010), such as dynamic models that can be run retrospectively (hindcast) and palaeolimnological reconstructions (Anderson *et al.*, 2006; Bennion & Battarbee, 2007). An integrated approach could play an important role in assessing the accuracy of simulations of aquatic ecosystem responses to future scenarios of individual and combined pressures (e.g. Anderson *et al.*, 2006; Dearing *et al.*, 2006), and therefore contribute to more effective management of water resources in the future.

Focusing on Lough Mask and its extensive and varied catchment, this chapter uses palaeolimnological (sediment-based DI-TP and sediment TP concentrations) data from two sediment cores (MK-11 and MK-12; Table 3.1) from the southwest part of the lake, in which preservation of diatom frustules was relatively good (see Section 5.3.4), and dynamic modelling data (DYCD hindcast in-lake daily temperature, nutrient and total chlorophyll *a* concentrations) for the deepest part of the lake, for the period 1905-2006 AD, to:

- 1/ compare reconstructions of lake trophic conditions from two independent approaches (dynamically-linked models and palaeolimnology);
- 2/ assess the usefulness of dynamically-linked models and palaeolimnology for reconstructing past trophic changes; and
- 3/ determine baseline trophic conditions, representing conditions prior to significant human impacts during the 20th century.

Details of the palaeolimnological and dynamic modelling methods, including model calibration and validation, used in the research are described in Chapter 3. The availability

of data for input to and calibrating and validating the models is described in Table 3.2. Due to gaps in data required to drive the dynamic models, hindcast in-lake temperature, nutrient and total chlorophyll *a* concentrations were limited to the following periods: 1905-1914 AD, 1931-1942 AD and 1950-2006 AD.

6.2 Results

6.2.1 Changes in drivers of trophic conditions 1901-2006 AD

Hindcast annual catchment TP loads were relatively stable from 1901 to 1950 AD (Figure 6.1) and increased after 1950 AD, particularly from 1970 AD where a significant change point was identified ($Q = 9.6$; $p \leq 0.01$). During the period 1901-1970 AD, the mean hindcast annual TP load was c. 18.8 kg TP km⁻² yr⁻¹ compared with c. 51.0 kg TP km⁻² yr⁻¹ between 1970 and 2006 AD. Hindcast annual catchment TP loads increased significantly, however, between 1970-2006 AD ($r^2 = 0.75$; $p < 0.01$; $v = 34$). Prior to 1970 AD, the majority of the hindcast annual catchment TP loading was attributable to land use (runoff and baseflow) (average = 61%; range = 26-75 %), which comprised mainly agricultural pasture (Table 2.3). During this period, the rural population contributed an average of 25 % (range = 16-34 %), while relatively minor contributions came from the urban population (average = 11 %; range = 5-20 %) and livestock (average = 4 %; range = 2-7 %) (Figure 6.1). Between 1970-2006 AD, the proportion of hindcast TP loading attributable to livestock sources increased dramatically to the order of 22-66 % (mean = 23,652 kg yr⁻¹ or 53 % of the total catchment TP load). As a result of this, the relative contributions from land use and rural population were reduced to c. 33 % (range = 19-59 %) and c. 7% (range = 5-12 %), respectively. However, the absolute loads for these sectors did not change greatly (Figure 6.1). The contribution from urban population also changed little (average = 6 %; range = 3-12 %). The majority of the hindcast TP load to Lough Mask came from the Robe and western subcatchments (Appendix U). Modelled in-lake water temperatures revealed strengthened thermal stratification in Lough Mask from the mid-1960s (Appendix V). Significant increases were evident in hindcast mean annual surface water temperatures ($r^2 = 0.62$; $p < 0.05$; $v = 40$) and deep water temperature (50 m) ($r^2 = 0.69$; $p < 0.05$; $v = 40$) and were evident in all seasons from 1965-2006 AD. These changes reflected the warming trend evident in air temperature data for the catchment (Appendix A).

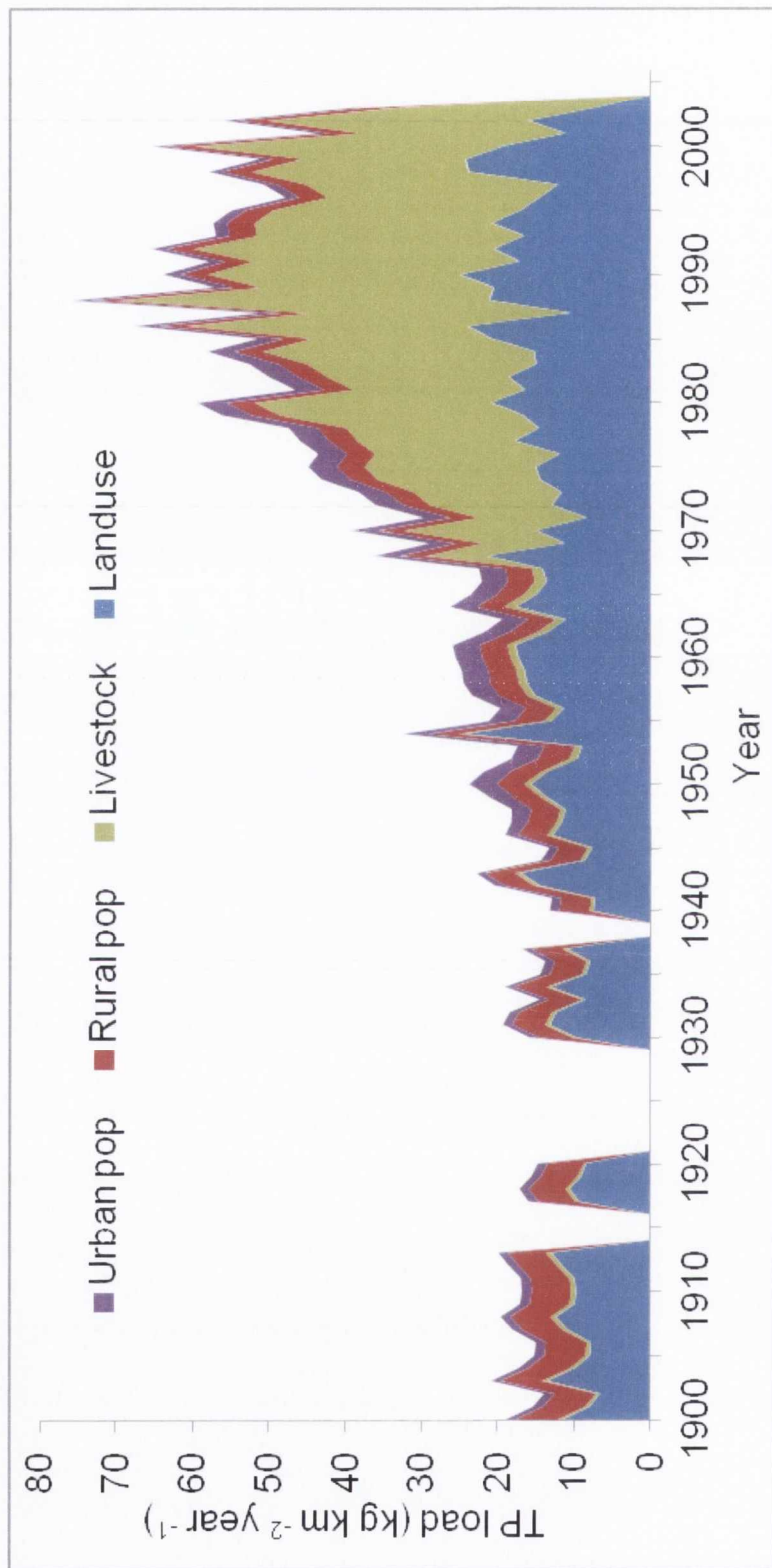


Figure 6.1 The relative contribution of land use runoff and baseflow, livestock, rural population and urban population to hindcast total catchment TP loading ($\text{kg km}^{-2} \text{ year}^{-1}$) to Lough Mask, 1901-2006 AD. Hindcast TP loading ($\text{kg km}^{-2} \text{ year}^{-1}$) for each of the main subcatchments, 1901-2006 AD is shown in Appendix U. Missing values reflect gaps in the model input data (see Table 3.2 for details)

6.2.2 Reconstructed trophic history 1905-2006 AD

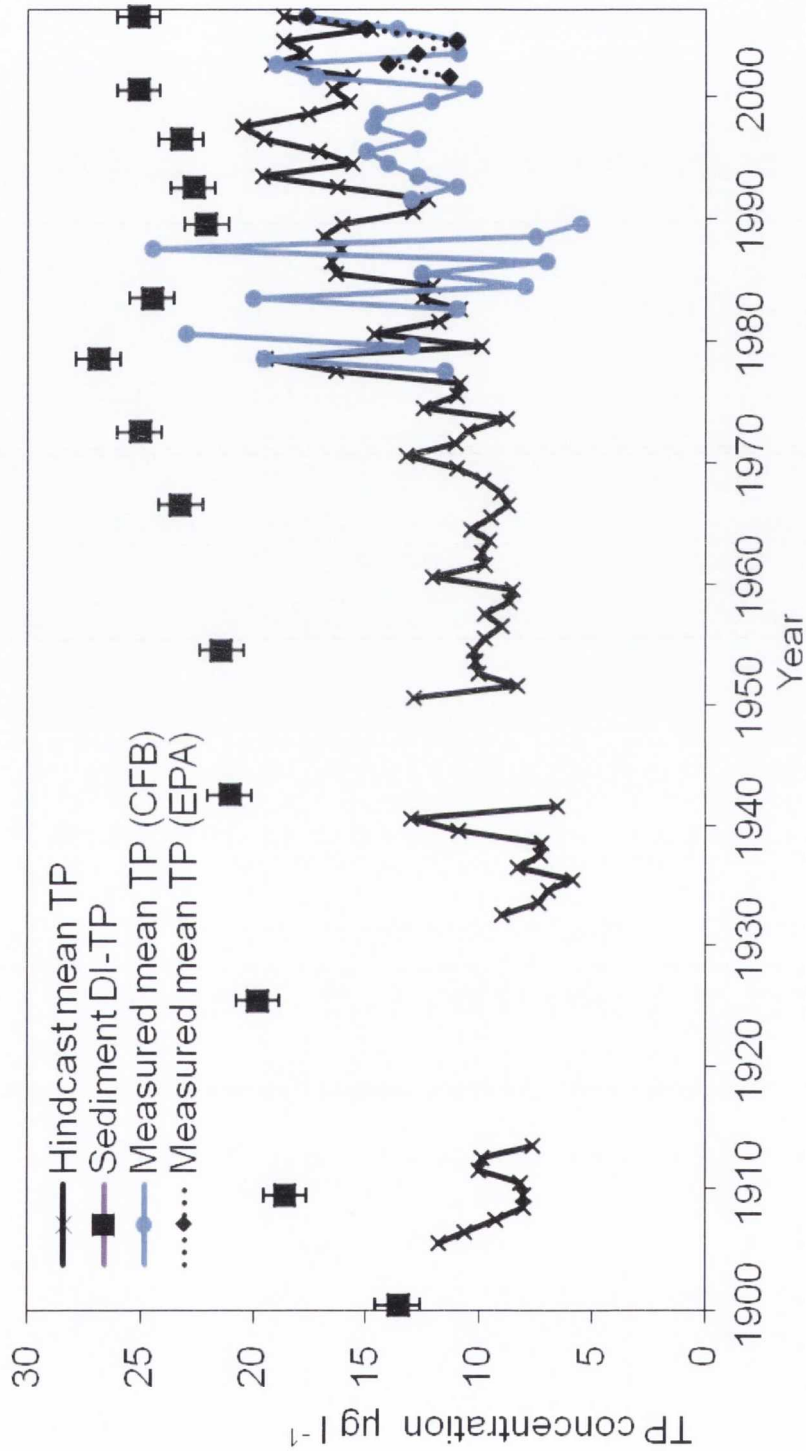
With the exception of the period c. 1982-1988 AD, when measured annual mean TP concentrations decreased, hindcast annual mean TP concentration data compared well with measured annual mean TP data for the lake, with both indicating relatively low nutrient conditions prior to 1970 AD and elevated nutrient conditions from 1970 AD onwards (Figure 6.2 a). Variations in DI-TP were similar to those evident from the measured data. However, DI-TP tended to be substantially greater than measured TP for the equivalent time period (Figure 6.2 a).

Sediment DI-TP also showed similar patterns of variation to hindcast modelled TP and were positively correlated for the 1905-2006 AD period ($r^2 = 0.56$; $p < 0.05$; $v = 13$). However, reconstructed DI-TP were consistently higher than hindcast modelled TP concentrations (Figure 6.2 a). Hindcast annual mean TP concentrations indicated oligotrophic conditions during the period 1905-1950 AD, while sediment-based DI-TP values indicated mesotrophic conditions during the same period (Table 6.1). From 1950-1970 AD, hindcast annual mean TP concentrations indicated oligo-mesotrophic conditions, while sediment-based DI-TP values were in the low eutrophic range. From 1970 AD onwards, both reconstructed datasets showed elevated trophic levels: hindcast TP concentrations indicated high mesotrophic conditions, while sediment-based DI-TP values were in the eutrophic range. During the period 1980-1990 AD, however, when hindcast mean TP concentrations continued to increase (from c. $14 \mu\text{g l}^{-1}$ to c. $16 \mu\text{g l}^{-1}$), reconstructed DI-TP concentrations decreased (from c. $27 \mu\text{g l}^{-1}$ to c. $22 \mu\text{g l}^{-1}$).

Sediment TP concentrations were relatively stable from 1901-1950 AD (mean = c. 0.67 mg g^{-1}). After 1950 AD sediment TP concentrations increased, particularly from 1970-2006 AD (mean = c. 0.89 mg g^{-1}) (Figure 6.2 b). A trend of increasing sediment TP concentrations is not evident in measured in-lake TP concentrations (Figure 6.2 b), however. Sediment TP concentrations were positively correlated with hindcast annual mean TP concentrations ($r^2 = 0.55$; $p < 0.05$; $v = 73$), and with sediment-based DI-TP levels ($r^2 = 0.66$; $p < 0.05$; $v = 13$) for the 1905-2006 AD period.

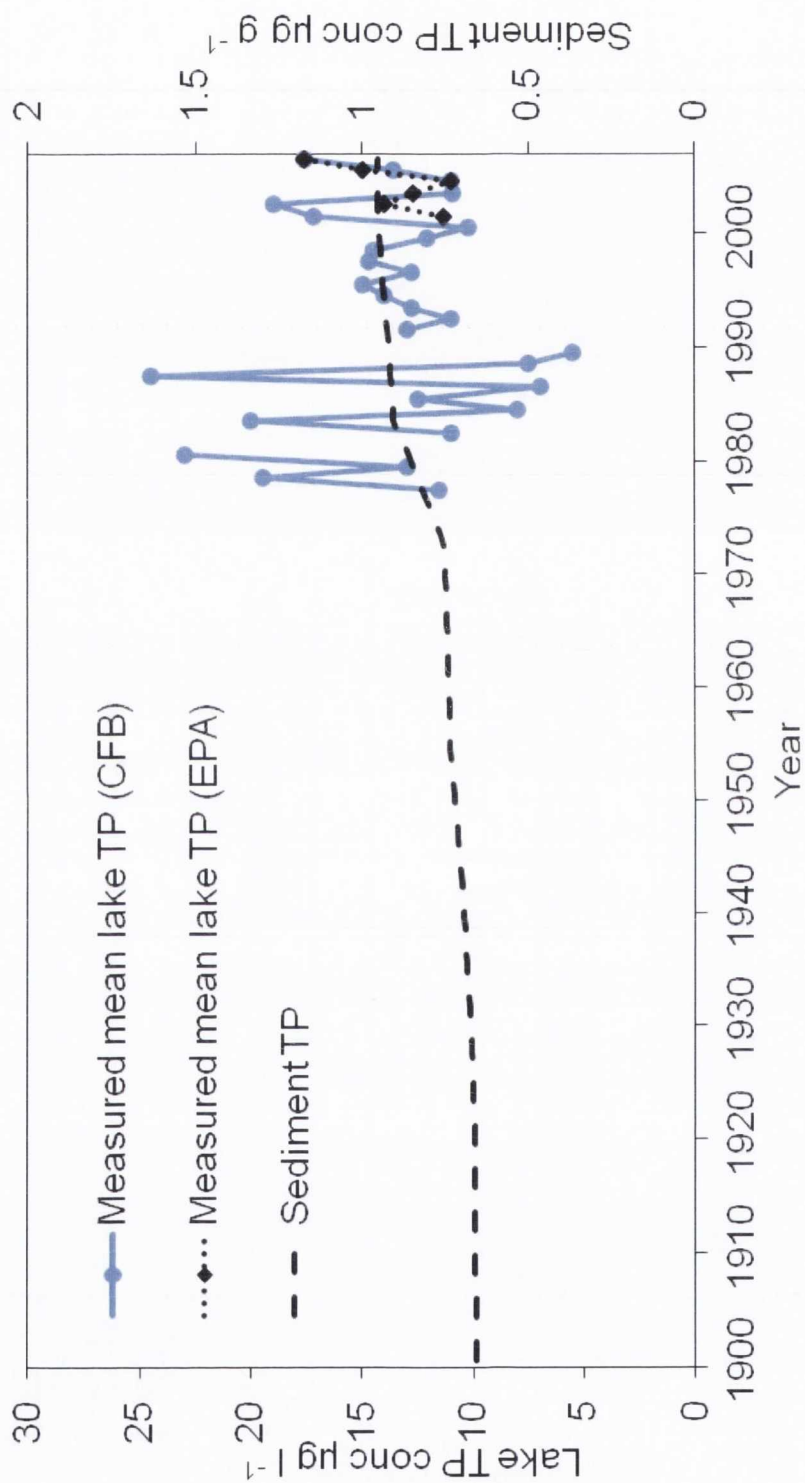
Table 6.1 Determining baseline trophic conditions using measured data (available from the Central Fisheries Board; Section 2.2.5), hindcast modelled and sediment-based reconstructions of in-lake TP and chlorophyll *a*, based on the modified OECD scheme (OECD, 1982) (see Table 3.3). * Time periods are approximated given that, due to data availability, some datasets did not provide data for an entire period (see Table 3.2 for details of data gaps)

Years AD*	1901-1950	1950-1960	1960-1970	1970-1980	1980-1990	1990-2000	2000 +
Measured							
mean TP		no data		meso	oligo	meso	
mean chlorophyll <i>a</i>		no data		meso			
Sediment							
DI-TP	meso	eutrophic					
Hindcast annual							
mean TP	oligo	low meso	oligo-meso	meso			
mean chlorophyll <i>a</i>	oligo	oligo-meso			meso	oligo-meso	
max chlorophyll <i>a</i>	oligo-meso	low-high meso					



(a)

Figure 6.2 Hindcast annual mean total phosphorus ($\mu\text{g l}^{-1}$), TP, sediment-based diatom-inferred TP ($\mu\text{g l}^{-1}$), DI-TP (core MK-12), and measured annual mean TP (from the Central Fisheries Board and the Environmental Protection Agency) concentrations (a), and sediment TP (mg g^{-1}) concentrations (core MK-12) and measured mean TP concentrations (lake) from the CFB and EPA (b)



(b)

Figure 6.2 (continued)

Hindcast annual mean chlorophyll *a* concentrations showed similar patterns of variations to the long-term measured data. However, hindcast annual maximum chlorophyll *a* levels differed substantially from the measured data (Figure 6.3). Hindcast annual mean chlorophyll *a* concentrations indicated similar trophic levels (oligo-mesotrophic) to hindcast mean TP concentrations in Lough Mask between 1905-1970 AD, but indicated lower trophic conditions (oligo-mesotrophic conditions) between 1970 and 2006 AD (Table 6.1; Figure 6.3). Similar trends of significant increases in hindcast annual mean chlorophyll *a* concentrations and in summer mean chlorophyll *a* concentrations (respectively, $r^2 = 0.46$; $p < 0.01$; $v = 40$ and $r^2 = 0.63$; $p < 0.05$; $v = 40$) were also evident. Hindcast annual maximum chlorophyll *a* concentrations indicated higher trophic conditions in the lake between 1905-1970 AD than hindcast annual mean values for TP or chlorophyll *a*, though still in the oligo-mesotrophic range (Table 6.1). Hindcast annual maximum chlorophyll *a* levels also increased between 1970-2006 AD to within the low to high mesotrophic range.

6.3 Discussion

Good agreement existed on the whole between patterns of variation in sediment-based DI-TP and hindcast in-lake TP concentration datasets over the 1905-2006 AD period, based on correlation analysis. The hindcast in-lake TP concentrations were a much closer approximation of monitored TP data for the 1975-2006 AD period than sediment based DI-TP, which overestimated measured values. Both reconstructions of trophic conditions support concern for recently observed nutrient enrichment in Lough Mask, in particular elevated trophic status, from oligotrophic to mesotrophic (Toner *et al.*, 2005; see Section 5.4). As might be expected, changes in hindcast in-lake TP concentrations and, to a lesser extent, chlorophyll *a* concentrations closely mirrored hindcast catchment TP loads for the simulation period. Hindcast catchment TP loading data indicated that anthropogenically-sourced P inputs were the principal driver of nutrient enrichment, in agreement with the findings of McGarrigle & Champ (1999), Donnelly (2001) and Donohue & Irvine (2003). Furthermore, hindcast catchment TP loading data indicated major changes in the sources of TP inputs to the lake, and thus drivers of nutrient enrichment, during the 20th century. Prior to 1970 AD, the main contributors to catchment TP loading were rural population and land use, compared with livestock post-1970 AD. In addition, the hindcast modelled and sediment-based results indicated that the commencement of nutrient enrichment was earlier

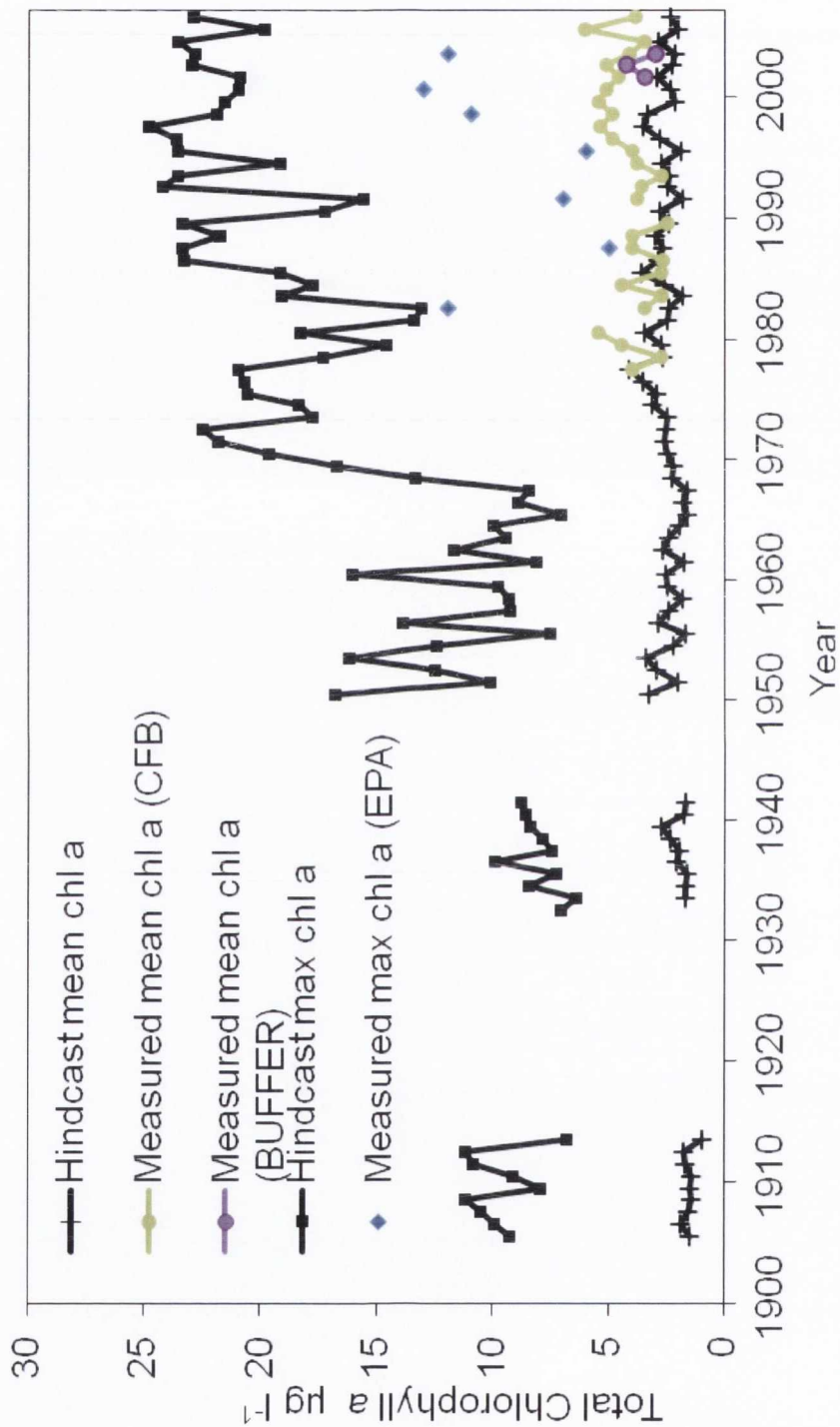


Figure 6.3 Hindcast and measured (from the Central Fisheries Board and BUFFER project) annual mean chlorophyll *a* ($\mu\text{g l}^{-1}$) and hindcast and measured (from the EPA) annual maximum chlorophyll *a* ($\mu\text{g l}^{-1}$)

than documented in the literature (mid-1980s) (McGarrigle & Champ, 1999; Toner *et al.*, 2005). The onset of warming and strengthened thermal stratification in Lough Mask from the mid-1960s also coincided with the start of elevated hindcast TP loading, linked to agricultural intensification, and with the effects of eutrophication. The results of this chapter also support the idea of multiple pressures contributing to deterioration in trophic status (Ormerod *et al.*, 2010). Climate and the combined effects of climate and agricultural intensification appear to be important drivers of eutrophication in Lough Mask (see Section 5.4).

However, marked differences also existed between the sediment-based and hindcast modelled datasets. Sediment-based DI-TP values were consistently higher than hindcast annual mean TP concentrations for the 1905-2006 AD period. Monitored data from Lough Mask were used to calibrate and validate hindcast in-lake data, and both monitored and modelled datasets compared well (Section 3.2.2.3). The DI-TP transfer function did not incorporate data from Lough Mask in its calibration dataset. Only seven of the 72 lakes forming the transfer function calibration dataset were classed in the same WFD typology category (based on altitude, water depth and alkalinity) (Anon, 2005) as Lough Mask, and the majority of lakes that were included were relatively small. The hindcast modelled data appear to provide a more accurate record of trophic changes in the lake than sediment-based data, which appear to have overestimated in-lake TP concentrations. These findings support the general consensus regarding DI-TP reconstructions, that is that they tend to overestimate in-lake TP concentrations. The DI-TP transfer function by Chen *et al.* (2008) used in this research has been found to overestimate in-lake TP concentrations in Lough Leane, southwest Ireland, when compared with measured data for a c. 20 year period (Dalton *et al.*, 2010). Most (WA) DI-TP transfer functions, e.g. Sayers (2001), Edlund & Kingston (2004) and Bennion *et al.* (2005), tend to overestimate measured TP concentrations. This is particularly the case in lakes where TP concentrations are generally low (Sayers, 2001). Some have also found that where TP levels are high, DI-TP models can underestimate concentrations (Bradshaw & Anderson, 2001). The benefits of using additional methods for reconstructing in-lake conditions, in addition to palaeolimnology, are therefore evident. While the DI-TP record is useful for investigating the nature and timing of in-lake responses to changes in nutrient loading, dynamic modelling can provide a better estimate of in-lake

conditions, as well as indicating the extent of changes in nutrient loading and the relative importance of nutrient sources.

There are several sources of uncertainty associated with the sediment-based DI-TP values. The sediment core used in this study was collected from the southwest part of the lake, whereas the hindcast in-lake model (DYCD) simulated conditions at the deepest point of the lake. Although similar trends in trophic history at the locations are evident from sediment-based data, a one-to-one relationship between the sediment-based, monitored and hindcast modelled datasets would not be expected given their differing nature, particularly in the context of temporal resolution. McGarrigle & Champ (1999) suggest that the southwest part of the lake has a water chemistry that reflects that of the western inflows, different to that of the open water of the lake. However, nutrient monitoring data (fortnightly to monthly data for the period 2001-2003) from 4 different locations in the lake (Section 2.2.5) indicates that nutrient levels were similar in the open water of the lake and, therefore, reconstructed trophic conditions should be comparable.

All models are simplifications of reality (Irvine *et al.*, 2005) and therefore both hindcast modelled and sediment-based reconstructed DI-TP datasets are inherently subject to error associated with how realistic the model or transfer function calculations are, and the accuracy of defined parameters in the models (e.g. species TP optima and nutrient uptake rates and growth rates of phytoplankton) used. The relationship between diatoms and TP, for example, can be complex (Brooks *et al.*, 2001). Moreover, diatoms can be influenced by many other factors, such as temperature, Si levels, stratification and mixing or water quality changes (Battarbee *et al.*, 2002). The pre-dominance of non-planktonic diatoms species in sediment samples, particularly small *Fragilaria*, which are more sensitive to changes in habitat availability than TP, can lead to overestimation of in-lake TP levels by transfer functions due to inaccurate estimates of TP optima (Sayer, 2001). The TP data used to calibrate the transfer function used in the current research were mainly summer measurements (Chen *et al.*, 2008), and were based on a relatively coarsely resolved sampling protocol (1- 9 samples per year). Overestimation of epilimnic TP levels using other DI-TP transfer functions, evident from other studies, is linked to the fact that DI-TP reflects summer TP values, rather than long-term average TP levels (e.g. Hall *et al.*, 1997).

Conversely, Bennion *et al.* (2001) found that diatom assemblages in Esthwaite Water (Cumbria, UK) reflected trends in increasing winter phosphate concentrations rather than the long-term measured TP data.

Other drivers of diatom productivity, such as pH, alkalinity and temperature, may be responsible for changes in diatom assemblages in the sediment record (Battarbee *et al.*, 2001) and influence the accuracy of DI-TP reconstructions. Chen *et al.* (2008) found that a pH-conductivity gradient explained the majority of the total variance in the diatom assemblages in their calibration dataset, and this is also the case for other diatom transfer function training sets (e.g. Reavie & Smol, 2001). Moreover, although P is often the limiting nutrient for phytoplankton growth in freshwaters, depletion of the Si reserves in the water column following diatom blooms, which is evident from algal monitoring data for Lough Mask (also see Section 2.2.5.3 for further details), is likely to influence DI-TP reconstructions.

Sediment diatom data for the southwest site indicated that the main species contributing to high DI-TP values during the 1905-2006 AD period was *A. formosa* Hassall (see Section 5.3.4). The TP optima defined for *A. formosa* in the DI-TP model by Chen *et al.* (2008), $36.0 \mu\text{g}^{-1}$ (Appendix O), was considerably higher than that defined in other diatom transfer function training sets, based on data from the same Ecoregion (DeNicola *et al.*, 2004) (Appendix O). The discrepancies between TP optima for *A. formosa* are likely to be due to sampling differences (Chen *et al.*, 2008). Thus, the transfer function approach to reconstructing lake TP levels is highly sensitive to the measured data used in the calibration process. Sediment-based DI-TP estimates for Lough Mask based on Chen *et al.* (2008) may be overestimated because of the high abundances of *A. formosa*, which has lower TP optima in other transfer function training sets (Appendix O), throughout the sediment core.

Other factors that may affect the accuracy of sediment-based DI-TP model estimates include the relatively low resolution of sediment-based reconstructions. The impacts of removal via the lake outflows, contamination from inflows, sediment resuspension, reworking of older sediments, bioturbation and post-depositional dissolution of diatoms in the sediment may also introduce error into sediment-based DI-TP estimates (Mackay *et al.*, 1998; Battarbee *et al.*, 2001; Battarbee *et al.*, 2005; Ryves *et al.*, 2006). Differential dissolution of diatoms is evident in the sediment core from the

deepest point (see Section 4.3.5 for further details) and therefore potential compositional biases may be an important factor influencing DI-TP reconstructions at the southwest site also.

Discrepancies between long-term trends in measured, hindcast modelled and sediment-based datasets occurred only during the period 1980-1990 AD, when measured TP and sediment-based DI-TP concentrations decreased and hindcast in-lake TP concentrations and sediment TP values increased. Elevated SARs were evident during the period 1980-1990 AD, concurrent with an increase in sheep numbers in the catchment, and may have been linked to high soil erosion rates caused by overgrazing by sheep, which is evident elsewhere in Ireland during the same period (Allott *et al.*, 2005; Dalton *et al.*, 2010). Alternatively, if the reductions in sediment-based DI-TP during this period are real, they may reflect a decrease in catchment TP loading that is not accounted for in the GWLF model, for example, internal P loading from the sediment.

The findings presented in Chapter 4 showed that trophic conditions in Lough Mask during the mid-late Holocene prior to significant human impact were characterised by oligotrophic conditions. The findings presented in this chapter, based on hindcast in-lake modelling and sediment-based data, indicate the persistence of oligotrophic to low mesotrophic conditions between 1905-1950 AD, prior to the commencement of substantial nutrient enrichment in the lake linked to climate warming and agricultural intensification in the catchment (see Section 5.4). Oligotrophic to low mesotrophic conditions prior to 1950 AD could therefore be considered suitable baseline trophic reference conditions, in the context of significant anthropogenic nutrient loading effects, and represents a more realistic target for restoration and prevention of deterioration than conditions that existed prior to the 20th century (Taylor *et al.*, 2006). The findings highlight the advantages of a combined approach to reconstructing past trophic conditions, in particular the potential benefits of dynamic modelling for implementing water quality policy, including for the establishment of baseline trophic conditions, defining targets for water quality restoration and elucidating aquatic ecological pressure-response relationships.

6.4 Conclusion

The findings of this study highlight the value of using more than one means of reconstructing past trophic conditions for providing long-term datasets to improve our understanding of aquatic ecological pressure-response relationships. Dynamic modelling can provide high resolution data and permits the roles of individual drivers of modelled trophic changes to be quantified. Sediment-based data can integrate information in the remains of biota preserved in the sediment on lake catchment complexity, such as variations in inflow water chemistry and in-lake ecological dynamics, which are not yet incorporated in dynamic models. Furthermore, use of both dynamic modelling and sediment-based data in the reconstruction of past aquatic variability can help elucidate the limitations of both approaches and highlight where future developments of such techniques should be focussed. The findings concur with previous suggestions that the applicability of sediment-based DI-TP transfer functions is limited. However, the results presented in this chapter showed that hindcast dynamic modelling techniques can provide a more reliable and useful means of reconstructing past lake trophic conditions than sediment-based methods. The results presented in this chapter also highlight the importance of high-resolution monitoring data for improving the performance of both hindcast and sediment-based models for reconstructing lake trophic histories. Oligotrophic to low mesotrophic conditions, which appear to have persisted prior to the commencement of nutrient enrichment in Lough Mask c. 1950 AD, could be used as target baseline trophic conditions for restoration.

Chapter 7

**Scenario-based ecological pressure-response modelling:
determining effective measures for achieving Water
Framework Directive objectives**

7.1 Abstract

Long and high resolution time series records of lake water quality are rare. Such records are essential for determining the extent of human modification and therefore in defining water quality targets for restoration. Dynamic modelling, still a relatively unused technique in water management, including in the context of the EU WFD, provides a potential means of testing the likely effectiveness of programmes of measures aimed at reducing pollution impacts. This chapter applies two dynamically-linked models, a catchment pressures model (GWLF) and an ecological response model (DYCD), in examining management challenges relating to deteriorating water quality in Lough Mask. The study site has undergone significant changes in catchment pressures over the last century, particularly agricultural intensification. In-lake responses to a series of scenarios that include changes in livestock numbers, land use and agricultural practices, and that incorporate current agricultural policies, were simulated for a six-year River Basin District management period (2000-2006 AD). Scenario calculations showed that current policies and trends are unlikely to result in improved water quality in the lake. Furthermore, the results highlight the difficulties in meeting the implementation schedule of the WFD in the absence of supplementary measures aimed at reducing nutrient loading from agricultural activity, such as the improvement of waste management practices or reductions in the nutrient content of cattle feed. In particular, basic measures for restoration of water quality in catchments dominated by livestock-based agriculture may not be successful. Supplementary measures (such as reductions in the intensity of agricultural activity, and nutrient management plans) are likely to be necessary to restore water quality to baseline trophic status in such catchments. This chapter demonstrates the role in decision support that dynamic modelling can potentially play, particularly in facilitating cost-effective implementation of the water quality objectives of legislation such as the WFD.

7.2 Introduction

The extent of deterioration in water quality as a result of anthropogenic activity, widely recognised as a major global environmental issue (Smol, 2008), has led to the development and implementation of legislation at national and international levels. In Europe, for example, most of the national legislation of EU member states has been subsumed within the WFD, 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 (Anon, 2005). One of the main challenges for achieving the aims of the WFD is an understanding of aquatic ecological pressure-response relationships, as this requires long-term and high-resolution datasets (Irvine *et al.*, 2005; Bennion & Battarbee, 2007) that are rarely available. High resolution climate and catchment pressure data are often available, however, for relatively long periods of time in the form of meteorological and documentary records.

The WFD management unit, the RBD, encourages an integrated catchment-scale approach to water quality management (Rekolainen *et al.*, 2003; Bennion & Battarbee, 2007). RBD management plans must be delivered for each RBD every six years (Rekolainen *et al.*, 2003; Yang & Griffiths, 2010) and have to address the following: characterisation of water bodies and assessment of their pressures and impacts; monitoring; setting of environmental objectives; and design and implementation of Programmes of Measures (POMs) to achieve environmental objectives for all water bodies. The first six-year RBD management cycle (including the deadline for the delivery of the first RBD management plans) commenced in 2009 in all EU member states (McNally, 2009). The timescale of the WFD for achieving good ecological status in all surface waters has been described as overambitious (Hering *et al.*, 2010).

POMs have been devised to mitigate pollution impacts, including impacts of nutrients (Crabtree *et al.*, 2009). These comprise basic measures, based largely on existing European regulations and policies; they may also comprise supplementary measures. The latter are to be applied in those cases where basic measures are not enough to achieve water quality targets (Kavanagh & Bree, 2009). Eutrophication, resulting from overenrichment by nutrients, in particular P, has become a major, widespread water quality issue (Smith & Schindler, 2009). Although point sources of P (e.g. urban industrial or sewage treatment works) are important, diffuse sources of P from agriculture have been identified as the main cause of nutrient enrichment in freshwaters (Jennings *et al.*, 2003; Sharpley *et al.*, 2009) and continue to prove a significant challenge to water quality improvement efforts in Ireland, where agricultural sources account for 31% of pollution incidents (Kavanagh & Bree, 2009). The relative contributions of point and diffuse sources generally vary according to location and site-specific factors (Bowes *et al.*, 2010) and are therefore difficult to anticipate in the absence of data.

The basic measure to address nutrient loading pressures from agriculture in Ireland is full enforcement of the Good Agricultural Practice for Protection of Waters Regulations 2010 (S.I. 610 of 2010), and implementation of similar codes of good practice in other EU member states (EU, 2010). These regulations in part implement Directive 91/676/EEC, commonly known as the Nitrates Directive (Howarth, 2011). Few studies have been carried out to test the effectiveness of POMs, or their effectiveness in conjunction with projected climate, population, land use and land management trends and policies. There is considerable uncertainty regarding the suitability and effectiveness of some measures (Kavanagh & Bree, 2009) and further research is recommended in RBD management plans (e.g. Canney, 2009). Long-term monitoring of measures for achieving good water quality has been suggested (Hering *et al.*, 2010). Mathematical modelling can provide a potential means of testing the likely effectiveness of particular POMs aimed at reducing pollution impacts, in addition to filling gaps in data, elucidating ecological pressure-response relationships and supporting decision making in various steps of the WFD implementation process (Irvine *et al.*, 2005; Volk *et al.*, 2009). Although successful implementation of the WFD will require modelling throughout management cycles, dynamic modelling is still a relatively unused technique in water management in the context of the WFD (Yang & Griffiths, 2010).

The aims of this chapter are to apply two dynamically linked models, a catchment pressures model (GWLF) and an ecological response model (DYCD) to Lough Mask to:

1. quantify the effects of potential changes in catchment pressures (e.g. human population, livestock numbers and agricultural practices) on the trophic status over a 6-year RBD management cycle,
2. place the modelled impacts in the context of deriving appropriate targets for water quality management, and
3. assess the usefulness of scenario-based dynamic modelling as a means of determining effective measures for achieving water quality targets for restoration.

Lough Mask is currently characterised as good ecological status according to the WRBD Management Plan (Canney, 2009), although previously the lake was classified as ‘at significant risk’ of failing to meet WFD good water quality requirements by 2015 (Anon, 2005). The defined WFD target for the lake is good ecological status (Canney, 2009). The coupled dynamic models, GWLF and DYCD (see Section 3.2.2 for details),

were used to hindcast daily nutrient and sediment loads and in-lake nutrient concentrations and primary productivity for a control period, 2000-2006 AD. Annual and seasonal mean TP, mean and maximum chlorophyll *a* concentrations were output from DYCD and used to assign trophic status according to the modified OECD classification used to classify lakes in Ireland (OECD, 1982).

Details of the dynamic modelling methods, including model calibration and validation, used in the research are described in Chapter 3. After analysis of the relative contribution of sources of hindcast modelled catchment P loading (presented in Chapter 6; Section 6.2.1), the measures set out in the WRBD management plan (Canney, 2009) and relevant literature, a broad range of management scenarios were derived to assess the potential impacts of changes in catchment pressures, including variations in human and livestock population levels, land use change, septic tank performance and slurry spreading period, on trophic conditions in Lough Mask, over the control simulation period (2000-2006 AD) (Table 7.1). The scenarios are described in detail in Section 3.2.2.3. Changes in catchment pressures based on published economic and policy trends were incorporated in some scenarios, while others were developed with the aim of deriving appropriate management measures for achieving water quality targets.

7.3 Results

7.3.1 Control simulation

Modelled annual mean TP concentrations in Lough Mask ranged from c. 16.7-18.5 $\mu\text{g l}^{-1}$, while modelled annual mean chlorophyll *a* concentrations ranged from c. 10.2-14.9 $\mu\text{g l}^{-1}$ indicating mesotrophic conditions (Figure 7.1). For modelled annual mean TP concentrations, the mean reduction required to reach oligotrophic values was 43 % (range = c. 40-45 %), while modelled annual mean chlorophyll *a* concentrations required a mean reduction of 33 % (range = c. 21-46 %) to reach oligotrophic values.

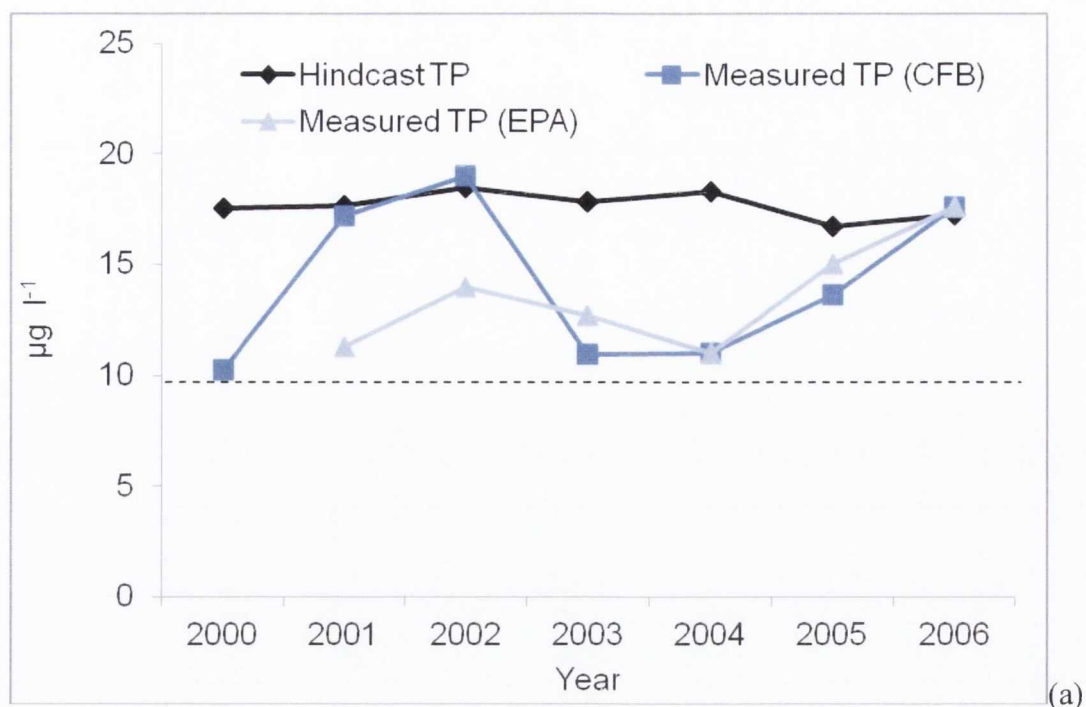
Of the catchment modelled annual TP loads to the lake for the control period (c. 54.4 $\text{kg km}^2 \text{yr}^{-1}$), the majority was derived from land use runoff and groundwater (c. 45%) followed by livestock (c. 43%), while human population contributed a relatively small proportion (c. 7%) via rural septic systems and c. 5% via urban STPs (Figure 7.2).

Table 7.1 Characterisation of management scenarios (see Section 3.2.2.3 for detailed descriptions)

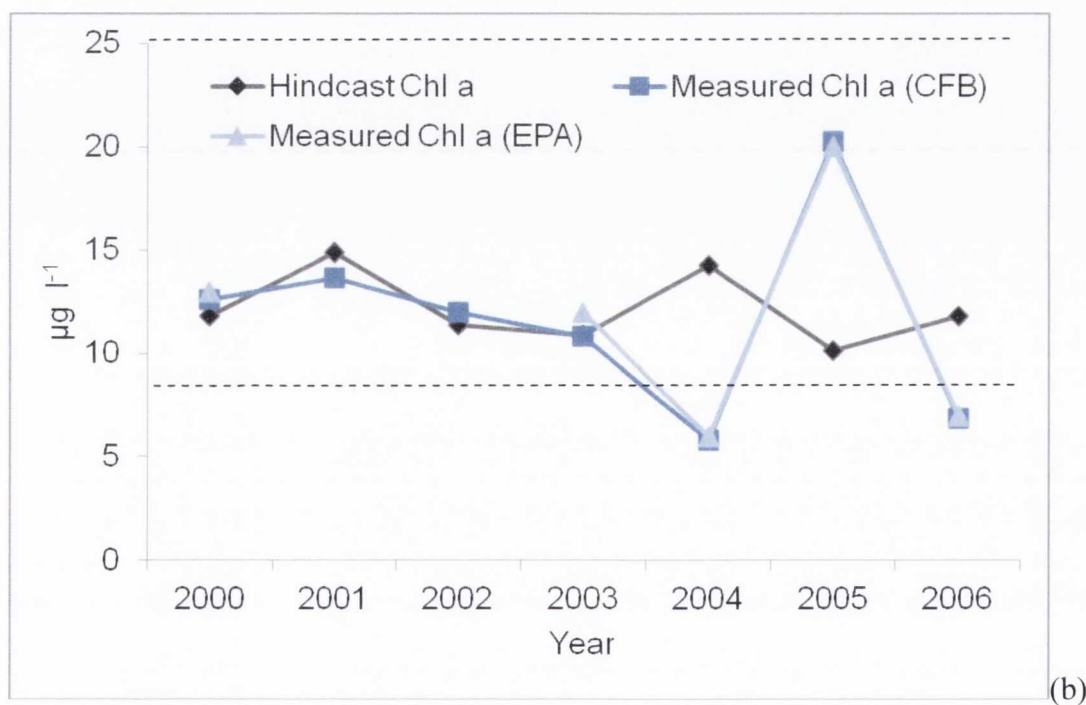
Scenario	Measure	Implementation in model*
0: Control	None	None
1: Livestock I	Reduction in cattle and sheep numbers	Cattle - 13%; Sheep - 13%
2: Livestock II	Total destocking of cattle; increase in sheep	Cattle - 100%; Sheep + 50%
3: Livestock II	Reduction in cattle	Cattle - 25%
4: Livestock III	Reduction in cattle	Cattle - 50%
5: Livestock IV	Reduction in P concentration of cattle feed to pre-1980 level	P output per head of cattle - 20%
6: Livestock V /agricultural practice I	Reduction in cattle & reduction in P concentration of cattle feed	Cattle - 50%; P output per head of cattle at pre-1980 level
7: Land use I	Decrease in productivity of agricultural grasslands	High productivity pasture - 50%; Low productivity pasture + 50%
8: Land use II	Change from predominantly pasture to arable land use	High productivity pasture - 50%; arable land + 50%
9: Septic systems	Upgrade of septic tanks	All septic tanks assigned to 'normal' category
10: Agricultural practice II	P-removal from slurry prior to land application	90% reduction in cattle P output per head used in calculation of slurry loads
11: Human pop	Increasing human population	Increase human pop 1.5% per annum
12: Land use III	Intensification of livestock-based agriculture	Increase P in runoff from high productivity grasslands + 25%; decrease cattle - 10%
13: Land use IV	Increase in forest cover (on agricultural grasslands and peatlands)	Increase in forest to 17% of total land use area; decrease in high productivity grasslands & unexploited peat bogs
14: Agricultural practice III	Change in permitted dates for slurry spreading	1 st April - 30 th September

Table 7.2 Mean difference (%) and standard deviation (in parentheses) between modelled summer and winter mean total phosphorus (TP) and mean chlorophyll *a* concentrations between each scenario and the control simulation

Year	SC1	SC2	SC3	SC4	SC5	SC6	SC7	SC8	SC9	SC10	SC11	SC12	SC13	SC14
Summer TP	6.3 (9.3)	-48.1 (13.5)	-1.8 (10.0)	-13.9 (8.6)	8.6 (7.3)	-22.8 (9.5)	13.9 (10.5)	14.2 (10.2)	0.0 (11.7)	-45.4 (12.8)	12.9 (10.1)	13.0 (9.9)	17.6 (8.2)	26.4 (11.4)
Winter TP	-11.9 (5.4)	-33.7 (3.1)	-14.9 (4.6)	-20.9 (4.0)	-12.3 (5.3)	-24.4 (3.5)	-9.2 (5.7)	-9.4 (5.6)	-20.4 (5.2)	-36.4 (2.8)	-10.9 (5.6)	-10.7 (5.5)	-9.2 (6.1)	-14.8 (3.8)
Summer mean	25.1 (14.3)	-64.3 (82.8)	20.1 (14.2)	12.6 (16.5)	27.5 (16.3)	-5.6 (24.7)	28.5 (14.3)	29.5 (14.4)	20.9 (14.4)	-57.3 (68.7)	31.6 (14.8)	29.8 (14.9)	38.1 (14.6)	25.3 (13.9)
chlorophyll <i>a</i>	-42.7 (1.4)	-106.5 (1.0)	-59.0 (1.5)	-58.5 (1.7)	-35.4 (2.0)	-66.6 (1.8)	-29.5 (2.3)	-32.7 (1.9)	-83.2 (1.3)	-106.9 (1.1)	-40.3 (2.0)	-21.1 (1.6)	4.3 (3.6)	29.0 (4.5)



(a)



(b)

Figure 7.1 Hindcast and measured annual mean TP (a) and annual mean chlorophyll *a* (b) concentrations in Lough Mask for the control simulation. Lower dashed line indicates oligo-mesotrophic boundary, upper dashed line indicates meso-eutrophic boundary

The relative contributions of the modelled TP loads from the main subcatchments to the modelled total catchment loads are detailed in Appendix U. Considerable seasonal variation was evident in the relative contribution of catchment sources to modelled TP loads. Modelled spring TP loads came primarily from livestock (c. 37%) and land use (c. 35%), whereas summer loads were sourced mainly from land use (c. 38%) and rural septic systems (c. 31%). Modelled autumn TP loads were sourced primarily from land use (c. 61%) followed by rural septic systems (c. 21%), while modelled TP loads for winter consisted mainly of land use (c. 55%) followed by livestock (c. 19%).

7.3.2 Management scenarios: in-lake trophic status

Modelled annual mean TP concentrations for Lough Mask (Figure 7.3 a) were reduced in all scenarios that involved reductions in livestock numbers or changes in agricultural practices (Scenarios 1-6 and 10), and Scenario 9 that included upgrading of rural septic systems (Figure 7.3 a; Table 7.2). For the remaining scenarios, which included changes in land use, increased human population and a reduction in the allowable period for slurry spreading, modelled annual mean TP concentrations were increased when compared with the control simulation. Only in Scenarios 2 (destocking of cattle, 92 %, and 50 % increase in sheep numbers), 4 (50 % reduction in the catchment livestock population), 6 (reduction in P output per head of livestock to pre-1980 levels and 50 % reduction in catchment livestock numbers) and 10 (P-reduction of cattle slurry before application to land) was the reduction in modelled annual mean TP concentrations large enough to reach requirements for oligotrophic conditions.

Modelled annual mean chlorophyll *a* concentrations were reduced in all scenarios. The greatest reductions (> 30 %) occurred for scenarios that included reductions in livestock by more than 50 % (Scenarios 2, 4 and 6), reduction in the P output per head of cattle to pre-1980 levels (Scenario 6) and reductions in the P content of slurry (Scenario 10) (Figure 7.3 b; Table 7.2). Only Scenarios 2 and 10 resulted in reductions in modelled annual mean chlorophyll *a* concentrations of > 33 % when compared with the control simulation, i.e. the reduction required to meet oligotrophic levels. Scenario 3 (a reduction in cattle numbers by 25 %) and 9 (upgrading of septic systems in the catchment) also resulted in substantial reductions in the modelled annual mean chlorophyll *a* concentrations (c. 25 % and c. 28 %, respectively). For all other

scenarios, the modelled annual mean chlorophyll *a* concentrations were reduced by < 25 %.

7.3.3 Management scenarios: catchment TP loading

Scenarios 2, 6 and 10 had the largest reductions in modelled annual mean TP concentrations (44 %, 25 % and 44 %, respectively) and annual mean chlorophyll *a* concentrations (72 %, 22 % and 67 %, respectively) relative to the control simulation.

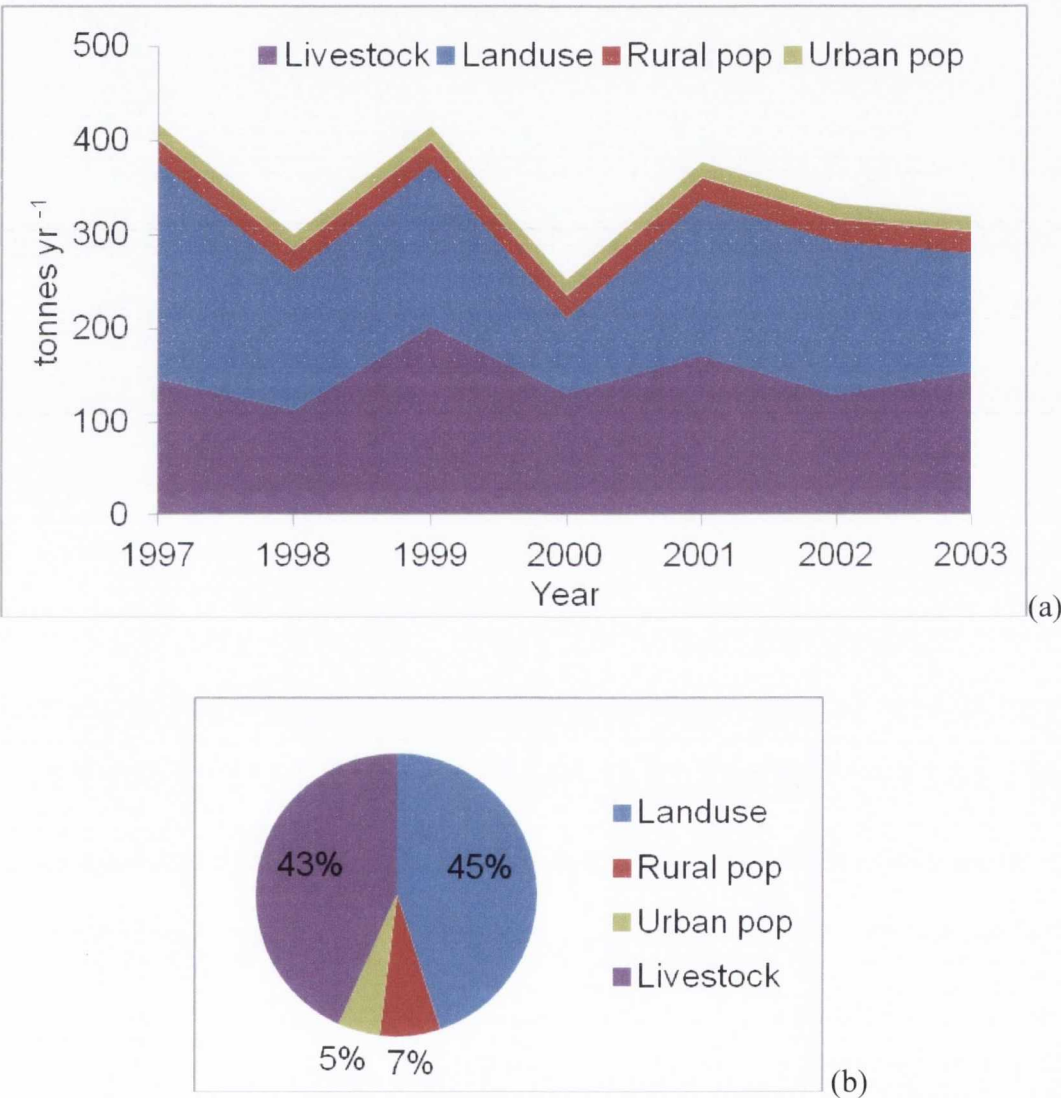
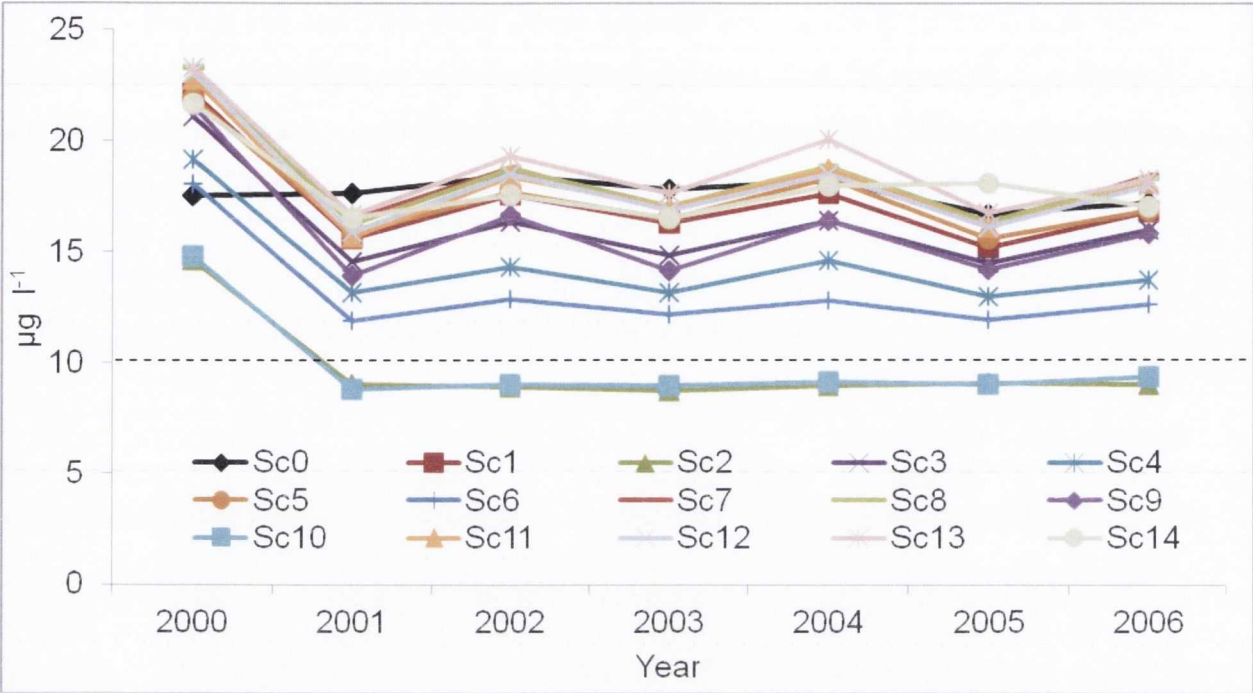


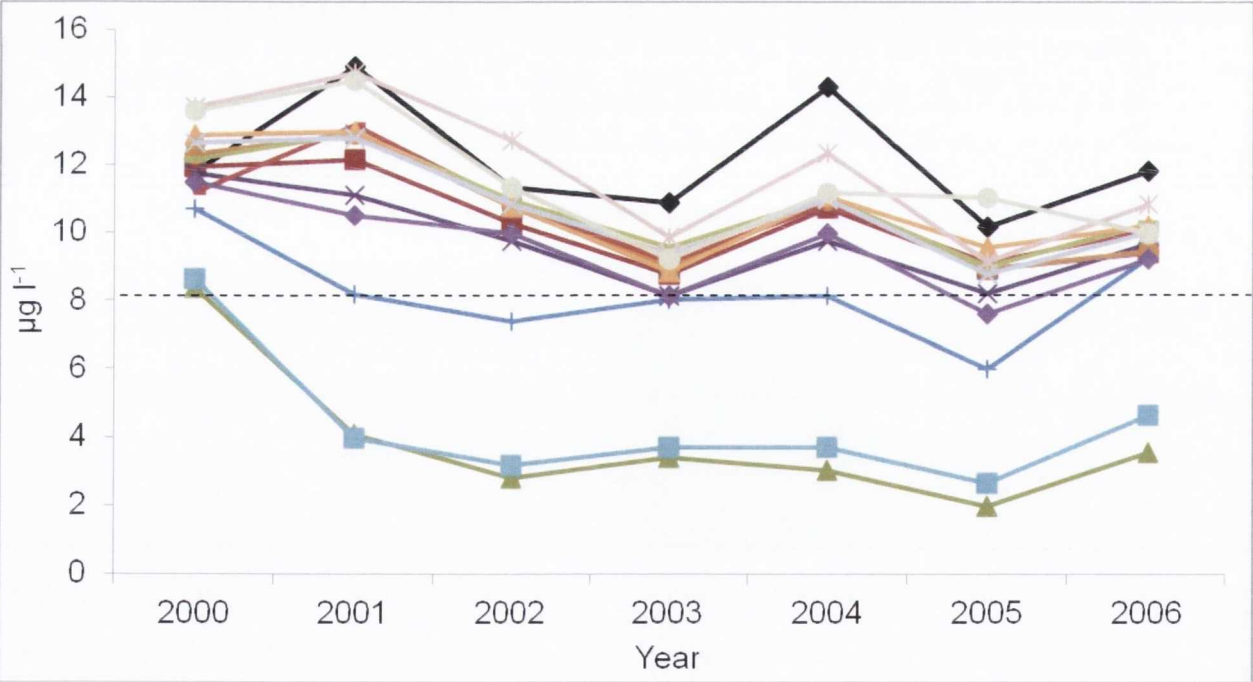
Figure 7.2 Relative contributions (%) of nutrient sources to modelled catchment TP loading (a) annual means (b) mean for the period 2000-2006 AD, for the control simulation

The reductions in modelled annual catchment TP loads for the latter scenarios were 44 %, 27 % and 23 % respectively, when compared with the control simulation.

Differences among the contributions of sources of P for the 3 scenarios are presented in Figure 7.4 (a-c) and described below. Modelled annual catchment TP loads for the 3 scenarios are provided in Appendix W.

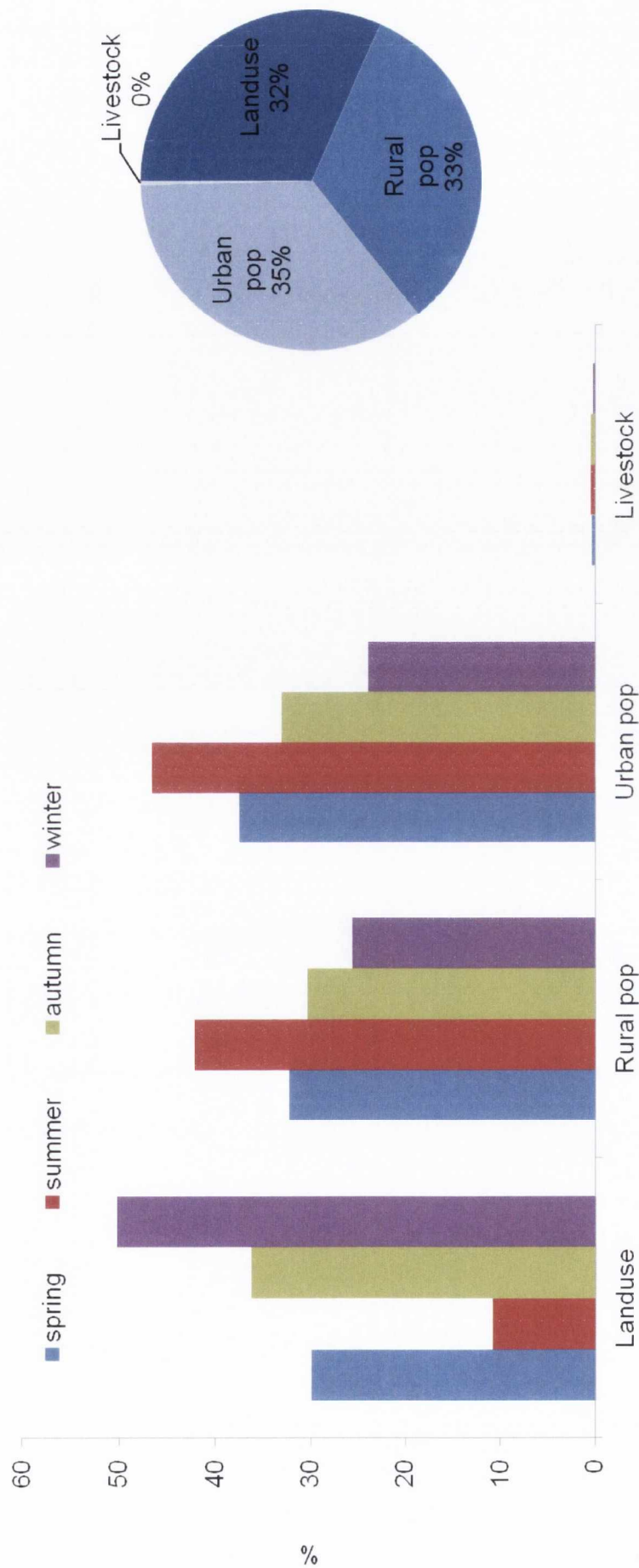


(a)



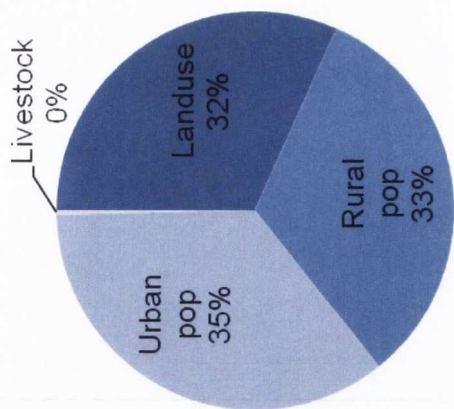
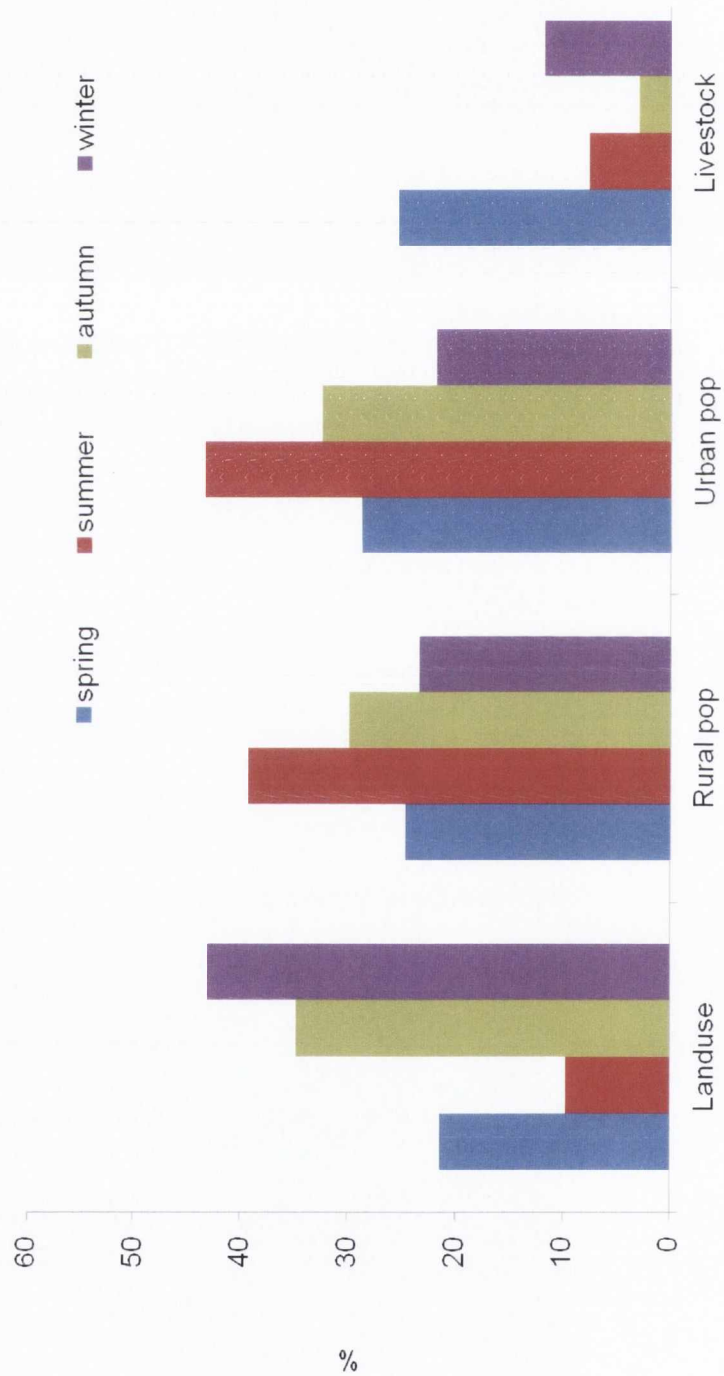
(b)

Figure 7.3 Modelled annual mean TP concentrations (a) and annual mean chlorophyll *a* concentrations (b) for Lough Mask for all scenarios. Dashed line indicates oligo-mesotrophic boundary



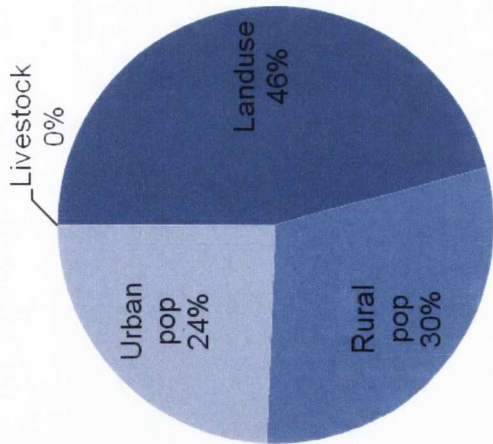
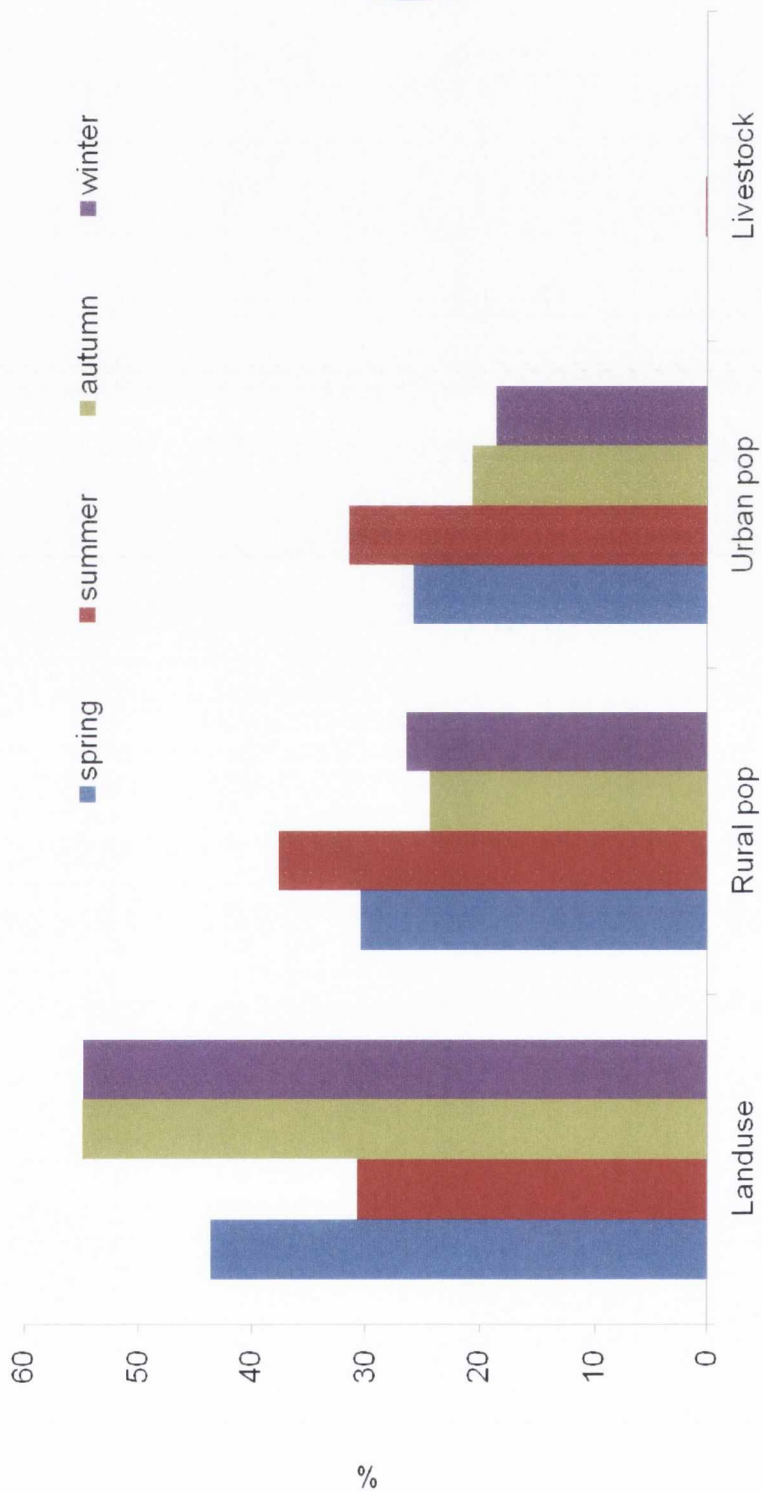
(a) Scenario 2

Figure 7.4 Variations in the relative contribution of catchment sources to modelled annual and seasonal TP loads for Scenarios 2 (a), 6 (b) and 10 (c)



(b) Scenario 6

Figure 7.4 (continued)



(c) Scenario 10

Figure 7.4 (continued)

Of the modelled annual TP load for Scenario 2 (mean = c. 17,695.0 kg yr⁻¹; σ = 4292.6 kg yr⁻¹), the contribution from livestock was reduced from c. 43 % in the control simulation to c. 0 %; the relative contributions from urban human population, rural human population and land use increased to c. 35 %, 33 % and 32 %, respectively. The reduction in the contribution of livestock was particularly evident in modelled spring and winter TP loads, where livestock comprised 0 % of the total TP load compared with c. 66 % and c. 41 %, respectively, in the control simulation. Reductions in the modelled annual mean TP load (mean = c. 23,307.2 kg yr⁻¹; σ = 4933.6 kg yr⁻¹) for Scenario 6 reflected reductions in the livestock and land use contributions when compared with the control period. Reductions in the relative proportion of livestock TP was most apparent in modelled spring and winter loads, while the reduction in the contribution from land use was most apparent in modelled autumn loads, followed by modelled summer and winter loads. Modelled annual TP loads (mean = c. 24,235.2 kg yr⁻¹; σ = 5138.9 kg yr⁻¹) for Scenario 10 were reduced mainly as a result of decreased livestock numbers (reduced to c. 0 % of the total TP load). Reductions in the livestock component were apparent in modelled summer and winter loads, but primarily in modelled spring loads (reduced from c. 66 % in the control simulation to c. 0 %). Scenario 9, involving complete upgrading of rural septic systems in the catchment, resulted in a c. 7 % reduction in modelled annual TP loads, evident primarily in modelled summer loads (reduced by c. 16 % when compared with the control simulation). The reduction in the allowable period for slurry spreading (Scenario 14) did not result in a reduction in modelled annual TP loads.

7.4 Discussion

Modelled annual mean TP and mean chlorophyll *a* concentrations indicated high mesotrophic conditions in Lough Mask for the duration of the control simulation period, 2000-2006 AD. Comparison of modelled data with available monitored data for annual mean TP and chlorophyll *a* concentration data for the lake revealed that the datasets were in reasonably good agreement for this period. Sediment-based TP reconstructions generally overestimated levels indicated by monitoring data. Long-term monitored annual mean data were based on relatively coarsely resolved monitoring data (< 5 times per year).

Available monitoring records, and the results presented in Chapter 5, suggest that substantial nutrient enrichment commenced in the lake in the 1970s, with evidence of oligotrophic conditions prior to c. 1950 AD. Evidence of nutrient enrichment thus appears to conflict with the current ecological status of Lough Mask, described as ‘good’ in the WRBD management plan. Moreover, even though the chemical status has yet to be determined according to the same plan, the latter states that basic measures, such as full enforcement of S.I. 610 of 2010 for addressing nutrient loading pressures from agriculture, will suffice for protection of deterioration of water quality (Canney, 2009). Analysis of the relative contributions of nutrient sources to modelled catchment TP loads indicated that agriculture, via both land use runoff and livestock, was the main source of nutrient loading and elevated nutrient levels in Lough Mask.

The effects of diffuse agricultural P loading on trophic conditions in lakes are well known (Jennings *et al.*, 2008; Bowes *et al.*, 2010; Keatley *et al.*, 2011). Basic measures to address nutrient loading from agricultural sources, i.e. the enforcement of S.I. 610 of 2010 (Howarth, 2011), which are incorporated in the control simulation, are unlikely to achieve good water quality in catchments where the predominant land use is agricultural grasslands, over a 6-year RBD management cycle. Together with evidence for substantial non-compliance of farmers with these regulations (> 30% of farms) (Canney, 2009), this presents a negative outlook for water quality restoration and prevention of deterioration.

Projected increases in the productivity of agricultural grasslands, as a result of the intensification of livestock-based farming, resulted in increased modelled annual mean TP concentrations. Projected changes in catchment land use and, to a lesser extent, human population, based on published policies and economic trends (e.g. Sweeney, 2003; CSO, 2008), are likely to result in further deterioration in water quality particularly elevated trophic status. Deterioration in lake trophic conditions have been linked to changes in land use and population elsewhere in Ireland (Jennings *et al.*, 2009), Europe (Kamari *et al.*, 2008) and worldwide (Hamilton *et al.*, 2010). However, there is substantial uncertainty regarding the outcome of current and future policies and, as a result, large variations in projections, particularly those relating to agricultural activity (van der Keur *et al.*, 2008). Moreover, the scenario results presented are subject to uncertainty associated with the effects of other potential pressures, in particular climate change (Falloon & Betts, 2010; Haasnoot *et al.*, 2011). There is considerable uncertainty

in the projections of future climate and their specific impacts on water and agriculture (Falloon & Betts, 2010). Projected changes in climate for the west of Ireland include increases in rainfall, frequency of flash flooding and diffuse nutrient loading in winter and warmer and drier summers (IPCC, 2007; Fealy *et al.*, 2010). The potential effects of such changes include the offset of recovery from eutrophication (Johnson *et al.*, 2010; Hamilton *et al.*, 2010) or reductions in the impacts of nutrient loading pressures (Fragoso *et al.*, 2011), and may interfere with the outcome of the current POMs for nutrient loading pressures. Thus, projected climate change must be considered in water quality management and current POMs may need to be reconsidered in light of the projected changes.

Destocking of cattle in the Lough Mask catchment resulted in the greatest improvement in modelled trophic conditions, a return to baseline (oligotrophic) status representing conditions prior to significant human impact. Projections of relatively low reductions in livestock numbers resulted in improved modelled trophic status also, but not to baseline conditions. In fact, reductions in livestock numbers by at least 50 % may be required to restore baseline conditions in Lough Mask, and in similar catchments dominated by intensive agriculture. Similar substantial reductions in livestock stocking density were also found to be the most effective measure for reducing nutrient output in catchments dominated by agriculture in the UK (Cardenas *et al.*, 2011) and elsewhere in Europe (Vagstad *et al.*, 2009). However, the effects of reducing cattle stocking densities can be site-specific. Capece *et al.* (2007) found that reducing stocking densities was not an effective measure for reducing nutrient loads to water in agricultural catchments in south Florida, because of a high retention of P in catchment soils from fertiliser applications in the past. The effects of reduced stocking densities on nutrient loads to water may also be offset by increased nutrient concentrations in livestock feed (Taylor *et al.*, 2012). Moreover, reductions in cattle stocking densities are considered a relatively expensive restoration measure to implement (Fezzi *et al.*, 2010).

Projected human population increases resulted in relatively small increases in eutrophication effects, and these were greatest in summer, when the relative contribution of septic tanks to the modelled catchment TP load was high. Ireland's non-compliance with EU directives, in particular the 1975 Directive on Waste (75/442/EEC) (IPA, 2009), means that more stringent monitoring and inspections of septic tank functioning and maintenance are likely to become standard practice. The importance of the septic tank

contribution to catchment TP loads, particularly during summer months, has also been highlighted elsewhere (Jennings *et al.*, 2009; Bowes *et al.*, 2010; Greene *et al.*, 2011; Macintosh *et al.*, 2011). In the scenario that tested the outcome of all septic tanks in the catchment operating effectively, i.e. full implementation of the EU Directive on Waste, the reduction in modelled annual TP loading was relatively low. The reduction in modelled summer TP loads, i.e. when high TP loading has the greatest potential for impacting trophic conditions, however, was more pronounced.

Kronvang *et al.*, (2009) identified the effectiveness of measures that include dietary reductions of nutrients in cattle feed and slurry processing of nutrients as a major knowledge gap. In this chapter, scenarios that involved changes in agricultural practices, a reduction in the P content of cattle feed (to pre-1980 AD levels), thereby reducing the P output per head of cattle, and P removal from slurry resulted in considerable reductions in modelled annual mean TP concentrations and annual mean chlorophyll *a* concentrations supporting the significance of such measures. Maguire *et al.* (2009) also found that changes in dietary and feed adjustments resulted in significant reductions in nutrient inputs to Chesapeake Bay. Furthermore, not only are such measures effective in controlling nutrient export from agricultural sources but they are also some of the more cost-effective measures (Sharpley *et al.*, 2009), when compared with the cost of reductions in the quantities of slurry spreading or reductions in stocking densities. Changing the period for slurry spreading from that permitted by S.I. 610 of 2010 to the optimum period recommended for slurry spreading in Ireland by Hyde & Carton (2005) resulted in elevated trophic status.

The results of this research indicate that the recovery of aquatic ecosystems from nutrient enrichment associated with agricultural intensification, which commenced in the latter part of the 20th century, is likely to be slow or non-existent even with full implementation of main basic measures for restoration. Even with full enforcement of S.I. 610 of 2010 in Ireland, recovery from agricultural P enrichment in soils may take from 7 to 15 years (Schulte *et al.*, 2010) and up to 20 years for groundwater (Fenton *et al.*, 2011). The findings also support suggestions that the aims of the WFD are too ambitious and basic measures are unlikely to succeed in meeting WFD objectives of good ecological status in the proposed time frame (Kavanagh & Bree, 2009; Volk *et al.*, 2009; Hering *et al.*, 2010; Hadjikakou *et al.*, 2011). Nevertheless, the results presented in this chapter indicate that WFD targets for agricultural catchments and reversal of

nutrient enrichment in lakes could be achieved relatively rapidly through implementing supplementary measures that involve changes in agricultural practices (such as reductions in the P content of cattle feed or removal of P from slurry used as fertiliser). In addition to being cost effective, such measures present a more feasible option for the agricultural sector than severe reductions in livestock numbers, which would be required to achieve comparable improvements in water quality.

Riparian zone management involving the establishment of vegetated buffer strips between land and watercourses to retain and reduce diffuse export of nutrients, common in some UK catchments, which was not included in the current study, may also provide a relatively cost-effective measure for addressing diffuse nutrient loading from agriculture (Smart *et al.*, 2001). Riparian zone management has not been investigated as a potential measure for P management in RBDs in Ireland. However, some studies have shown that biochemical processes in vegetated buffer strips can actually result in increased P loss from soils to streams (e.g. Smart *et al.*, 2001).

The scenario results presented are inherently subject to uncertainty associated with the models and other potential pressures, such as climate change. The scenario data presented are based on the accuracy of literature values chosen for model parameters (e.g. particulate and dissolved nutrients for land uses, per capita nutrient output per head for the human and animal populations, and phytoplankton growth rates) and how realistic model calculations are. Well-known techniques for estimating uncertainty in relatively simple water quality models have not been developed to cater for complex models like DYCD with many model parameters (Trolle *et al.*, 2011). Both models have, however, been used extensively in other lakes and have been found to make accurate predictions of nutrient concentrations and phytoplankton populations (e.g. Burger *et al.*, 2007; Trolle *et al.*, 2008), with or without manual calibration (which was performed in this study) (Trolle *et al.*, 2011). Furthermore, proposals to abolish the EU milk quota scheme in 2015 are predicted to lead to an increase in dairy cattle by c. 11 % in Ireland (European Commission, 2009), and therefore increased diffuse nutrient loading.

7.5 Conclusion

In conclusion, the findings of the research presented indicate that:

- basic measures for restoration of water quality in catchments dominated by livestock-based agriculture are unlikely to be successful,
- supplementary measures, such as reductions in the intensity of agricultural activity, lower stocking density on land or nutrient management planning (that includes removal or treatment of slurry or reductions in the nutrient content of cattle feed) may be necessary to restore water quality to baseline trophic status in such catchments, and
- integrated dynamic catchment and in-lake modelling can be used to help identify where POMs should be focussed to improve water quality and, ultimately, test the efficiency of POMs before their costly implementation.

Chapter 8

General Discussion

The main aim of this research project was to determine the extent to which a multidisciplinary approach, combining palaeolimnology, historical catchment and climate data and dynamic modelling, could contribute to improvements in both understanding of trophic pressure-response relationships and, ultimately, aquatic management. Lough Mask, a large and complex lake in the west of Ireland, was a particular focus for the study. In this final chapter, first the limitations and strengths of the methods and data are critiqued. Then the research questions relating to Chapters 4, 5, 6 and 7 are addressed. Finally, the key findings arising from the research questions are discussed in detail and suggestions are made for future research.

8.1 Critique of the research

This study sought to investigate whether a multidisciplinary approach, combining palaeolimnology and dynamically-linked models, can contribute to understanding aquatic ecological pressure-response relationships and thereby assist the management of lakes. The findings demonstrated that a dynamic modelling approach provides a cost-effective, time-efficient and useful means of managing lake ecosystems and implementing water quality policies. The provision of long-term, otherwise unavailable, data relating to lake ecological pressures and responses using two independent and complementary techniques can also provide greater confidence in the accuracy of the reconstructed ecological pressure-response relationships. Analysis of the discrepancies between sediment-based and dynamically-modelled reconstructions of in-lake conditions helped to elucidate the limitations of the techniques and indicated where further development efforts to improve the techniques should be focussed.

Problems associated with the palaeolimnological approach, and the uncertainty in the lake sediment-based reconstructions in particular, were major challenges in the research. Initial difficulties in the sediment-based research included locating good and reliable locations for sediment coring. Sediment coring attempts around the southeast part of the lake, where one of the water quality sampling sites used in the BUFFER project was located, were unsuccessful. K. Rogers (WRBD, pers. comm.) reported generally low levels of sediment accumulation in the southeast part of the lake, and this might explain the difficulties encountered in coring. Additional sediment coring was carried out in the deep channel-like subbasin at the western side of the lake, but did not yield as reliable or as long sediment cores as that already obtained for the deepest point

coring site. Furthermore, the complex and non-uniform nature of sediment accumulation in Lough Mask (detailed in Section 4.4), in addition to the low number of dates and dating resolution for the older part of the sediment record, mean that interpretations of the sediment-based data, particularly for the Robe and deepest point coring sites, need to be treated with caution. The complexity of the study site used in this research, in terms of basin morphology and in-lake processes, which are not fully understood, mean that the sediment-based data may be subject to considerable errors that are impossible to quantify (Whitmore *et al.*, 1996). For example, wind-induced mixing and resuspension of sediment in the lake are not well-understood and difficult to quantify, and are likely to have an important influence on the quality of the sediment records.

Interpretations of the sediment-based data are subject to further uncertainty associated with poor subfossil preservation in some parts of the sediment record. Differential diatom dissolution, evident in the sediment core from the deepest point, and the associated compositional biases in sediment diatom assemblages add to the uncertainty in the sediment-based interpretations of past environmental changes. Moreover, interpretations of long-term ecological pressure-response relationships are subject to uncertainty associated with the depauperate horizons in the diatom and macrofossil records.

The site-specific nature of lake sediment records evident in the current study and elsewhere (e.g. Taylor *et al.*, 2006) limit the extent to which the interpretations based on one study site can be extrapolated in a regional or wider context. This was addressed to some extent in the current study by examining the findings in the context of palaeoenvironmental data from the same region and farther afield. Difficulties in matching sediment, instrumental and modelling datasets for statistical comparisons included the differences in their temporal resolutions, often considerable potential errors associated with the data and the several different approaches that can be taken. In addition, the possibility of lagged in-lake responses to changing ecological pressures further restricts the interpretations of these statistical comparisons.

Furthermore, the interpretations are subject to the inherent uncertainty involved in modelling. All modelling exercises include varying levels of uncertainty in the estimates produced. These relate to the errors associated with model structure, the

driving data and the data used for parameterisation of the models. Models are effectively simplifications of reality. Therefore, models will inevitably only include the dominant processes contributing to the parameters of interest. Sources of uncertainty in the catchment modelling include the suitability of the meteorological data used, inaccuracies in the measured flow data used for model calibration and error relating to input nutrient data, including error associated with sampling methods and analysis. Further uncertainty is associated with the selection of appropriate input data from the literature, where catchment data were not available. The uncertainty arising from the catchment modelled streamflow and nutrient loads is carried forward in the input data used to run the ecological response model, and is potentially propagated. Additional uncertainty is also associated with the model parameter values used for phytoplankton and zooplankton groups in CAEDYM, which were based on a combination of literature optimised values. Further uncertainty in the scenario-based modelling predictions includes that associated with the projected changes in catchment pressures themselves and potential pressures that were not incorporated in the scenarios.

The application of the approach was also limited by the lack of suitable and high resolution monitoring data required for calibrating and validating the models. A particular weakness of the current study was the absence of contemporary lake water and inflow monitoring Si data, and sediment-based Si data for Lough Mask, for the purpose of calibrating the dynamic models and investigating the controls of Si limitation in Lough Mask during the mid-late Holocene. The importance of Si limitation in Lough Mask was unknown prior to the current study, and due to the financial and time constraints these data could not be collected. Si concentration data would provide further insight into the possibility of lagged biological responses to changes in climate and catchment pressures, in addition to improving the modelled in-lake responses.

Interpretations of long-term ecological pressure-response relationships were limited by uncertainty in the sediment-based techniques relating to the relatively low resolution of the sedimentary record. In addition, interpretations of long-term ecological pressure-response relationships are subject to uncertainty associated with the depauperate horizons in the diatom and macrofossil records or possible breaks in sedimentation, which may be linked to interactions between climate and catchment conditions. Comparisons with regional palaeoenvironmental data showed that the sediment-based data could provide a valuable record of long-term environmental change. Moreover, the

findings present some new and preliminary insights into the potential drivers of the absence of diatom remains in sediment records, from lakes in temperate locations, which are poorly-understood (Podrیتskea & Gajewski, 2007).

The complexity of the study lake basin was inevitably simplified in the application of the 1-dimensional in-lake response model (DYCD), the assumptions of which may not hold true. Therefore, the hindcast modelling approach may not fully incorporate the spatial complexity of Lough Mask, evident from the sediment-based data presented in this thesis. However, the application of a more spatially-detailed in-lake model would not be viable given their highly-complex nature and unrealistic, in terms of cost and time, data requirements for calibration and validation (Mirchi *et al.*, 2009). Moreover, measured nutrient data from four different locations within the lake (including the locations of the three sediment coring sites in this study) between 2001-2003 AD from the BUFFER project (Section 2.2.5) revealed that spatial variations in nutrient concentrations in the lake are low.

8.2 Research questions

In Chapter 4, the first research question ‘how have trophic conditions varied over the long term in a complex lake?’ was addressed by examining a mid-Holocene to Anthropocene record of variations in sedimentary biological, lithological and geochemical proxies. In Chapter 5, the second research question ‘what are the relative roles of climate variability and human pressures in driving trophic changes in a west of Ireland lake during the 20th century?’ was investigated, using both palaeolimnological and hindcast modelling techniques. Research Question 3, ‘can a multidisciplinary approach, combining palaeolimnological and dynamic modelling methods, be used to elucidate long-term trophic dynamics?’, was addressed in Chapter 6. Chapter 7 focussed on Research Question 4, ‘can dynamic modelling be used to design and test the effectiveness of water quality management plans?’, providing a demonstration of the broader practical relevance of the research.

8.2.1 Research Question 1: How have trophic conditions varied over the long term in a complex lake?

Sediment-based data from Lough Mask showed that trophic conditions varied throughout the mid to late Holocene but stayed within the oligotrophic range. Variations in the preservation of diatoms in the sediment cores indicated the pervasiveness of post-depositional diatom dissolution and recycling of Si from the sediment to the water column. Both diatom dissolution and Si recycling are inherently linked to climatic variability because Si concentrations depend mainly on catchment and in-lake processes, such as influx of Si from the catchment and in-lake biological uptake of Si (Neal *et al.*, 2005). Although internal lake processes are often more important determinants of in-lake Si concentrations (Nõges *et al.*, 2008), the findings presented in Chapter 4 revealed that climate-driven variations in precipitation may play an important role in dictating Si levels in the lake, and therefore the extent of diatom dissolution at the sediment-water interface. An overlap between horizons with depauperate assemblages of diatoms and macrofossil remains and those of oscillations in precipitation levels evident throughout mid-late Holocene records in Ireland and northwest Europe is evident in the Lough Mask sediment cores. This is supported by variations in sediment lithological and geochemical proxies. A possible mechanism for this relationship may be the effects of the relative influx of groundwater-dominated versus surface water-dominated inflows from the catchment on Si concentrations in the lake (Neal *et al.*, 2005). During relatively wet climatic periods, increased inflow is dominated by surface water (runoff), where the waters are mainly derived from the acidic- and organic-rich soil layer where acidic conditions prevail, and there is very limited inorganic material for weathering. During relatively dry periods, the relative contribution of groundwater to inflows is greater than the surface runoff contribution. Groundwaters are enriched with Si due to interactions with inorganic components of bedrock (e.g. aluminosilicates) that can weather and partially neutralize acidic waters from the soil zone reside, and are enriched with Ca, magnesium and bicarbonate.

Si concentrations in lakes can be reduced by biological uptake by diatoms, which occurs during the spring and summer groundwater flow-dominated periods. As P can promote diatom growth, increased levels of P can lead to a marked depletion of Si concentrations in the water column (Conley *et al.*, 2000). Si concentrations can be increased, however, during periods of high precipitation due to an increased supply of

weathered silicates from the catchments (Weyhenmeyer *et al.*, 2004; Nöges *et al.*, 2008). Aside from biological uptake and precipitation levels, other factors including in-lake processes, such as mixing (Nöges *et al.*, 2008), influence Si levels and diatom dissolution; all these factors may act alone or in combination in determining the preservation of diatoms in the sediment record from a particular site (see Section 8.3.1).

Evidence of human-induced pressures, primarily indicators of increased soil erosion, occur from as early as c. 1000 BP in the sediment record from the deepest point in Lough Mask. However, moderate nutrient enrichment, indicated by a switch from a *C. kuetzingiana*-dominated assemblage to one characterised by *F. crotonensis*, *T. flocculosa* and *A. formosa*, is evident in all three sediment coring sites in Lough Mask. The difference in timing of the onset of moderate nutrient enrichment between the three coring sites may well be a result of the relatively poor resolution of the sediment record, sediment dating uncertainties and variable preservation of diatoms and macrofossils in the sediment core from the deepest point. More substantial eutrophication that commenced during the 19th century was linked to high human population, intensive agricultural activity and modification of the catchment drainage network (see Chapter 2 for further details). Alternating periods of low to relatively high diatom concentrations, possibly linked to interactions between precipitation, catchment hydrology and Si cycling persisted throughout the Anthropocene. The main phase of eutrophication commenced in c. 1950-2006 AD. From c. 1970 AD, eutrophication appears to have been driven by climate warming, and associated with enhanced thermal stratification, and agricultural intensification.

The relationship between climate and Si dynamics and diatom productivity is complex and not fully understood (Nöges *et al.*, 2008). The interactions between precipitation, catchment hydrology and Si dynamics, and their implications, are discussed in more detail in Section 8.3.1. The trophic history of the site in the context of regional and site-specific changes in human activity is discussed further in Section 8.3.2, while the roles of coupled dynamic pressure-response models and palaeolimnological data in lake management are discussed in Section 8.3.3.

8.2.2 Research Question 2: what are the relative roles of climate variability and human pressures in driving trophic changes in a west of Ireland lake during the 20th century?

Palaeolimnological, hindcast modelling and catchment historical data for Lough Mask, presented in Chapter 5, provide new insights into multiple and interacting climate and human drivers of aquatic chemical and trophic variability during the 20th century. Moreover, evidence for the importance of the influence of oceanic climate conditions in driving aquatic trophic variability during the 20th century was presented. Few studies (e.g. Jennings *et al.*, 2000; Blenckner *et al.*, 2007) have investigated the long-term relationship between in-lake trophic conditions and variations in the NAO, which controls variations in winter climate conditions in western Europe (George *et al.*, 2010). Moreover, climate warming and agricultural activity were seemingly important factors influencing lake trophic conditions from c. 1970 AD. The results indicate that climate warming may play a more important role in dictating lake primary productivity than previously thought, and highlight the potential for the combined effects of multiple pressures, in this case climate warming and agricultural intensification, on trophic conditions.

Variations in lake water chemistry and trophic conditions in Lough Mask appear to be linked to interactions between climate (variations in precipitation, associated with the NAO, and climate warming), catchment hydrology and human activity. The importance of climate warming (and associated enhanced thermal stratification) and human (mainly agricultural) activity increased post-c. 1970 AD. Changes in the NAO, in particular a trend towards positive values, have been linked to milder and wetter winters in Britain and Ireland since the 1960s (George *et al.*, 2010). The results also indicate the possibility for an increased influence of other climatic phenomena, such as the AO or the EA-WR, on in-lake trophic conditions after c. 1970 AD. Little is known about the possible influence of the AO or the EA-WR on trophic variability in western Europe.

Lake eutrophication linked to increased diffuse nutrient loading, as a result of dramatic increases in livestock numbers and intensification of agricultural activity in the latter half of the 20th century, is well-documented in Ireland and in Europe (e.g. Keatley *et al.*, 2011). The NAO-related precipitation-nutrient availability relationship evident in Lough Mask over the 20th century is well-documented in other published studies.

Positive NAO values are linked to increased wind speeds, temperatures and precipitation in northern Europe (Jennings *et al.*, 2000). High precipitation is generally associated with enhanced runoff and resulting increased diffuse nutrient loading from anthropogenic sources (Greene *et al.*, 2011). The findings from the current study suggest that precipitation-driven eutrophication, as a result of increased diffuse nutrient runoff from agricultural land surfaces, becomes more evident post-c. 1970 AD. This has important implications for primary productivity in the lake. The potential for Si depletion as a result of diatom growth is increased with increased nutrient loading and, therefore, the potential for the dominance of other phytoplankton groups, such as cyanophytes is increased. Thus, effective management of lake ecosystems and predicting in-lake responses to future climate change may be more difficult than anticipated. Climate variability is likely to be an important, geographically-specific determining factor in the success of future catchment management plans. Moreover, consideration of the effects of multiple pressures, such as climate and agriculture, acting in combination is also likely to be important for successful catchment management.

8.2.3 Research Question 3: can a multidisciplinary approach, combining palaeolimnological and dynamic modelling methods, be used to elucidate long-term trophic dynamics during the 20th century?

The findings presented in Chapter 6 showed the benefits of using a multidisciplinary approach, combining palaeolimnological and dynamic modelling methods to reconstruct long-term trophic variability in lakes. Relatively few studies have compared reconstructions of long-term trophic conditions using different independent methods (e.g. Bennion *et al.*, 2005; Johnson *et al.*, 2010). The two independent reconstructions of trophic conditions for Lough Mask, for the last c. 100 years, were in reasonably good agreement in terms of their indicated trophic status category. However, the sediment-based transfer function approach substantially overestimated in-lake TP levels, and is therefore unreliable. However, the hindcast modelling approach performed reasonably well in reconstructing in-lake trophic conditions. The results presented in Chapter 6 ascertained the usefulness of the multidisciplinary approach for establishing baseline trophic conditions in lakes. In addition, the use of dynamic modelling allowed the relative contributions of different pressures driving changes in trophic conditions to be distinguished, and could potentially be used in lake management to assess the effectiveness of potential changes in pressures under different management scenarios.

The application of the multidisciplinary approach was limited by a lack of suitable and high resolution monitoring data required for more thorough calibration and validation of the dynamic models (see Section 6.3). In the current study, differential diatom dissolution in the sediment record, most likely as a result of post-depositional dissolution due to variations in the availability of Si in the water column, was found to influence sediment-based reconstructions (see Section 4.4 and 8.3.1). Si monitoring data were not available for model calibration in the current study. The lack of understanding of the mechanisms involved in Si cycling has also been identified as an important issue in aquatic modelling in marine systems (Dixit & Van Cappellen, 2002), and is likely to be important in modelling lake ecosystems.

Furthermore, the application of the multidisciplinary approach is subject to uncertainty (outlined in Section 8.1). In general, uncertainty in dynamic models is related mainly to uncertainty in parameter estimations (Hession & Storm, 2000). In the current study, the largest uncertainty is likely to be associated with parameters relating to the loss of nutrients from agricultural sources, and has been estimated to be no greater than that associated with relatively simple export coefficient models (Dalton *et al.*, 2010). Furthermore, the dynamically-linked models, GWLF and DYCD, have been used extensively in other lakes and have been found to make accurate predictions of lake trophic conditions (e.g. Trolle *et al.*, 2008; Naden *et al.*, 2010; Pierson *et al.*, 2010), with or without manual calibration (Trolle *et al.*, 2011). Manual calibration was performed in the current study.

The findings relating to Research Question 3 build on the suggestions by Anderson *et al.* (2006) and Johnson *et al.* (2010) regarding the benefits and limitations of a combined dynamic modelling and palaeolimnological approach to investigating lake ecological pressure-response relationships, particularly in the context of lake management. The approach can be used to elucidate long-term trophic dynamics provided certain requirements, in particular an understanding of the important controls of trophic conditions and a thorough calibration and validation of the dynamic modelling and sediment-based techniques, using suitable and high resolution monitoring data, are met. Moreover, more widespread application of the multidisciplinary approach and targeted monitoring programmes, for more thorough calibration and validation of the models, are necessary to improve the reliability of this approach.

8.2.4 Research Question 4: can dynamic modelling be used to design and test the effectiveness of water quality management plans?

Although the need for improved calibration and validation of dynamic models used in the current study has been highlighted (Section 8.1), the findings presented in Chapter 7 provide a demonstration of how a scenario-based dynamic modelling approach could potentially be used to design and test the effectiveness of lake management plans and, in the context of the WFD, POMs. Moreover, the benefits of a scenario-based modelling approach, in particular the provision of different management options that can be assessed in terms of their cost- and time-effectiveness, are palpable.

There is considerable uncertainty regarding the suitability of current POMs, in the context of implementing the WFD, in Ireland and in Europe (Taylor *et al.*, 2012). However, few studies have tested the effectiveness of POMs. Although scenario-based modelling is highly recommended for designing and reviewing the effectiveness of water quality management plans (Irvine *et al.*, 2005; Becker *et al.*, 2010; Kundzewicz *et al.*, 2010), the approach has not been applied in this context in Ireland prior to this study.

In the current study, the basic measure outlined in current POMs in Ireland and much of Europe for restoring water quality in agriculturally-impacted catchments, i.e. Good Agricultural Practice for Protection of Waters Regulations 2010 (S.I. 610 of 2010), was deemed ineffective for restoring baseline trophic conditions. From a range of supplementary measures or management options, tested using the scenario-based approach, two relatively cost-effective options (removal or treatment of slurry and reductions in the nutrient content of cattle feed) for RBD management that would restore baseline trophic conditions over a relatively short timeframe in an agriculturally-impacted catchment were found. The findings also highlighted the benefits of other potential options for RBD management for reducing catchment nutrient loads, including the full enforcement of the EU Directive on Waste (i.e. effective operation of domestic septic tanks).

The use of dynamic modelling for effective catchment management could considerably reduce the need for costly and time consuming monitoring programmes that are currently used in RBD management in Ireland and elsewhere in Europe. Moreover, the scenario-based modelling approach employed could also be used to develop more

effective water quality-relevant policies in agriculturally-impacted lake catchments. Given that the aims of the WFD have been deemed as over-ambitious by many (e.g. Volk *et al.*, 2009; Hadjikakou *et al.*, 2011), because of the short timeframe and high cost of implementation, the benefits of scenario-based modelling for use in lake management at catchment (RBD) and national levels are even more apparent.

8.3 Key findings

From the above, the key findings from the research are: the importance of interactions between climate, climate, catchment and in-lake processes in driving variations in lake water quality; the record of human impacts at Lough Mask; and the value of coupled dynamic pressure-response models and palaeolimnological data to lake management. These key findings form the basis of the following discussion.

8.3.1 The importance of interactions between climate, catchment and in-lake processes in driving variations in lake water quality

The findings presented in Chapters 4 and 5 highlighted the importance of the interactions between climate, catchment and in-lake processes in influencing changes in lake chemical and biological conditions. In this section, these interactions are explained (Figure 8.1) and the findings are discussed in the context of other palaeoenvironmental records from the west of Ireland and then in terms of their wider relevance. The interpretations outlined in this section are made with caution and are inevitably dependent on the assumptions and uncertainties outlined in Section 8.1.

8.3.1.1 Interactions between climate and catchment processes and diatom preservation

Variations in sedimentary proxies in the current study may reflect interactions between precipitation levels, hydrological routing in the catchment and Si availability in the lake that resulted in periods of post-depositional dissolution of diatoms in the sediments.

Si in lake water is fundamentally derived from the weathering of silicates and aluminosilicates in the bedrock and soils (Berner & Berner, 1996; Drever, 1997), and is greatly influenced by intense internal biological cycling (Conley, 2002), variations in

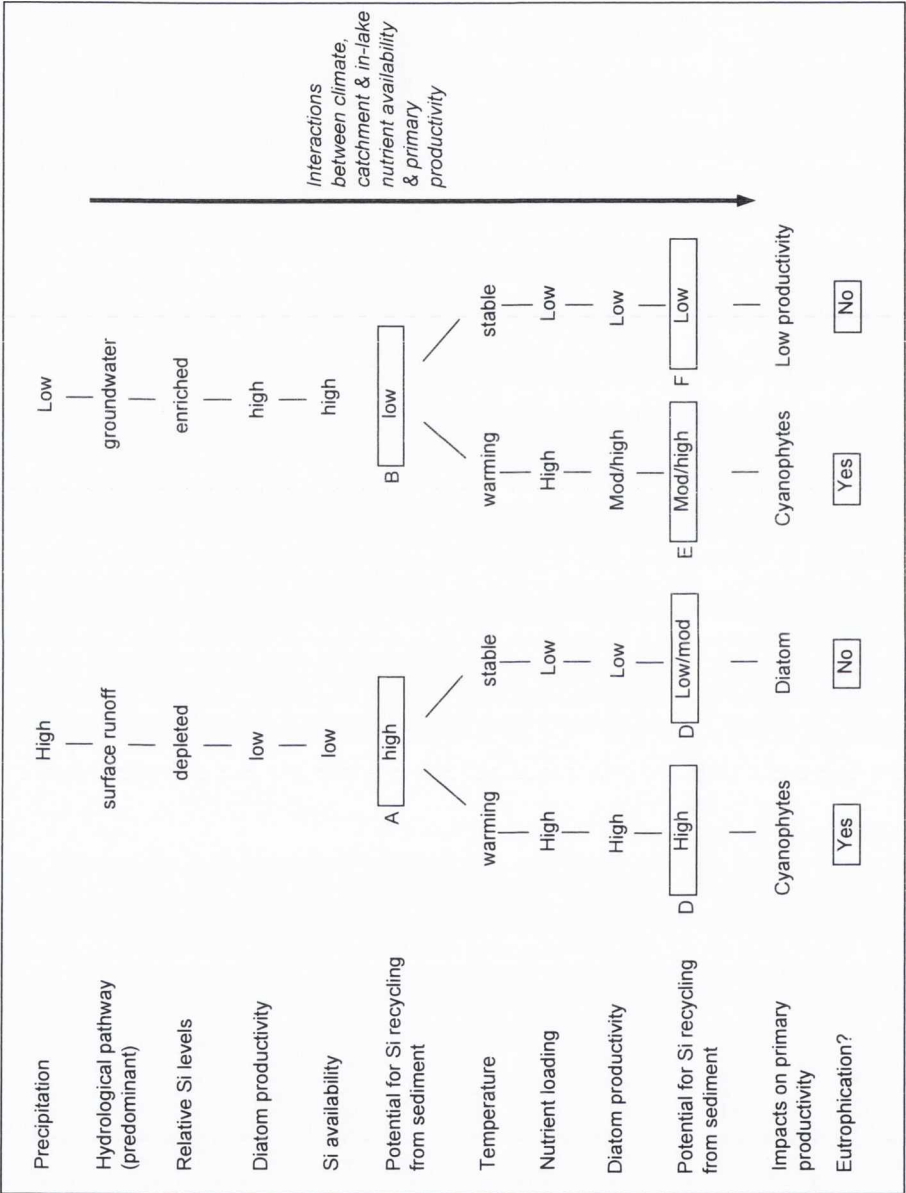


Figure 8.1 A simplified summary of the possible interactions between climate, catchment and in-lake processes in driving variations in lake water quality. The impacts of the main interactions are labelled A-F and are described in Section 8.3.1. Note: this diagram is not exhaustive and only interactions evident in the current study are included

inorganic and biogenic mineral stability (Jongmans *et al.*, 1997; Van Breemen *et al.*, 2000 a, b; Conley *et al.*, 2000; Conley, 2002; Hoffland *et al.*, 2003; Berner & Berner, 1996), climate conditions and catchment hydrology (Meybeck, 1980; White & Blum, 1995). During periods of relatively high precipitation the predominant hydrological flow path is surface runoff. Where surface waters flow through organic soils or the acidic soil zone, where there is limited inorganic material with Si- and silicate-bearing minerals for weathering or soils with low permeability and limited time for weathering, runoff can be depleted in Si (Neal *et al.*, 2005). During relatively drier periods the relative contribution of surface runoff to streamflow is reduced; the predominant hydrological flow path is via groundwater rather than runoff, particularly in karstified catchments (Sophocleous, 2002). Thus, during relatively dry periods, the influence of groundwater inputs from the limestone-dominated parts of the catchment increases. Groundwaters can be relatively enriched with Si due to greater interaction with Si- and silicate-bearing minerals in bedrock (Neal *et al.*, 2005). During relatively wet periods, the groundwater component that is relatively enriched in Si is diluted by surface runoff and, therefore, Si concentrations are reduced during high flow conditions (Figure 8.1 A). During relatively dry periods, streamflow is composed primarily of groundwater that is relatively enriched in Si and therefore Si concentrations are higher during low flow (Figure 8.1 B).

8.3.1.2 *The role of in-lake processes and the Si cycle*

Si plays a major role in determining the phytoplankton species composition in freshwater systems (Lund, 1950, 1954; Harris, 1986) and is the main growth limiting nutrient for diatoms (Wetzel, 2001). The importance of biogenic processes in regulating Si concentrations in freshwater is well recognised (e.g. Berner & Berner, 1996). Spring phytoplankton growth, dominated by diatoms, can lead to a potential for Si uptake to the extent that further diatom growth is restricted until the concentration increases later in the year. Human-induced eutrophication can lead to modification of the Si cycle (Conley *et al.*, 1993). For example, in the St Lawrence River - Great Lakes system (USA), the largest freshwater system in the world, Si depletion is recognised as an important factor dictating the ecological response to nutrient enrichment since the early 1980s (Schelske, 1986). Anthropogenic nutrient enrichment promotes diatom growth to the point where all of the available Si in the water column is utilised and diatom growth ceases (Neal *et al.*, 2005). Diatom growth in most lakes in Ireland is terminated by Si depletion, for example, following the spring bloom (e.g. Gibson *et al.*, 2000). The

combination of Si-depleted conditions and high nutrient availability in the water column can result in major changes in phytoplankton community composition, and diatoms can be replaced by cyanophytes and green algae (Wetzel, 2001). Si depletion can be an indicator of increasing eutrophication as P levels increase allowing diatoms to exhaust Si supplies (Jewson *et al.*, 1981). Changes in phytoplankton community composition can further enhance water quality problems associated with eutrophication (Figure 8.1: C) (Paerl *et al.*, 2010). This is evident in Lough Mask where two peaks in cyanophytes (in summer and late autumn/winter) followed the diatom peaks (see Section 2.2.5).

There are several other factors that may affect Si dynamics and diatom growth in a lake and, therefore, provide alternative explanations for the patterns evident in the sediment record from Lough Mask. In-lake processes, such as Si recycling from the sediment, changes in light conditions, mixing, washout, parasitism, benthic grazing and possible interactions between these factors are likely to also play a role in dictating Si dynamics in lakes (Jewson *et al.*, 1981). Jewson *et al.* (1981) found that stormy weather can interrupt diatom growth due to changes in light conditions. Gibson *et al.* (2000) found that in-lake processes are potentially more important than catchment processes in determining the available Si in Lough Neagh, located in northwest Ireland. Gibson *et al.* (2000) found that factors such as removal of diatoms via outflow, parasitism and grazing by zooplankton did not have any significant influence on diatom populations. However, silicate recycling at the sediment-water interface was found to be an important process influencing diatom growth. Following Si depletion in the water column, as a result of uptake by diatoms, the potential for Si recycling and dissolution of diatoms accumulating at the sediment surface is increased (Battarbee *et al.*, 2005). The length of time required to replenish Si in the lake water column depends on interactions between climate and catchment geomorphological units (Drever, 1997). Gibson *et al.* (2000) found that sediment release of Si from the sediment, which can increase during calm weather conditions, was a major source of Si for diatom growth the following spring in Lough Neagh. Without Si release from the sediment the maximum spring diatom crop would be only about one-third of that actually observed. Furthermore, the possible role of benthic animals and temperature in sediment Si release, or the role of an interaction between temperature and benthos activity and the possibility of interactions or potential feedback effects, is not well-understood (Gibson *et al.*, 2000). Si recycling may be delayed depending on temperature and benthic animal activity (Gibson *et al.*, 2000). A more

complete understanding of the mechanisms involved in Si cycling is likely to be important in modelling lake ecosystems. Moreover, the importance of delayed or lagged pollution-response patterns needs to be considered in lake water quality management, in particular in designing effective management plans.

8.3.1.3 Interactions between warming, nutrient loading and Si recycling

Human-induced eutrophication and climate warming, evident from c. 1970 AD, add to the complexity of interactions described in Sections 8.3.1.1 and 8.3.1.2 (Figure 8.1) and have important implications for phytoplankton community composition. During relatively wet climate periods, when the potential for Si recycling from the sediment is high, high nutrient loading and warming may promote diatom growth and Si depletion. If Si depletion occurs when catchment nutrient loading is high, then the likely result is eutrophication and the persistence of nuisance algal groups that are P limited, such as cyanophytes (Figure 8.1: C).

In contrast, low nutrient loading and relatively stable temperatures during wetter climatic periods would result in relatively low primary productivity, as availability of Si and nutrients, such as P, is low (Figure 8.1: D). Eutrophication and increased primary productivity are also likely outcomes of low precipitation levels combined with high anthropogenic nutrient loading and relatively warmer temperatures (Figure 8.1: E). The increase in diatom growth during relatively drier climatic periods may also lead to Si depletion in the water column (Figure 8.1: E) and the dominance of other algal groups, such as cyanophytes. In the absence of anthropogenic nutrient loading and climate warming (Figure 8.1: D and F), primary productivity would be relatively low and phytoplankton assemblages would most likely be characterised by diatoms.

The interactions described in this section are potentially complicated by other catchment and in-lake processes that may be responsible for the variations in preservation of diatoms in the sediment cores from Lough Mask. In fact, in-lake processes are likely to play an important role in influencing diatom preservation and may also be linked to climatic variations. Gibson *et al.* (2000) suggests the possible role for oxygen conditions in bottom waters in influencing Si release from the sediment by limiting the activity of benthic animals. Increased SARs, linked to instability in the lake water column, increased erosion of material or a large influx of drainage waters from the

catchment could also influence diatom preservation with dilution effects on. However, neither increased SARs or increased influx of allochthonous material from the catchment are evident during the periods of poor diatom preservation in the sediment cores, although this may be a consequence of the quality of chronological control. In addition to in-lake processes, several other catchment (including hydromorphological modification, land use change and agricultural activity) and climate processes influence the interpretations in the current study, particularly for the Anthropocene part of the sediment record. In Lough Mask, the climate signal may well be complicated by hydromorphological modifications which took place following widespread human depopulation and the Great Famine (Coxon & Drew, 2000).

To investigate further the possible role of climate in determining in-lake conditions and diatom preservation in the sediment, described in this section, the findings from the current research were compared with available reconstructed precipitation level data (from the west of Ireland and northwest Europe) (summarised in Figure 8.2). The comparisons described below are dependent on the accuracy and resolution of sediment dating and sampling data from each of the studies, which were variable. The timing of periods of low diatom and macrofossil concentrations in the current research closely track the timing of relatively wet climatic periods evident in palaeoenvironmental records from other sites in the west of Ireland and in northwest Europe during the mid-late Holocene (Figure 8.2), including bog sediment records (Chambers *et al.*, 1997; Chambers *et al.*, 2010), fluvial sediment records (Turner *et al.*, 2010), stalagmites (McDermott *et al.*, 1999) and lake sediment records (Dalton, 1999; Holmes *et al.*, 2007; Holmes *et al.*, 2010). Loughaunyella, located in the west of Ireland, was the only site where diatom preservation issues in the sediment were reported (Dalton, 1999). Horizons with depauperate assemblages of diatoms were omnipresent in sediment cores from Loughaunyella (Figure 8.2) and their occurrence was linked to increased inputs of allochthonous sediment to the lake (Dalton, 1999). Loughaunyella is located in a catchment underlain by alkaline bedrock with extensive peat cover (Holland, 2009), in contrast to other lakes included in the comparison, which comprise mainly sandstone bedrock and have little or no groundwater influence. Therefore, the interactions between climate, hydrology, Si cycling and nutrient availability described in this section may also apply to Loughaunyella.

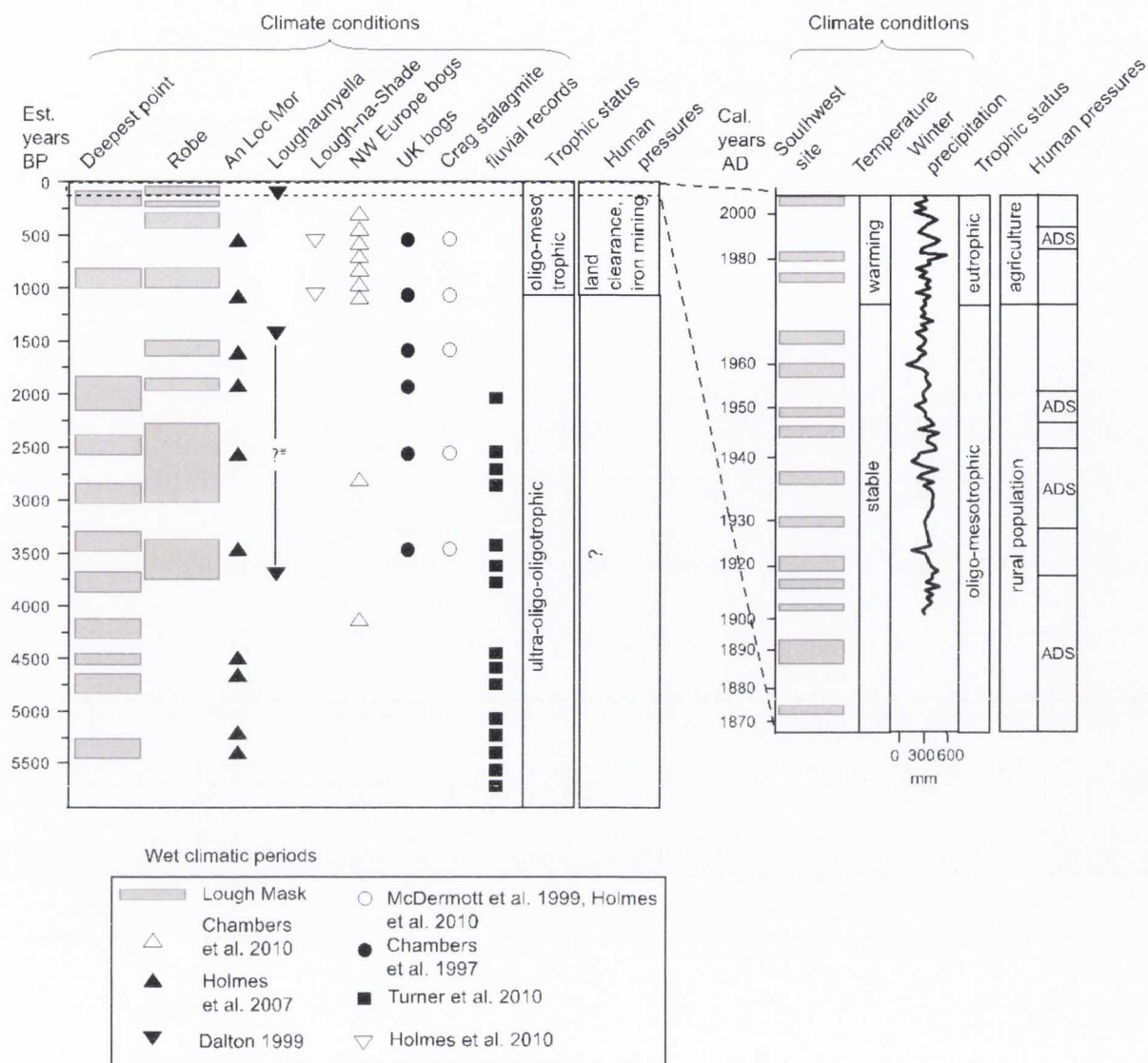


Figure 8.2 A comparison between the environmental history of Lough Mask showing variations in trophic conditions in the lake over the last c. 6000 years and potential climate and human drivers of change, and climate conditions indicated by lake sediment or other palaeoenvironmental studies

8.3.1.4 The role of climate and multiple pressures

Evidence from the current study suggests that the underlying drivers of lake water quality during the 20th century are linked to the NAO. These findings are in line with other studies based on contemporary monitoring data that have been reported elsewhere in Ireland (Jennings *et al.*, 2000; Aherne & Farrell, 2002). The influence of the NAO on lake conditions has been highlighted in lakes in the UK (Monteith & Shilland, 2007), and in northwest Europe (Larsen & Holmes, 2006). Nöges *et al.* (2008) did not find any

significant relationship between phytoplankton productivity in lakes in Europe and the NAO, and suggests that this is due to the dampening effect of in-lake processes (such as morphology, mixing and residence time) on the climate signal. However, Nõges *et al.* (2008) noted that relatively low Si concentrations in lakes, located in Sweden, Estonia and Northern Germany, during late winter/early spring occurred in high NAO years perhaps reflecting a diluting effect of increased winter flow. Early spring development of diatoms in years with high NAO has been described for the same lakes in Sweden (Gerten & Adrian, 2000) and Germany (Weyhenmeyer *et al.*, 1999) and in other European lakes (Adrian *et al.*, 1995; Weyhenmeyer *et al.*, 1999). A particular weakness of the current study was the absence of contemporary lake water and inflow monitoring Si data, and sediment-based Si data for Lough Mask, for investigating such interactions and the possibility of lagged biological responses to changes in climate and catchment pressures.

Analysis of the long-term datasets available in the current study suggested an increased influence of climate warming (and associated thermal stratification), linked to the NAO, on in-lake conditions post-c. 1970 AD. From c. 1970 AD, the influence of other climatic phenomena on in-lake ecological variability, such as the EA-WR or the AO, which are not well-understood, may have also increased. The AO is effectively an alternative expression of the NAO that incorporates data from more sites in its calculation (Thompson & Wallace, 1998). According to Monteith & Shilland (2007), based on c. 20 years of monitoring data, the deposition of chloride (derived from seasalts) in lakes in the UK is more strongly related to the AO than the NAO (Monteith & Shilland, 2007). Significant changes (increases) in the AO are also evident since the 1970s (Monteith & Shilland, 2007), and may have contributed to the variations in Si levels and the preservation of diatoms suggested by the current study. The findings indicate that lake chemical and biological responses to human pressures in a relatively complex lake, located in close proximity to the Atlantic Ocean in particular, are highly dependent on hydrological and climatic conditions. An understanding of multiple and interacting aquatic pressures and responses is vital for effective management of similar lake ecosystems, and for predicting the aquatic ecological impacts of future environmental change. The findings highlight the importance of considering multiple pressures and the role of interacting pressures in dictating in-lake dynamics.

8.3.2 *The record of human impacts at Lough Mask*

Evidence from the sediment record from the deepest point indicated human impacts at Lough Mask from possibly as early c. 1000 BP. This may have been linked to human settlement and associated woodland clearance (O'Connell *et al.*, 1986) or early agricultural activity (Overland & O'Connell, 2008) evident in the west of Ireland at this time. However, interpretation of the sediment record is subject to considerable uncertainty, particularly for the older part of the record, due to low and non-uniform SAR and differential dissolution of diatoms. Moreover, human impacts are not evident from the sediment record from the Robe site at this time, and may therefore not have affected the entire catchment.

Assuming that the sediment dating and sediment proxy data are reliable for the more recent upper part of the sediment record from Lough Mask, more substantial human impacts in the form of the commencement of moderate eutrophication are evident with the onset of the Anthropocene. Early 19th century eutrophication is consistent with high human population densities and intensive tillage-based agricultural activity (O'Grada, 1995) and associated high catchment soil erosion and nutrient loading in the west of Ireland at this time (Huang & O'Connell, 2000). The persistence of eutrophication and increased allochthonous sediment inputs, during the mid-late 19th century are, however, inconsistent with rapid recovery from eutrophication evident in other lakes in the region, associated with dramatic declines in human population and the relaxation of agricultural pressures following the Great Famine (1845-1850 AD) in Ireland (Donohue *et al.*, 2010). However, the overall eutrophication trend during the 19th century, evident in Lough Mask, is complicated by periods of poor diatom preservation and dissolution (described in Section 8.3.1), perhaps linked to flooding events during the mid-19th century (Donohue *et al.*, 2010).

Trophic conditions in Lough Mask during the mid-late 19th century are also likely to reflect locally-specific human pressures at this time, in particular extensive hydromorphological modifications in the catchment in the form of ADS, which took place following widespread human depopulation and the Great Famine (Coxon & Drew, 2000). The impacts of ADS on in-lake trophic conditions are not well-understood (Krause & King, 1994). However, more rapid surface water flow and dekarstification in catchments underlain by limestone bedrock (Coxon & Drew, 1986; Coxon & Drew,

2000) and increased sediment and nutrient load capacity of inflows (Bhattarai & O'Connor, 2004) are known. Thus, ADS are likely to result in nutrient enrichment effects in lakes. Peaks in allochthonous sediment inputs to Lough Carra were evident between c. 1852-1875 AD, also linked to ADS in the catchment (Donohue *et al.*, 2010).

In addition, major changes in food production in Ireland between 1850 AD and 1914 AD from primarily tillage to livestock-based land uses (Turner, 2002) are also likely to have contributed to moderate eutrophication during the mid-late 19th century. Huang & O'Connell (2000) linked changes in sedimentation in Ballydoo Lough, also located in the west of Ireland, during this period to intensification of livestock-based agricultural activity. Moderate eutrophication in other parts of Ireland, e.g. Crans Lough, Co. Tyrone (Taylor *et al.*, 2006; Dalton *et al.*, 2009) Lough Heron (Anderson, 1997) and Lough Neagh (Battarbee, 1978; Zhou *et al.*, 2000; Foy *et al.*, 2003), at this time has also been linked to increased diffuse nutrient loading sourced from agricultural sources. In Lough Neagh, eutrophication was linked to increased point sources nutrient loading from newly-developed urban sewerage networks (Foy *et al.*, 2003). Total C to total N (C:N) ratios in sediments that range between c. 4-6 generally indicate a large proportion of sewage derived organic matter (Brennan *et al.*, 1994). However, this was not evident in the current study.

In contrast, nutrient enrichment effects were not evident in the sediment records from many other lakes in the region, including Lough Feeagh and Lough Bunnaveela (Dalton *et al.*, 2010), Lough Leane (Douglas & Murray, 1987), Lough Currane (Treacy, 2011), Lough Inchiquin and several smaller lakes, located in the west of Ireland, examined by Taylor *et al.* (2006), or in lakes located elsewhere in Ireland, e.g. Lough Neagh (Foy *et al.*, 2003), until much later. The eutrophication history of Lough Erne (located in northwest Ireland), which has similar catchment characteristics to Lough Mask, is also similar to that of Lough Mask. Eutrophication during the early 20th century, evident from increased SARs and changes in diatom assemblages in the sediment record, and was linked to increased influxes of domestic effluent from the catchment following the construction of piped water and storm drains (Battarbee, 1986). More pronounced eutrophication post-c. 1970 AD was linked to diffuse nutrient loading from agriculture, expansion of the sewerage network, the introduction of synthetic detergents and the development of rural septic tank systems (Zhou *et al.*, 2000). Early eutrophication is also evident outside of Ireland at this time, for example, in lakes in the

UK (Fritz, 1989) and Denmark (Bradshaw *et al.*, 2006), and was also linked mainly to nutrient loading from agricultural sources.

The aquatic impacts of region-wide changes in human pressures can vary between lakes in the same region. Differences in the trophic histories of lakes located in the same region are also likely to reflect variations in local factors, such as catchment conditions (e.g. the nutrient-buffering capacity of catchments soils or variations in land use) and human activity (e.g. agricultural activity and ADS) (Taylor *et al.*, 2006). Moreover, the complexity of trophic responses is further complicated by the site-specific nature of lake responses to climate variability, which is also evident in the current study (see Section 8.2.1) and elsewhere (e.g. Battarbee *et al.*, 2005; Blenckner, 2005). The findings support the suggestions of Taylor *et al.* (2006) that general type-specific or region-specific dates for reference conditions for lakes, which are used to determine water quality targets, may be inappropriate. In particular, the findings are in agreement with a growing body of literature suggesting the need for lake reference conditions to be defined on a site-specific basis, based in Ireland (Girvan & Foy, 2006; Taylor *et al.*, 2006) and elsewhere in Europe (Davy-Bowker *et al.*, 2006; Battarbee *et al.*, 2008; Carvahlo *et al.*, 2008; Carvahlo *et al.*, 2009; Johnson *et al.*, 2010; Bennion *et al.*, 2011b).

8.3.3 The roles of coupled dynamic pressure-response models and palaeolimnological data in lake management

The current study provided a demonstration of the benefits, limitations and practical relevance of dynamically-linked models, when run retrospectively and compared with palaeoenvironmental data, for lake management. The findings are subject to the uncertainty and assumptions outlined in Section 8.1. Although the resolutions of the hindcast modelled and sediment-based datasets differ considerably, the approach potentially provides a novel and effective means of managing lake ecosystems. The benefits of using the coupled approach in lake management include: establishing reference conditions (Chapter 4) and water quality targets (Chapter 6); an improved understanding of trophic pressure-response relationships (Chapters 4 and 5) and the provision of a range of alternative nutrient management options that can be assessed based on cost- and time-effectiveness, for water quality management plans, and for implementing water quality-relevant policy (Chapter 7).

8.3.3.1 *Benefits and limitations of a coupled dynamic modelling-palaeolimnological approach to lake management*

A major issue with the application of models in environmental management is their validation or non-falsification, or evaluation of the model performance using independent data that were not used to construct the model (Ljung, 1999). This is rarely possible because of the lack of available monitoring data, particularly for relatively complex and linked models with high data requirements (Jakeman *et al.*, 2006). Although palaeolimnological techniques cannot solve the problem of non-falsification, they can provide an additional reconstructed dataset for comparison with the modelled data.

Anderson *et al.* (2006) indicate the potential for validation of hindcast modelled data with palaeolimnological data. However, this is problematic and is severely constrained by the relatively coarser temporal resolution of the sediment-based data. In addition, sediment dating errors are often much greater than the temporal scale of change under investigation. Moreover, the palaeolimnological reconstructions are also based on models that require independent validation. This type of approach has been applied used in climate studies, to attempt to validate climate models where, for example, pollen records have been used as palaeoclimate proxies to validate climate models for use in predicting future climate variability (e.g. Brovkin *et al.*, 2003; Claussen *et al.*, 2003). The approach has also been used for vegetation dynamics models (e.g. Tinner *et al.*, 2003). The coupled dynamic modelling-palaeolimnology approach can help elucidate long-term and complex interactions between different aquatic pressures and responses (see Section 8.3.1), and the relative roles of multiple stressors on an ecosystems (Anderson *et al.*, 2006). Additional benefits of the coupled approach include their potentially complementary nature, as each method can provide vital information for lake management that is not apparent using the other method. Of course, both approaches could also provide two incorrect reconstructions of past conditions.

Difficulties in defining water quality targets based on reference conditions are linked to the lack of long-term and high-resolution monitoring data (Bennion *et al.*, 2011a), and the potential for complex and site-specific trophic histories (see Section 8.3.2). A coupled dynamic pressure-response modelling and palaeolimnological approach, which provides two independent and long-term water quality datasets, can

help to establish meaningful baseline trophic conditions and effective water quality targets (see Chapter 6). Natural ecological variability or pristine reference conditions, which would not have been detectable using dynamic modelling alone, can be determined from long-term palaeolimnological data (see Chapter 4). Dynamic modelling also allows the contributions of different drivers of in-lake responses to be distinguished and changes in their roles over time to be assessed (see Chapter 5), which can be difficult to achieve using palaeoecological data in isolation (Smol, 2008). Because of the complexity of the information preserved in lake sediment records, the focus often tends to be on a specific environmental driver (Anderson *et al.*, 2006). The findings of the current research demonstrated the importance of considering the interactive effects of multiple climate and human drivers of change in lake ecosystems (see Chapter 5). Knowledge of the relative contributions of different drivers of change is vital for focussing water quality management efforts (Smol & Douglas, 2007; Ormerod, 2010).

Few studies have tested the effectiveness of POMs (Taylor *et al.*, 2012), even though this has been recommended at national (Clenaghan *et al.*, 2005) and international levels (Yang & Griffiths, 2010). There is also considerable uncertainty regarding the suitability of current water quality management plans, particularly in agriculturally-impacted catchments in Ireland (Kavanagh & Bree, 2009) and more generally (Howarth, 2011). Scenario-based dynamic pressure-response modelling, validated through comparisons with palaeolimnological and monitoring data is a potentially powerful tool for designing water quality management plans (see Chapter 7) and supporting management decisions at catchment level (Irvine *et al.*, 2005; Sutherland, 2006). In the current study, scenario-based dynamic modelling provided a range of alternative management options for achieving water quality targets that could be assessed in terms of cost- and time-effectiveness (see Chapter 7).

The ability of models to replicate complex aquatic ecological pressure-response relationships is, however, limited by the availability of high quality and high resolution monitoring datasets required for calibration and validation procedures (Davis, 1994; Anderson *et al.*, 2006). The findings of the current research indicate that sediment-based reconstructions tend to overestimate trophic levels in the water column for the most recent part of the sediment record (see Section 6.3) and, therefore, may be unreliable. The findings also suggest that improvements to the calibration and validation procedures

of models by acquiring more suitable and high resolution monitoring datasets would improve the effectiveness of the dynamic modelling-palaeolimnological approach.

Moreover, a major challenge facing the application of dynamic models in environmental management and decision making is the estimation of uncertainty in model predictions (Linstead *et al.*, 2010) (see Section 8.1). Estimates of uncertainty in catchment nutrient loads for the version of GWLF used in the current study (Dalton *et al.*, 2010) suggest that there are potentially large margins of error in the estimates. However, these margins of error are comparable to those associated with export coefficient models (e.g. Johnes, 1996; Bennion *et al.*, 2005). Quantifying the uncertainty of model predictions is a complex task because of the potentially large number of parameters and the complexity of pressure-response relationships (Linstead *et al.*, 2010). This complexity, together with unrealistic time and resource constraints, means that uncertainty analysis is rarely performed (Jakeman *et al.*, 2006). Moreover, the statistical methods available for estimating uncertainty in modelling have not yet been developed to cater for uncertainty estimation in complex models like DYCD with many model parameters (Trolle *et al.*, 2011). The importance of uncertainty in model output, however, depends on the purpose of modelling and relative uncertainty can be important (Jakeman *et al.*, 2006). For decision support purposes in water quality management where the rank order of the potential impacts of alternative scenarios or management measures are assessed, minimal uncertainty is much less important than where models are used for forecasting, and cost, benefit and risk must be gauged (Jakeman *et al.*, 2006).

8.3.3.2 *Methods used in lake management*

Currently, water quality management in Ireland and elsewhere in Europe, which is based on the implementation of the WFD, is based primarily on monitoring data (e.g. Anon, 2006). Given the paucity of long-term monitoring datasets available, and the long histories of human impacts on lakes evident in the current study, water quality targets based on monitoring data alone are likely to be inaccurate and associated water quality management plans and restoration attempts are unlikely to be successful. While high quality and high frequency targeted monitoring data are the only way of grounding other methods of water management, and are essential for recording extreme and episodic pollution events (Jordan *et al.*, 2007), monitoring programmes are often costly and have

high time and resource requirements (Taylor *et al.*, 2012). In contrast, the potential benefits, particularly the cost-effective and time-efficient achievement of water quality targets, of using dynamic modelling as a tool for managing lake water quality in conjunction with monitoring data were evident from the current study. Although in the current study the approach was, to an extent, limited by the lack of suitable monitoring data, the application of the approach was reasonably successful. The relevance of the coupled approach is supported by its successful application in another lake, Lough Leane, southwest Ireland (Dalton *et al.*, 2010). Together with the success of dynamic modelling approaches to water quality management elsewhere, including in the USA and Australia (Irvine *et al.*, 2005; Zhang *et al.*, 2010), the benefits of dynamic modelling are likely to have greater relevance and wider applicability in Ireland, and more generally.

In contrast to Ireland and many countries in Europe, dynamic modelling is a fundamental part of water quality management operations in the US Environmental Protection Agency (e.g. Di Luzio *et al.*, 2002). For example, modelling is used to fill gaps in monitoring data, determine measures for achieving water quality targets and forms the basis for informing and setting priorities in environmental policy development and implementation (Committee on Models in the Regulatory Decision Process, National Research Council, 2007). Moreover, there has been a general acknowledgement in the scientific community of the benefits of modelling, in conjunction with high quality and focussed monitoring, in water quality management (Irvine *et al.*, 2005; Højberg *et al.*, 2007). Despite this, the application of modelling techniques in Ireland and Europe remains rare. Moreover, the application of modelling in water management is limited by a lack of understanding of the relative importance of key ecological processes and lack of data available for their parameterisation and, therefore, some would argue that models should be used more for exploring processes than for making projections (Anderson *et al.*, 2006). Moreover, limited application of modelling has been linked to lack of the required skills, lack of time, lack of confidence in models and lack of awareness on how models can be used in practice (Højberg *et al.*, 2007; Linstead *et al.*, 2010).

The findings of the current study highlight the benefits and potential of a dynamic modelling approach to lake management, for example, at RBD level, and for ensuring cost-effective implementation of water quality policies in a reasonable timeframe. Moreover, the findings support the view that a modelling approach has the potential to help unravel multiple climate and human impacts on key ecological processes (e.g.

Anderson *et al.*, 2006), and could potentially improve our ability to predict aquatic responses to future changes in climate and catchment pressures. However, given the large uncertainty involved in future climate projections, the application of ecological models that can reliably incorporate and run climate scenarios is still at an early stage (Hayhoe *et al.*, 2011), and further research on quantifying and understanding uncertainty in modelling output is needed (Littel *et al.*, 2011). The current findings showed that natural ecological variability and the limitations of the models must be considered before the approach can be used effectively to manage lake ecosystems. Further improvements to the performance of the models using additional targeted monitoring programmes (for calibration and validation) would be necessary to improve the reliability of the approach. Moreover, adoption of dynamic modelling in lake management in the near future in Europe is dependent on the full enforcement of the recommendations of the WFD, and will only take place when additional issues, such as accurate validation, quantification of uncertainty and the lack of awareness regarding the role of modelling in water quality management and the lack of expertise, are addressed.

8.4 Future Research

To gain a better understanding of ecological pressure-response relationships in complex lakes, and to establish the wider applicability of dynamic modelling in lake management, the methodological approach employed in this research needs to be applied at a wider range of lake sites. To-date, the approach employed has only been employed at one other site in Ireland, Lough Leane, southwest Ireland (Dalton *et al.*, 2010). However, both applications have been reasonably successful, highlighting the potentially-wider relevance of the approach.

The analysis of additional sediment proxies, in particular the sedimentary record of ultraviolet radiation-specific algal pigments (Leavitt & Hodgson, 2001) and biogenic Si (Leng *et al.*, 2009) could also contribute to the interpretations made in the current study regarding natural trophic variability, controls on diatom preservation in the sediment and interactions between trophic pressures and responses. The evidence presented suggests a possible role for Si recycling in dictating in-lake response patterns to climatic variability and human pressures. Further investigations into Si dynamics in lakes could provide insight into the occurrence of lagged or delayed responses in primary productivity to increased nutrient availability (see Section 8.3.1). Additional and more

focussed monitoring programmes, aimed at improving the calibration and validation procedures of the models, would improve the reliability of the modelling-palaeolimnological approach.

The site-specific nature of aquatic ecological pressure-response relationships evident in the current study and elsewhere (e.g. Blenckner, 2005; Taylor *et al.*, 2006) has important implications for the management of lake ecosystems. In particular water quality targets defined on the basis of regional- or type-specific reference conditions (e.g. Anon, 2005) are likely to be inappropriate. Alternative site-specific or regional lake-type schemes for defining reference conditions are deserving of further research. Furthermore, given the spatially-heterogeneous nature of the geology, hydrology, topography and soil types of the Irish ecoregion, relative to its small size (Cross, 1998), and the fact that climatic, particularly precipitation, gradients are steep (George *et al.*, 2010), there is likely to be an even greater need for lake management to take place on a site-specific basis.

The complex interactions between multiple climate and human pressures and in-lake responses, evident in the current study, are particularly challenging for lake management. Lakes located in close proximity to the Atlantic Ocean are particularly sensitive to climatic variability, and climate-induced ecological variability must be considered when devising lake management plans and assessing the success of restoration attempts in the future. Future climate change projections for the west of Ireland include a 40% increase in winter rainfall and temperature increases between 2-3.5 °C, based on current greenhouse gas emissions (IPCC, 2007; Fealy *et al.*, 2010). The frequency of flooding events are also projected to increase in the west of Ireland (Fealy *et al.*, 2010; George *et al.*, 2010), and the western European region (IPCC, 2007). Based on these climate projections, the findings of this study indicate that:

- increasing winter precipitation and the frequency of flooding events, which has been associated with increased streamflow in winter, elevated soil erosion rates, increased nutrient loading and changes in the growth and seasonal dynamics of phytoplankton (Jennings *et al.*, 2008; Dalton *et al.*, 2010; Fealy *et al.*, 2010; George *et al.*, 2010) could either exacerbate eutrophication further and deplete Si resources in the water column,
- increasing winter precipitation, in the absence of significant nutrient loading, may result increases in the relative contribution of surface runoff to streamflow over

- groundwater inputs. Thus, the potential for Si depletion and changes in the growth and seasonal dynamics of phytoplankton may increase, and
- increasing temperatures may exacerbate eutrophication effects, because of strengthened thermal stratification and increased stability in the water column. This may promote Si depletion in the water column, which could lead to the predominance of nuisance algal groups, such as cyanophyte.

Moreover, given that NAO changes to more positive values are likely to continue (George *et al.*, 2010; Nickus *et al.*, 2010), and evidence presented in this study indicates that the NAO and the increased frequency of precipitation and diffuse nutrient loading, enhanced eutrophication may be even more likely in the future. Dynamic modelling provides a potentially useful approach for improving the certainty of future predictions of lake ecological responses to climate and catchment changes. However, in order to maximise the benefits and the reliability of dynamic-modelling and palaeolimnological-based approaches, improvements in the calibration of the models using focussed monitoring programmes will be vital.

Chapter 9

Conclusion

9.1 Thesis summary

The main aim of this study was to determine the extent to which a multidisciplinary approach, combining dynamic modelling, palaeolimnology and historical catchment and climate data could contribute to an improved understanding of lake ecological pressure-response relationships and, ultimately, assist in the management of lakes. The thesis investigated four specific research questions, which are addressed in Chapters 4, 5, 6 and 7. Given that little is known about natural trophic variability in complex lakes, mainly because of the paucity of long-term monitoring data, the first research question (see Chapter 4) was ‘how have trophic conditions varied over the long-term in a complex lake?’ Deciphering the links between multiple climate and human drivers of trophic variability in lakes is particularly challenging because of their inherent complexity and potential for similar effects. Thus the second research question (see Chapter 5), ‘what are the relative roles of climate variability and human pressures in driving trophic changes in a west of Ireland lake during the 20th century?’, addressed these challenges using a range of instrumental, palaeolimnological and dynamic modelling data. Given the absence of sufficient long-term monitoring data on lake trophic variability, and the lack of knowledge of long-term trophic pressure-response relationships in lake ecosystems, Research Question 3 (see Chapter 6), ‘can a multidisciplinary approach, combining palaeolimnological and dynamic modelling methods, be used to elucidate long-term trophic dynamics?’, investigated whether a multidisciplinary approach, involving two independent methods - palaeolimnological and dynamic modelling, could be used to elucidate long-term trophic dynamics. Although the benefits of a dynamic modelling approach to lake management and the implementation of water quality policy are well-known, the approach is not widely used for these purposes. Thus the fourth research question (see Chapter 7), ‘can dynamic modelling be used to design and test the effectiveness of water quality management plans?’, addressed this issue using a scenario-based dynamic modelling approach.

9.2 Research findings

The main findings relating to the research questions are detailed below.

Research Question 1: ‘How have trophic conditions varied over the long term in a complex lake?’

Sediment-based data biological, lithological and geochemical proxy data covering the mid-late Holocene were used to address the first research question, which sought to investigate the range of trophic variability and the possible controls of trophic variability in Lough Mask, a complex lake located in the west of Ireland, during the last c. 6000 years. Two key findings emerged from the results relating to the first research question:

- Interactions between climate, catchment conditions and in-lake processes

Trophic conditions during much of the mid-late Holocene in Lough Mask were in the oligotrophic range, based on sediment biological and geochemical data. Natural trophic variability appears to have been driven by complex interactions between climate, catchment conditions and in-lake processes. Post-depositional diatom dissolution and recycling of Si from the sediment appear to be linked to climatic variability, in particular variations in the levels of precipitation, via changes in the relative influence of groundwater versus surface water influx from the catchment. Although internal lake processes are often more important determinants of in-lake Si levels, the findings of the current research revealed that climate-driven variations in precipitation may play an important role. However, the relationship between climate and Si cycling in lakes is complex and site-specific, and often difficult to decipher because of the importance of in-lake processes, which are difficult to quantify.

- Early human impacts

Sediment-based data indicated relatively early human-induced pressures in the Lough Mask catchment, during the 19th century, linked to high human population, intensive agricultural activity and modification of the catchment drainage network. The findings highlight the site-specific nature of long-term trophic histories in lakes, which often reflect a combination of regional- and local-scale factors. Moreover, the findings indicate the need for lake reference conditions, used to determine water quality targets, to be defined on a site-specific basis.

Research Question 2: ‘What are the relative roles of climate variability and human pressures in driving trophic changes in a west of Ireland lake during the 20th century?’

A range of historical catchment and climate data, palaeolimnological data, and hindcast catchment and in-lake modelling data, for the last c. 100 years, were analysed to address the second research question. The findings demonstrated the value of a multidisciplinary approach to elucidating aquatic ecological pressure-response relationships in a complex west of Ireland lake, including the role of climate variability in influencing in-lake trophic variability.

Prior to c. 1970 AD, variations in lake water chemistry and trophic conditions in Lough Mask were linked to variations in climate, in particular winter precipitation levels and the NAO, and human population. Post-c. 1970 AD, nutrient enrichment effects were more pronounced and were linked to elevated summer temperatures and enhanced thermal stratification, and agricultural intensification. Climate warming and associated enhanced thermal stratification appeared to be the main driver of eutrophication post-c. 1970 AD, followed by agricultural intensification. The results indicated that climate warming may play a more important role in dictating lake primary productivity than previously thought. The results also highlighted the potential for the effects of multiple pressures, in this case climate warming and agricultural intensification, on lake trophic conditions. The possibility of influences of other climatic phenomena in western Europe on lake trophic variability was also highlighted. Future climate changes may attenuate the response of water bodies to measures aimed at alleviating cultural eutrophication pressures.

Research Question 3: ‘Can a multidisciplinary approach, combining palaeolimnological and dynamic modelling methods, be used to elucidate long-term trophic dynamics?’

Palaeolimnology and hindcast modelling could potentially be used to reconstruct long-term trophic variability in lakes. The results of both methodological approaches used to reconstruct past trophic conditions were in reasonably good agreement in terms of their indicated trophic status category, and in particular highlighted the usefulness of the multidisciplinary approach for establishing baseline trophic conditions in lakes. However,

comparisons between the two independent reconstructions of trophic conditions highlighted some important limitations of the techniques. The sediment-based transfer function did not replicate measured lake TP levels. However, the hindcast modelling approach performed reasonably well in reconstructing in-lake trophic conditions.

Improvements to the accuracy and reliability of the both dynamic and sediment-based modelling techniques suggested here could be achieved relatively easily using more detailed and targeted monitoring programmes for model calibration.

Research Question 4: ‘Can dynamic modelling be used to design and test the effectiveness of water quality management plans?’

A scenario-based modelling approach demonstrated the broader practical relevance of the findings of the current study to lake catchment management and the implementation of the water quality policy. Such an approach could potentially be used to design and test the effectiveness of lake management plans, in particular POMs in the context of the WFD. The findings showed that current policies and trends, including basic measures outlined in current RBD management plans in Ireland and elsewhere in Europe are unlikely to result in improved water quality, and that supplementary measures would be required to meet the implementation schedule of the WFD. Scenario-based modelling could considerably reduce the need for costly and time consuming monitoring programmes that are currently used in RBD management. Moreover, scenario-based modelling could contribute to the development of more effective water quality-relevant policies. Dynamic ecological modelling is a valuable tool that could be used in decision support in water quality management, and in particular in facilitating cost-effective implementation of water quality objectives of legislation such as the WFD.

9.3 Overall aim

The findings of the current research indicate the immense potential of dynamically-linked models, when run retrospectively and compared to palaeolimnological data, in lake management and in ensuring the successful implementation of water quality policies. The

main difficulty in applying the coupled modelling and palaeolimnological approach is the very different temporal resolutions of the datasets produced by the methods. However, the approach can provide valuable and complimentary information on aquatic ecological pressure-response relationships, natural ecological variability in lakes, the relative roles of climate and human drivers of aquatic ecological responses, and provide appropriate management options for water quality restoration.

Before the multidisciplinary approach can be used reliably in lake management, however, improvements to the parameterisation, calibration and validation procedures in the models are vital. This can only be achieved by acquiring additional larger and higher-resolution monitoring datasets than those available in the current study, and by testing the approach at a wider range of lake sites, with varying catchment characteristics. The findings of the research highlight the relevance of a dynamic modelling approach to the management of lake ecosystems, not only in Ireland but more generally. Given the extent of projected future changes in climate and environmental pressures, this type of approach to lake management is likely to prove even more valuable. However, improvements to the practical applicability of the coupled approach will depend on how widespread testing and use of the models will be and on the relevance of future monitoring programmes.

References

- Adrian, R., O'Reilly, C.M., Zagarese, H., Baines, S.B., Hessen, D.O., Keller, W., Livingstone, D.M., Sommaruga, R., Straile, D., Van Donk, E., Weyhenmeyer, G.A. & Winder, M. (2009) Lakes as sentinels of climate change. *Limnology and Oceanography*, **54**, 2283-2297.
- Adrian, R., Deneke, R., Mischke, U., Stellmacher, R. & Lederer, P. (1995) A long-term study of the Heiligensee (1975-1992). Evidence for effects of climatic change on the dynamics of eutrophied lake ecosystems. *Archiv für Hydrobiologie*, **133**, 315-337.
- Aherne, J. & Farrell, E.P. (2002) A survey of lakes in the Republic of Ireland: hydrochemical characteristics and acid sensitivity. *Ambio*, **31**, 452-459.
- Ahn, Y.S., Mizugaki, S., Nakamura, F. & Nakamura, Y. (2006) Historical change in lake sedimentation in Lake Takkobu, Kushiro Mire, northern Japan over the last 300 years. *Geomorphology*, **78**, 321-334.
- Allan, J.D. & Johnson, L.J. (1997) Catchment-scale analysis of aquatic ecosystems. *Freshwater Biology*, **37**, 107-111.
- Allott, N., McGinnity, P. & O'Hea, B. (2005) Factors influencing the downstream transport of sediment in the Lough Feeagh catchment, Burrishoole, Co. Mayo, Ireland. *Freshwater Forum*, **23**, 126-38.
- Anderson, N.J. (1989) A whole-basin diatom accumulation rate for a small eutrophic lake in northern Ireland and its palaeoecological implications. *Journal of Ecology*, **77**, 926-946.
- Anderson, N.J. (1997) Historical changes in epilimnetic phosphorus concentrations in six rural lakes in Northern Ireland. *Freshwater Biology*, **38**, 427-440.
- Anderson, N.J. (1998) Variability of diatom-inferred phosphorus profiles in a small lake basin and its implications for histories of lake eutrophication. *Journal of Paleolimnology*, **20**, 47-55.
- Anderson, N.J. (1990a) Variability of diatom concentration and accumulation rates in sediments of a small lake basin. *Limnology and Oceanography*, **35**, 497-508.
- Anderson, N.J. (1990b) Variability of sediment diatom assemblages in an upland, wind-stressed lake (Loch Fleet, Galloway, S. W. Scotland). *Journal of Paleolimnology*, **4**, 43-59.

- Anderson, N.J., Bugmann, H., Dearing, J.A. & Gaillard, M.J. (2006) Linking palaeoenvironmental data and models to understand the past and to predict the future. *Trends in Ecology and Evolution*, **21**, 696-704.
- Anderson, N. J., Rippey, B. & Gibson, C.E. (1993) A comparison of sedimentary and diatom-inferred phosphorus profiles: implications for defining pre-disturbance nutrient conditions. *Hydrobiologia*, **253**, 357-366.
- Anon (2005) Article 5 The characterisation and analysis of Ireland's river basin districts. In accordance with Section 7 (2 & 3) of the European Communities (Water Policy) Regulations 2003 (SI 722 of 2003). National Summary Report (Ireland). *Compendium of public submissions and responses*.
- Anon (2006) *Ireland Water Framework Directive Monitoring Programme. Prepared to meet the requirements of the EU Water Framework Directive (2000/60/EC) and National Regulations implementing the Water Framework Directive (S.I. No. 722 of 2003) and National Regulations implementing the Nitrates Directive (S.I. No. 788 of 2005)*. Environmental Protection Agency (Ireland), Wexford.
- Appleby, P.G. (2001) Chronostratigraphic Techniques in Recent Sediments. *Tracking Environmental Change Using Lake Sediments. Vol. 1: Basin Analysis, Coring and Chronological Techniques* (eds W.M. Last & J.P. Smol) pp. 155-202. Kluwer Academic Publishers, Dordrecht.
- Appleby, P.G. (2008) Three decades of dating recent sediments by fallout radionuclides: a review. *The Holocene*, **18**, 83-93.
- Appleby, P.G. & Oldfield, F. (1983) The assessment of ^{210}Pb data from sites with varying sediment accumulation rates. *Hydrobiologia*, **103**, 29-35.
- Appleby, P.G. & Oldfield, F. (1992) Application of ^{210}Pb to sedimentation studies. Uranium-series Disequilibrium. *Applications of Earth, Marine & Environmental Sciences* (eds M.R.S.H. Ivanovich) Oxford University Press, Oxford.
- Arnold, J.G., Allen, P.M., Muttiah, R. & Bernhardt, G. (1995) Automated base flow separation and recession analysis techniques. *Ground Water*, **33**, 1010-1018.
- Arnold, J.G., Srinivasan, R., Muttiah, R.S. & Williams, J.R. (1998) Large area hydrological modelling and assessment. Part I: Model development. *Journal of American Water Works Association*, **34**, 73-89.
- Aumann, C.A. (2007) A methodology for developing simulation models of complex systems. *Ecological Modelling*, **202**, 385-396.

- Austin, P., Mackay, A.W., Palushkina, O. & Leng, M. (2007) A high resolution diatom-inferred palaeoconductivity and lake level record of the Aral Sea for the last 1600 yr. *Quaternary Research*, **67**, 383-393.
- Barber, K.E., Chambers, F.M. & Maddy, D. (2003) Holocene palaeoclimates from peat stratigraphy: macrofossil proxy climate records from three oceanic raised bogs in England and Ireland. *Quaternary Science Reviews*, **22**, 521-539.
- Barbiero, R.P. (2000) A multi-lake comparison of epilithic diatom communities on natural and artificial substrates. *Hydrobiologia*, **438**, 157-170.
- Battarbee, R.W. (1978) Observations on the recent history of Lough Neagh and its drainage basin. *Philosophical Transactions of the Royal Society of London B*, **281**, 303-345.
- Battarbee R.W. (1986) The eutrophication of Lough Erne inferred from changes in the diatom assemblages of ^{210}Pb - and ^{137}Cs -dated sediment cores. *Proceedings of the Royal Irish Academy B*, **86**, 141-168.
- Battarbee, R.W. (1991) Recent palaeolimnology and diatom based environmental reconstruction. *Quaternary Landscapes* (eds L.C.K. Shane & E.J. Cushing) University of Minnesota Press, Minneapolis.
- Battarbee, R.W. (1999) The importance of palaeolimnology to lake restoration. *Hydrobiologia*, **395/396**, 149-159.
- Battarbee, R.W. (2000) Palaeolimnological approaches to climate change, with special regard to the biological record. *Quaternary Science Reviews*, **19**, 107-124.
- Battarbee, R.W. (2010) Aquatic ecosystem variability and climate change – a palaeoecological perspective. *Climate Change Impacts on Freshwater Ecosystems* (eds M. Kernan, R.W. Battarbee & B. Moss) pp.119-215. Wiley-Blackwell, Chichester.
- Battarbee, R.W., Anderson, N.J., Bennion, H. & Simpson, G.L. (in press) Combining limnological and palaeolimnological data to disentangle the effects of nutrient pollution and climate change on lake ecosystems: problems and potential. *Freshwater Biology*.
- Battarbee, R.W., Carvalho, L., Jones, V.J., Flower, R.J., Cameron, N.G., Bennion, H. & Juggins, S. (2001) Diatoms. *Tracking Environmental Change Using Lake Sediments. Vol. 3: Terrestrial, Algal and Siliceous Indicators* (eds J.P. Smol, H.J.B. Birks & W.M. Last) pp. 155-202. Kluwer Academic Publishers, Dordrecht.

- Battarbee, R.W., Grytnes, J.A., Thompson, R., Appleby, P.G., Catalan, J., Korhola, A., Birks, H.J.B., Heegaard, E. & Lami, A. (2002) Comparing palaeolimnological and instrumental evidence of climate change for remote mountain lakes over the last 200 years. *Journal of Paleolimnology*, **28**, 161-179.
- Battarbee, R.W., Howells, G., Skeffington, R.A. & Bradshaw, A.D. (1990) The causes of lake acidification, with special reference to the role of acid deposition. *Philosophical Transactions of the Royal Society of London B*, **327**, 339-347.
- Battarbee, R.W. & Kneen, M.J. (1982) The use of electronically counted microspheres in absolute diatom analysis. *Limnology and Oceanography*, **27**, 184-188.
- Battarbee, R.W., Mackay, A.W., Jewson, D.H., Ryves, D.B. & Sturm, M. (2005) Differential dissolution of Lake Baikal diatoms: correction factors and implications for palaeoclimatic reconstruction. *Global and Planetary Change*, **46**, 75-86.
- Battarbee, R.W., Monteith, D.T., Juggins, S., Simpson, G.L., Shilland, E.W., Flower, R.J. & Kreiser, A.M. (2008) Assessing the accuracy of diatom-based transfer functions in defining reference pH conditions for acidified lakes in the United Kingdom. *The Holocene*, **18**, 57-67.
- Becker, A., Soncini-Sessa, R., Castelletti, A., Hattermann, F.F., Willems, P., Stalnacke, P., Laurans, Y. & de Lange, W.J. (2010) How can models help implementing the Water Framework Directive? Water Framework Directive: model supported implementation - a water manager's guide. (eds F.F. Hattermann & Z.W. Kundzewicz) pp. 11-53. International Water Association, London.
- Bengtsson, L., Hellstrom, T. & Rakoczi, L. (1990) Redistribution of sediments in three Swedish lakes. *Hydrobiologia*, **192**, 167-181.
- Bennett, K.D. (1996) Determination of the number of zones in a biostratigraphic sequence. *New Phytologist*, **132**, 155-179.
- Bennett, K.D. (2002) *Documentation for psimpoll 4.1 and pscomb 1.03*. Quaternary Geology, Department of Earth Sciences, Uppsala University, Sweden.
- Bennett, K.D. & Fuller, J.L. (2002) Determining the age of the mid-Holocene Tsuga Canadensis (hemlock) decline, eastern North America. *The Holocene*, **12**, 421-429.
- Bennion, H. (1994). A diatom-phosphorus transfer function for shallow, eutrophic ponds in southeast England. *Hydrobiologia*, **275/276**, 391-410.

- Bennion, H., Appleby, P.G. & Phillips, G.L. (2001) Reconstructing nutrient histories in the Norfolk Broads, UK: implications for the role of diatom-total phosphorus transfer functions in shallow lake management. *Journal of Paleolimnology*, **26**, 181-204.
- Bennion, H. & Battarbee, R. (2007) The European Union Water Framework Directive: opportunities for palaeolimnology. *Journal of Paleolimnology*, **38**, 285-295.
- Bennion, H., Battarbee, R.W., Sayer, C.D., Simpson, G.L. & Davidson, T.A. (2011b) Defining reference conditions and restoration targets for lake ecosystems using palaeolimnology: a synthesis. *Journal of Paleolimnology*, **45**, 533-544.
- Bennion, H., Johnes, P., Ferrier, R., Phillips, G. & Haworth, E. (2005) A comparison of diatom phosphorus transfer functions and export coefficient models as tools for reconstructing lake nutrient histories. *Freshwater Biology*, **50**, 1651-1670.
- Bennion, H., Juggins, S. & Anderson, N.J. (1996) Predicting epilimnetic phosphorus concentrations using an improved diatom-based transfer function and its application to lake eutrophication Management. *Environmental Science and Technology*, **30**, 2004-2007.
- Bennion, H., Simpson, G.L., Anderson, N.J., Clarke, G., Dong, X., Hobæk, A., Guilizzoni, P., Marchetto, A., Sayer, C.D., Thies, H. & Tolotti, M. (2011a) Defining ecological and chemical reference conditions and restoration targets for nine European lakes. *Journal of Paleolimnology*, **45**, 415-431.
- Berner, E.K. & Berner, R.A. (1996) *Global Environment: Water, Air and Geochemical cycles*. pp. 376. Prentice Hall, Upper Saddle River, New Jersey.
- Bertahas, I., Dimitriou, E. & Karaouzas, I. (2006) Climate change and agricultural pollution effects on the trophic status of a Mediterranean lake. *Acta Hydrochimica et Hydrobiologica*, **34**, 349-359.
- Beven, K. (2009) *Environmental Modelling: An Uncertain Future?* pp. 330. Routledge, London.
- Bhattacharai, K.P. & O'Connor, K.M. (2004) The effects over time of an arterial drainage scheme on the rainfall-runoff transformation in the Brosna catchment. *Physics and Chemistry of the Earth*, **29**, 787-794.
- Bianchi, M., Boyle, M. & Hollingsworth, D. (1999) A comparison of methods for trend estimation. *Applied Economics Letters*, **6**, 103-109.

- Bicknell, B.R., Imhoff, J.C., Donigian, A.S. & Johanson, R.C. (1997) *Hydrologic simulation program - FORTRAN (HSPF) Users Manual for release 11*. EPA-600/R-97/080, United States Environmental Protection Agency, Athens, Georgia, U.S.A.
- Biggs, R., Raudsepp-Hearne, C., Atkinson-Palombo, C., Bohensky, E., Boyd, E., Cundill, G., Fox, H., Ingram, S., Kok, K., Spehar, S., Tengo, M., Timmer, D. & Zurek, M., (2007) Linking futures across scales: a dialog on multiscale scenarios. *Ecology and Society*, **12**, 17 [online] URL: <http://www.ecologyandsociety.org/vol12/iss1/art17/>.
- Binfield, J., Donnellan, T., Hanrahan, K. & Westhoff, P. (2008) *Baseline 2008 Outlook for EU and Irish Agriculture*. FAPRI Ireland Partnership/Teagasc (Ireland), Galway.
- Birks, H.H. (2001) Plant Macrofossils. *Tracking Environmental Change Using Lake Sediments. Vol. 3: Terrestrial, Algal and Siliceous Indicators* (eds J.P. Smol, H.J.B. Birks & W.M. Last) pp. 49-74. Kluwer Academic Publishers, Dordrecht.
- Birks, H.H. (2007) Plant macrofossil methods and studies. *Encyclopedia of Quaternary Science* (eds S.A. Elias) Elsevier, Amsterdam.
- Birks, H.H. & Birks H.J.B (2006) Multi-proxy studies in paleolimnology. *Vegetation History and Archaeobotany*, **15**, 235-251.
- Birks, H.H. & Bjune, A.E. (2010) Can we detect a west Norwegian tree line from modern samples of plant remains and pollen? Results from the DOORMAT project. *Vegetation History and Archaeobotany*, **19**, 325-340.
- Birks, H.J.B. (1995) Quantitative palaeoenvironmental reconstructions. *Statistical modelling of Quaternary science data* (eds D. Maddy & J.S. Brew) pp.161-254. Quaternary Research Association, Cambridge.
- Birks, H.J.B. (1996) Statistical approaches to interpreting diversity patterns in the Norwegian mountain flora. *Ecography*, **19**, 332-340.
- Birks, H.J.B. & Gordon, A.D. (1985) *Numerical Methods in Quaternary Pollen Analysis*. pp. 317. Academic Press, London.
- Birks, H.J.B., Line, J.M., Juggins, S., Stevenson, A.C. & ter Braak, C.J.F. (1990) Diatoms and pH Reconstruction. *Philosophical Transactions of the Royal Society London B*, **327**, 263-278.
- Björck, S. & Wohlfarth, B. (2001) ^{14}C chronostratigraphic techniques in paleolimnology. *Tracking Environmental Change Using Lake Sediments. Vol. 1: Basin Analysis, Coring and Chronological Techniques* (eds W.M. Last & J.P. Smol) pp. 205-245. Kluwer Academic Publishers, Dordrecht.

- Blaauw, M. & Heegard, E. (2012) Age-depth modelling. *Tracking Environmental Change Using Lake Sediments. Vol. 5: Data Handling and Statistical Techniques* (eds H.J.B. Birks, S. Juggins, A.F. Lotter & J.P. Smol) pp. 379-413. Kluwer Academic Publishers, Dordrecht.
- Blenckner, T. (2005) A conceptual model of climate-related effects on lake ecosystems. *Hydrobiologia*, **533**, 1-14.
- Blenckner, T., Adrian, R., Arvola, L., Jarvinen, M., Maberly, S., Padisak, J., Straile, D., Teubner, K. & Weyhenmeyer, G. (2010) The impact of climate change on lakes in northern Europe. *The impact of climate change on European lakes*, Aquatic Ecology Series 4 (eds D.G. George) pp. 339-358. Springer.
- Blenckner, T., Adrian, R., Livingstone, D.M., Jennings, E., Weyhenmeyer, G.A., Nic Aonghusa, C., George, D.G., Jankowski, T., Järvinen, M., Nöges, T., Straile, D. & Teubner, K. (2007) Large-scale climatic signatures in lakes across Europe, a meta-analysis. *Global Change Biology*, **13**, 1314-1313.
- Blenckner, T. & Hillebrand, H. (2002) North Atlantic Oscillation signatures in aquatic and terrestrial ecosystems - a metaanalysis. *Global Change Biology*, **8**, 203-212.
- Bloemendal, J. (1982) *The quantification of rates of total sediment influx to Llyn Goddionduon, Gwynedd*. Ph.D. thesis, University of Liverpool.
- Borcard, D., Legendre, P. & Drapeau, P. (1992) Partialling out the spatial component of ecological variation. *Ecology*, **73**, 1045-55.
- Borja, A., Galparsoro, I., Solaun, O., Muxika, I., Tello, E., Uriarte, A. & Valencia, V. (2006) The European Water Framework Directive and the DPSIR, a methodological approach to assess the risk of failing to achieve good ecological status. *Estuarine, Coastal and Shelf Science*, **66**, 84-96.
- Bowes, M.J., Neal, C., Jarvie, H.P., Smith, J.T. & Davies, H.N. (2010) Predicting phosphorus concentrations in British rivers resulting from the introduction of improved phosphorus removal from sewage effluent. *Science of the Total Environment*, **408**, 4239-4250.
- Boyle, J.F. (2001) Inorganic geochemical methods in palaeolimnology. *Tracking Environmental Change Using Lake Sediments. Vol. 2: Physical and Geochemical Methods* (eds W.M. Smol & J.P. Last) pp. 83-141. Kluwer, Dordrecht.

- Bradbury, J.P. (1978) *A paleolimnological comparison of Burntside and Shagawa Lakes, Northeastern Minnesota*. EPA 600/3 78 004. U.S. Environmental Protection Agency, Corvallis.
- Bradshaw, E.G. & Anderson, N.J. (2001) Validation of a diatom–phosphorus calibration set for Sweden. *Freshwater Biology*, **46**, 1035-1048.
- Bradshaw, E.G., Nielsen, A.B. & Anderson, N.J. (2006) Using diatoms to assess the impacts of prehistoric, pre-industrial and modern land-use on Danish lakes. *Regional Environmental Change*, **6**, 17-24.
- Brancelj, A., Šiško, M., Muri, G., Appleby, P., Lami, A., Shilland, E., Rose, N.L., Kamenik, C., Brooks, S.J. & Dearing, J.A. (2002) Lake Jezero v Ledvici (NW Slovenia) – changes in sediment records over the last two centuries. *Journal of Paleolimnology*, **28**, 47-58.
- Brennan, M.T., Wilson, J.G., Jeffrey, D.W., Dowley, A., Jennings, E. & Hussey, M. (1994) *Particulate Nutrient Inputs and Their Role in Macroalgal Development in Dublin Bay. Report to STRIDE Measure 3 Environment Sub-programme*. Department of the Environment (Ireland), Dublin.
- Brönmark, C. & Hansson, L. (2005). *The Biology of Lakes and Ponds*. pp.285. University Press, Oxford.
- Brooks, S.J., Bennion, H. & Birks, H.J.B. (2001) Tracing lake trophic history with a chironomid–total phosphorus inference model. *Freshwater Biology*, **46**, 513-533.
- Brovkin, V., Levis, S., Loutre, M., Crucifix, M., Claussen, M., Ganopolski, A., Kubatzk, C. & Petoukhov, V. (2003) Stability analysis of the climate-vegetation system in the northern high latitudes. *Climate Change*, **57**, 119-138.
- Brugam, R., McKeever, K. & Kolesa, L. (1998) A diatom-inferred water depth reconstruction for an Upper Peninsula, Michigan lake. *Journal of Paleolimnology*, **20**, 267-276.
- Buishand, T.A. (1982) Some methods for testing the homogeneity of rainfall records. *Journal of Hydrology*, **58**, 1-27.
- Burger, D.F., Hamilton, D.P. & Pilditch, C. (2007) Modelling the relative importance of internal and external nutrient loads on water column nutrient concentrations and phytoplankton biomass in a shallow polymictic lake. *Ecological Modelling*, **211**, 411-423.

- Burns, R.T. & Moody, L.B. (2002) Phosphorus Recovery from Animal Manures using Optimized Struvite Precipitation. *Proceedings of Coagulants and Flocculants: Global Market and Technical Opportunities for Water Treatment Chemicals 2002*. Chicago.
- Butler, C.J., Coughlin, A.D.S. & Fee, D.T. (1999) Precipitation at Armagh Observatory 1838-1997. *Biology and Environment: Proceedings of the Royal Irish Academy B*, **98**, 123-140.
- Canney, P. (2009) *Final River Basin Management Plan for the Western River Basin District in Ireland (2009-2015)*. pp.129. Galway County Council (on behalf of relevant local authorities), Galway.
- Capece, J.C., Campbell, K.L., Bohlen, P.J., Graetz, D.A. & Portier, K.M. (2007) Soil phosphorus, cattle stocking rates, and water quality in subtropical pastures in Florida, USA. *Rangeland Ecology and Management*, **60**, 19-30.
- Cardenas, L.M., Cuttle, S.P., Crabtree, B., Hopkins, A., Shepherd, A., Scholefield, D. & del Prado, A. (2011) Cost effectiveness of nitrate leaching mitigation measures for grassland livestock systems at locations in England and Wales. *Science of the Total Environment*, **409**, 1104-1115.
- Carignan, R. & Flett, R.J. (1981) Postdepositional mobility of phosphorus in lake sediments. *Limnology and Oceanography*, **26**, 361-366.
- Carol, D., Dearing, J. & Roberts, R. (1998) Land-use history and sediment flux in a lowland lake catchment: Groby Pool, Leicestershire, UK. *The Holocene*, **8**, 383-394.
- Carper, G.L. & Bachmann, R.W. (1984) Wind resuspension in Sediments in a Prairie Lake. *Canadian Journal of Fisheries and Aquatic Sciences*, **41**, 1763-1767.
- Carvalho, L. & Defew, L.H. (2005) Eutrophication pressures. *Relationships between pressures, chemical status and biological quality elements: analysis of the current knowledge gaps for the implementation of the Water Framework Directive. REBECCA Report D4* (eds A.S. Heiskanen & A.G. Solimini).
- Carvalho, L. & Kirika, A. (2003) Changes in shallow lake functioning: response to climate change and nutrient reduction. *Hydrobiologia*, **506**, 789-796.
- Carvalho, L., Solimini, A., Phillips, G., Pietiläinen, O., Moe, J., Cardoso, A.C., Lyche-Solheim, A., Ott, I., Søndergaard, M., & Tartari, G. (2009) Site-specific chlorophyll reference conditions for lakes in Northern and Western Europe. *Hydrobiologia*, **633**, 59-66.

- Carvalho, L., Solimini, A., Phillips, G., van den Berg, M., Pietilainen, O., Lyche-Solheim, A., Poikane, S. & Mischke, U. (2008) Chlorophyll Reference Conditions for European Lake Types used for Intercalibration of Ecological Status. *Aquatic Ecology*, **42**, 203-211.
- Catalan, J., Ventura, M., Brancelj, A., Granados, I., Thies, H., Nickus, U., Korhola, A., Lotter, A.F., Barbieri, A., Stuchlik, E., Lien, L., Bitušík, P., Buchaca, T., Camarero, L., Goudsmit, G.H., Kopáček, J., Lemcke, G., Livingstone, D.M., Müller, B., Rautio, M., Šiško, M., Sorvari, S., Šporka, F., Strunecký, O. & Toro, M. (2002) Seasonal ecosystem variability in remote mountain lakes: implications for detecting climatic signals in sediment records. *Journal of Paleolimnology*, **28**, 25-46.
- Cerling, T.E. (1999) Paleorecords of C4 plants and ecosystems. *C4 Plant Biology* (eds R.F. Sage & R.K. Monson) pp. 445-469. Academic Press, London.
- Cerosaletti, P.E., Fox, D.G. & Chase, L.E. (2004) Phosphorus Reduction through Precision Feeding of Dairy Cattle. *Journal of Dairy Science*, **87**, 2314-2323.
- Central Fisheries Board (CFB) (2002) *2002 Annual Report of the Central and Regional Fisheries Boards and the Fisheries Cooperative Societies*. pp. 71. Central and Regional Fisheries Boards (Ireland), Dublin.
- Chambers, F.M., Barber, K.E., Maddy, D. & Brew, J. (1997) A 5500-year proxy-climate and vegetation record from blanket mire at Talla Moss, Borders, Scotland. *Holocene*, **7**, 391-399.
- Chambers, F.M., Daniell, J.R.G., Alm, J., Bartlett, S., Begeot, C., Bingham, L., Blaauw, M., Blundell, A., Chambers, F., Charman, D., Daniell, J., Evershed, R., Karofeld, E., Korhola, A., Kuester, H., Laine, J., Magny, M., Mauquoy, D., McClymont, E., Mitchell, F., Oksanen, P., Pancost, R., Sarmaja-Korjonen, K., Seppä, H., Sillasoo, Ü., Steffanini, B., Steffens, M., Tuittila, E-S., Välranta, M., van der Plicht, J., van Geel, B. & Yeloff, D. (2010) Peatland archives of late-Holocene climate change in northern Europe. *PAGES news*, **18**, 4-6.
- Charles, D.F., Dixit, S.S., Cumming, B.F. & Smol, J.P. (1991) Variability in diatom and chrysophyte assemblages and inferred pH: paleolimnological studies of Big Moose L. N.Y. *Journal of Palaeolimnology*, **40**, 143-163.
- Charman, D.J. (2010) Centennial climate variability in the British Isles during the mid-late Holocene. *Quaternary Science Reviews*, **29**, 1539-1554.

- Charman, D.J., Blundell, A., Chiverrell, R.C., Hendon, D. & Langdon, P.G. (2006) Compilation of non-annually resolved Holocene proxy climate records: stacked Holocene peatland palaeo-water table reconstructions from northern Britain. *Quaternary Science Reviews*, **25**, 336-350.
- Chen, G., Dalton, C., Leira, M. & Taylor, D. (2008) Diatom-based total phosphorus (TP) and pH transfer functions for the Irish Ecoregion. *Journal of Paleolimnology*, **40**, 143-163.
- Christoffersen, K., Andersen, N., Søndergaard, M., Liboriussen, L. & Jeppesen, E. (2006) Implications of climate-enforced temperature increases on freshwater pico and nanoplankton populations studied in artificial ponds during 16 months. *Hydrobiologia*, **560**, 259-266.
- Claussen, M., Ganopolski, A., Brovkin V., Gerstengarbe, F.W. & Werner P. (2003) Simulated global-scale response of the climate system to Dansgaard/Oeschger and Heinrich events. *Climate Dynamics*, **21**, 361-370.
- Clenaghan, C., Clinton, F. & Crowe, M. (2005) Phosphorus Regulations 2005: National Implementation Report. Environmental Protection Agency (Ireland), Wexford.
- Clesceri, N.L., Curran, S.J. & Sedlak, R.I. (1986). Nutrient loads to Wisconsin Lakes: part 1. Nitrogen and Phosphorus export coefficients. *Water Resources Bulletin*, **22**, 983-990.
- Cohen, A.S. (2003) *Paleolimnology: The History and Evolution of Lake Systems*. University Press, Oxford.
- Committee on Models in the Regulatory Decision Process, National Research Council (2007). *Models in Environmental Regulatory Decision Making. Board on Environmental Studies and Toxicology*. The National Academies Press, Washington D.C.
- Conley, D.J. (2002) Terrestrial ecosystems and global biogeochemical silica cycle. *Global Biogeochemical Cycles*, **16**, 1121-1129.
- Conley, D.J., Schelske, C.L. & Stoermer, E.F. (1993) Modification of the biogeochemical cycle of silica with eutrophication. *Marine Ecology Progress Series*, **101**, 179-192.
- Conley, D.J., Stalnacke, P., Pitkanen, H. & Wilander, A. (2000) The transport and retention of dissolved silicate by rivers in Sweden and Finland. *Limnology and Oceanography*, **45**, 1850-1853.

- Coxon, C. & Drew, D.P. (1986) Groundwater flow in the lowland limestone aquifer of eastern Co. Galway and eastern Co. Mayo, western Ireland. *New Directions in Karst* (eds K. Paterson & M. Sweeting) pp. 259-280. Norwich.
- Coxon, C. & Drew D.P. (2000) Interdependence of groundwater and surface water in lowland karst areas of western Ireland: management issues arising from water and contaminant transfers. *Groundwater in the Celtic Regions: Studies in Hard Rock and Quaternary Hydrogeology* (eds N.S. Robins & B.D.R. Misstear) *Geological Society Special Publications*, **182**, 81-88.
- Crabtree, B., Kelly, S., Green, H., Sqibbs, G. & Mitchell, G. (2009) Water Framework Directive catchment planning: a case study apportioning loads and assessing environmental benefits of programmes of measures. *Water Science and Technology*, **59**, 407-416.
- Cross, J.R. (1998) An Outline and Map of the Potential Natural Vegetation of Ireland. *Applied Vegetation Science*, **1**, 241-252.
- Crutzen, P.J. & Stoermer, E.F. (2000) The Anthropocene. *Global Change Newsletter*, **41**, 17-18.
- CSO (Central Statistics Office) (2008) *Population and labour force projections 2011-2041*. Stationary Office, Dublin.
- Cummins, T. & Farrell, E.P. (2003) Biogeochemical impacts on blanket peatland streams of clearfell harvesting and reforestation I: phosphorus. *Forest Ecology and Management*, **180**, 545-555.
- Dai, T., Wetzel, R.L., Tyler, R.L. & Lewis, E.A. (2000) *BasinSim 1.0: A windows based watershed modeling package*. Virginia Institute of Marine Science, College of Williams and Mary.
- Dalton, C. (1999) *A palaeolimnological investigation of acidity in humic lake waters in Connemara, western Ireland*. PhD thesis, University College London, London.
- Dalton, C., Jennings, E. & Taylor, D. (2009) Palaeolimnology and the Water Framework Directive. *Biology and Environment. Proceedings of the Royal Irish Academy B*, **109**, 161-74.
- Dalton, C., Jennings, E., Taylor, D., O'Dwyer, B., Murnaghan, S., Bosch, K., de Eyto, E. & Sparber, K. (2010) *Past, current and future Interactions between pressures, chemical status and bioLogical qUality eleMents for lakes IN contrAusting*

- catchments in Ireland (ILLUMINATE, EPA/ERTDI Project # 2005-W-MS-40). Final Report. Environmental Protection Agency (Ireland), Dublin.*
- Daly, K. (1999) *An environmental appraisal of the phosphorus dynamics of Irish grassland soils*. Unpublished PhD thesis, Trinity College, University of Dublin.
- Daly, K., Mills, P., Coulter, B. & McGarrigle, M. (2002) Landscape and Watershed Processes. Modelling Phosphorus Concentrations in Irish Rivers Using Land Use, Soil Type, and Soil Phosphorus Data. *Journal of Environmental Quality*, **31**, 590-599.
- Daly, K. & Styles, D. (2005) *Eutrophication from Agricultural Sources – Phosphorus Chemistry of Mineral and Peat Soils in Ireland (2000-LS-2.1.1b-M2)* Final Report. Environmental Protection Agency (Ireland), Dublin.
- Davis, M.B. (1994) Ecology and paleoecology begin to merge. *Trends in Ecology and Evolution*, **9**, 357-358.
- Davy-Bowker, J., Clarke, R.T., Johnson, R.K., Kokes, J., Murphy J.F. & Zahrádková, S. (2006) A comparison of the European Water Framework Directive physical typology and RIVPACS-type models as alternative methods of establishing reference conditions for benthic macroinvertebrates. *Developments in Hydrobiology*, **188**, 91-105.
- Dean, W.E. (1974) Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *Journal of Sedimentary Petrology*, **44**, 242-248.
- Dean, W.E. (1981) Carbonate minerals and organic matter in sediments of modern north temperate hard-water lakes. *Society of Economic Paleontologists and Mineralogists Special Publication*, **31**, 213-231.
- Dearing, J.A., Battarbee, R.W., Dikau, R., Larocque, I. & Oldfield, F. (2006) Human–environment interactions: learning from the past. *Regional Environmental Change*, **6**, 1-17.
- Deevey (1955) The obliteration of the hypolimnion. *Memorie dell'Istituto Italiano di Idrobiologia*, **8**, 9-38.
- de Freitas, H.A., Pessenda, L.C.R., Aravena, R., Gouveia, S.E.M., Ribeiro, A. d-S. & Boulet, R. (2001) Late Quaternary vegetation dynamics in the southern Amazon basin inferred from carbon isotopes in soil organic matter. *Quaternary Research*, **55**, 39-46.

- Delany, R. (1988) *Ireland's Inland Waterways*. pp. 200. Appletree Press, Belfast.
- DeNicola, D.M., de Eyto, E., Wemaere, A. & Irvine, K. (2004) Using epilithic algae communities to assess trophic status in Irish lakes. *Journal of Phycology*, **40**, 481-495.
- Department of Agriculture, Food and Forestry (1996) *Growing for the Future, Strategic Plan for the Development of the Forestry Sector in Ireland*. Department of Agriculture, Food and Forestry, Dublin.
- Department of Environment (1997) *Managing Ireland Rivers & Lakes: a Catchment-Based Strategy Against Eutrophication*. Department of Environment, Dublin.
- Desellas, A.M., Paterson, A.M., Sweetman, J.N. & Smol, J.P. (2011) Assessing the effects of multiple environmental stressors on zooplankton assemblages in Boreal Shield lakes since pre-industrial times. *Journal of Limnology*, **70**, 41-56.
- Diefendorf, A.F., Patterson, W.P. & Mullins, H.T. (2006) Evidence for high-frequency late Glacial to mid-Holocene (16,800 to 5500 cal yr B.P.) climate variability from oxygen isotope values of Lough Inchiquin, Ireland. *Quaternary Research*, **65**, 78-86.
- Di Luzio, M., Srinivasan, R. & Arnold, J.G. (2002) Integration of watershed tools and SWAT model into BASINS. *Journal of American Water Resources Association*, **38**, 1127-1141.
- Dixit, S. & Van Cappellen, P. (2002) Surface chemistry and reactivity of biogenic silica. *Geochimica et Cosmochimica Acta*, **66**, 2559-2568.
- Dokulil, M.T. & Herzig, A. (2009) An analysis of long-term winter data on phytoplankton and zooplankton in Neusiedler See, a shallow temperate lake, Austria. *Aquatic Ecology*, **43**, 715-725.
- Dokulil, M.T. & Teubner, K. (2011) Eutrophication and Climate Change: Present Situation and Future Scenarios. *Eutrophication: causes, consequences and control*, **2011**, 1-16.
- Donnelly, K. (2001) *The response of Lough Conn and Lough Mask, two Irish western lakes, to total phosphorus loading, 1995-1999*. PhD thesis, University College Dublin.
- Donohue, I. & Irvine, K. (2003) *Key nutrient transport mechanisms important for the prediction of nutrient and phytoplankton concentrations in European standing waters. Preliminary report on the monitoring of the Carra/Mask Catchment, Counties Mayo & Galway (v. 2)*. BUFFER project (EVK1-1999-00094). Trinity College, Dublin.

- Donohue, I., Leira, M., Hobbs, W., León-Vintró, L., O'Reilly, J. & Irvine, K. (2010) Rapid ecosystem recovery from diffuse pollution after the Great Irish Famine. *Ecological Applications*, **20**, 1733-1143.
- Donohue, I., McGarrigle, M. & Mills, P. (2006) Linking catchment characteristics and water chemistry with the ecological status of Irish rivers. *Water Research*, **40**, 91-98.
- Donohue, I., Styles, D., Coxon, C. & Irvine, K. (2005) Importance of spatial and temporal patterns for assessment of risk of diffuse nutrient emissions to surface waters. *Journal of Hydrology*, **304**, 183-92.
- Douglas, R.W., Menary, W. & Jordan, P. (2007) Phosphorus and sediment transfers in a grassland river catchment. *Nutrient Cycling in Agro-ecosystems*, **77**, 199-212.
- Douglas, D.J. & Murray, D.A. (1987) Palaeolimnological studies of Irish lakes 1: Lough Leane, Killarney, Co. Kerry. *Irish Journal of Environmental Science*, **IV**, 33-41.
- Dreßler, M., Schwarz, A., Hübener, T., Adler, S. & Scharf, B.W. (2011) Use of sedimentary diatoms from multiple lakes to distinguish between past changes in trophic state and climate: evidence for climate change in northern Germany during the past 5,000 years. *Journal of Paleolimnology*, **45**, 223-241.
- Drever, J.I. (1997) *The Geochemistry of Natural Waters*. pp.436. Prentice Hall, New Jersey.
- Dunford, R.W., Donoghue, D.N.M. & Burt, T.P. (2012) Forest land cover continues to exacerbate freshwater acidification despite decline in sulphate emissions. *Environmental Pollution*, **167**, 58-69.
- Eakins, J.D. & Morrison, R.T. (1978) A new procedure for the determination of lead-210 in lake and marine sediments. *International Journal of Applied Radiation and Isotopes*, **29**, 531-536.
- Edlund, M. & Kingston, J. (2004) *Expanding a Sediment Diatom Reconstruction Model to Eutrophic Southern Minnesota Lakes (CFMS Contract No. A45276). Final report to Environmental Outcomes Division*. St. Paul. Minnesota Pollution Control Agency. Minnesota.
- Engstrom, D.R. & Wright, H.E. (1984) Chemical stratigraphy of lake sediments as a record of environmental change. *Lake Sediments and Environmental History* (eds E.Y. Hawarth & J.G.W. Lund) pp.11-67. Leicester University Press, Leicester.
- Elliott, A., Jones, I.D. & Thackeray, S.D. (2006) Testing the sensitivity of phytoplankton communities to changes in water temperature and nutrient load in a temperate lake. *Hydrobiologia*, **559**, 1573-5117.

- European Commission (2003) *A Long Term Policy Perspective for Sustainable Agriculture*. European Commission, Brussels.
- European Commission (2009) Economic Impact of the Abolition of the Milk Quota Regime. Regional Analysis of the Milk Production in the EU. European Commission, Brussels.
- European Diatom Database (EDDI) (2009). Pages visited
<http://craticula.ncl.ac.uk/EDDI/jsp/index.jsp>
<http://craticula.ncl.ac.uk/Eddi/jsp/datasetdesc.jsp?DatasetId=TP> 02.02.2008
<http://craticula.ncl.ac.uk/Eddi/jsp/datasetdesc.jsp?DatasetId=NWEuro> 05.02.2008
- European Environment Agency (EEA) (2000) *CORINE land cover technical guide Addendum 2000. EEA technical Report No. 40* (eds M. Bossard, J. Feranec & J. Ptahel) pp. 105. EEA, Copenhagen.
- European Parliament and Council (2000) Water Framework Directive 2000/60/EC establishing a framework for community action in the field of water policy. *Official Journal of the European Communities*, **L327**, 1-73.
- European Union (2010) *The EU Nitrates Directive*. Publications Office, Brussels.
- Evans, B.M., Lehning, D.W., Corradini, K.J., Petersen, G.W., Nizeyimana, E., Hamlett, J.M., Robillard, P.D. & Day, R.L. (2002) A Comprehensive GIS-Based Modeling Approach for Predicting Nutrient Loads in Watersheds. *Journal of Spatial Hydrology*, **2**, 1-18.
- Ewen, J., Parkin, G. & O'Connell, E. (2000) SHETRAN: distributed basin flow and transport modelling system. *Journal of Hydrologic Engineering*, **5**, 250-258.
- Falloon, P. & Betts, R. (2010) Climate impacts on European agriculture and water management in the context of adaptation and mitigation - The importance of an integrated approach. *Science of the Total Environment*, **408**, 5667-5687.
- Fassio, A., Giupponi, C., Hiederer, R. & Simota, C. (2005) A decision support tool for simulating the effects of alternative policies affecting water resources: an application at the European scale. *Journal of Hydrology*, **304**, 462-76.
- Fealy, R., Allott, N., Broderick, C., de Eyto, E., Dillane, M., Erdil, R.M., Jennings, E., McCrann, K., Murphy, C., O'Toole, C., Poole, R., Rogan, G., Ryder, E., Taylor, D., Whelan, K. & White, J. (2010) *RESCALE: Review and Simulate Climate and Catchment Responses at Burrishoole, Final Summary Report*. Marine Institute, Galway.

- Fenton, O., Schulte, R.P.O., Jordan, P., Lalor, S.T.J. & Richards, K.G. (2011) Time lag: a methodology for the estimation of vertical and horizontal travel and flushing timescales to nitrate threshold concentrations in Irish aquifers. *Environmental Science and Policy*, **14**, 419-431.
- Fezzi, F., Hutchins, M., Rigby, D., Batemana, I.J., Posen, P. & Hadley, D. (2010) Integrated assessment of Water Framework Directive nitrate reduction measures. *Agricultural Economics*, **41**, 123-134.
- Flanagan, P.J. & Toner, P.F. (1975) *A preliminary survey of Irish lakes*. An Foras Forbartha, pp. 164.
- Flower, R.J. & Ryves, D.B. (2009) Diatom preservation: differential preservation of sedimentary diatoms in two saline lakes. *Acta botanica Croatica*, **68**, 381-399.
- Flower, R.J., Rippey, B., Rose, N.L., Appleby, P.G. & Battarbee, R.W. (1994) Palaeolimnological evidence for the acidification and contamination of lakes by atmospheric pollution in western Ireland. *Journal of Ecology*, **82**, 581-596.
- Foged, N. (1977) Freshwater diatoms in Ireland. *Bibliotheca Phycologica*, **34**, 221.
- Forrest, F., Reavie, E.D. & Smol J.P. (2002) Comparing limnological changes associated with 19th century canal construction and other catchment disturbances in four lakes within the Rideau Canal system, Ontario, Canada. *Journal of Limnology*, **61**, 183-197.
- Foy, R.H., Lennox, S.D. & Gibson, C.E. (2003) Changing perspectives on the importance of urban phosphorus inputs as the cause of nutrient enrichment in Lough Neagh. *Science of the Total Environment*, **310**, 87-99.
- Foy, R.H. (1992) A phosphorus loading model for Northern Irish lakes. *Water Research*, **26**, 633-638.
- Fragoso Jr., C.R., Motta Marques, D.M.L., Ferreira T.F., Janse, J.H. & van Nes, E.H. (2011) Potential effects of climate change and eutrophication on a large subtropical shallow lake. *Environmental Modelling and Software*, **26**, 1337-1348.
- Free, G., Little, R., Tierney, D., Donnelly, K. & Caroni, R. (2007) *WATER FRAMEWORK DIRECTIVE A Reference Based Typology and Ecological Assessment System for Irish Lakes Preliminary Investigations (2002-W-FS-1-M1) Synthesis Report*. pp. 51. Environmental Protection Agency (Ireland), Wexford.
- Fritz, S.C. (1989) Lake Development and Limnological Response to Prehistoric and Historic Land-Use in Diss, Norfolk, U.K. *Journal of Ecology*, **77**, 182-202.

- Fritz, S.C. (2008) Deciphering climatic history from lake sediments. *Journal of Paleolimnology*, **39**, 5-16.
- Gal, G., Hipsey, M.R., Parparov, A., Wagner, U., Makler, V. & Zohary, T. (2009) Implementation of ecological modeling as an effective management and investigation tool: lake Kinneret as a case study. *Ecological Modelling*, **220**, 1697-1718.
- Genty, T., Bruno, B., Robin, P. & Mostafa, B. (2008) Neutralization of acid mine drainage in anoxic limestone drains: a laboratory study. *Hydrology and Earth System Sciences*, **12**, 353-362.
- George, D.G. (2000) De-coupling natural and anthropogenic sources of variation in the lakes of the English Lake District. *Verhandlungen der Internationalen Vereinigung der Limnologie*, **27**, 321-325.
- George, D.G. & Harris, G.P. (1985) The effect of climate on long-term changes in the crustacean zooplankton biomass of Lake Windermere, UK. *Nature*, **316**, 536-539.
- George, G., Jennings, E. & Allott, N. (2010) The Impact of Climate Change on Lakes in Britain and Ireland. *The Impact of Climate Change on European Lakes* (eds D.G. George), Aquatic Ecology Series 4, pp. 359-386. Springer.
- George, D.G., Maberly, S.C. & Hewitt, D.P. (2004) The influence of the North Atlantic Oscillation on the physical, chemical and biological characteristics of four lakes in the English Lake District. *Freshwater Biology*, **49**, 760-774.
- Gerten, D. & Adrian, R. (2000) Climate-driven changes in spring plankton dynamics and the sensitivity of shallow polymictic lakes to the North Atlantic Oscillation. *Limnology and Oceanography*, **45**, 1058-1066.
- Gibson, C.E. (1984) Sinking rates of planktonic diatoms in an unstratified lake; a comparison of field and laboratory observations. *Freshwater Biology*, **14**, 507-515.
- Gibson, C.E., Wang, G. & Foy, R. H. (2000) Silica and diatom growth in Lough Neagh: the importance of internal recycling. *Freshwater Biology*, **45**, 285-293.
- Gilbert, R. (2003) Spatially irregular sedimentation in a small, morphologically complex lake: implications for paleoenvironmental studies. *Journal of Paleolimnology*, **29**, 209-220.
- Girvan, J.R. & Foy, R.H. (2006) Trophic stability in an Irish mesotrophic lake: Lough Melvin. *Aquatic Conservation: Marine and Freshwater Ecosystems*, **16**, 623-636.

- Glew, R., Smol, J.P. & Last, W.M. (2001) Sediment core collection and extrusion. *Tracking Environmental Change Using Lake Sediments. Vol 1: Basin Analysis, Coring and Chronological Techniques* (eds W.M. Last & J.P. Smol) pp.285-287. Kluwer Academic Publishers, Dordrecht.
- Gonzales-Medeiros, J.J., Perez-Cid, B., & Fernande-Gomez, E. (2005) Analytical phosphorus fractionation in sewage sludge and sediment samples. *Analytical and Bioanalytical Chemistry*, **381**, 873-878.
- Gordon, A.D. & Birks, H.J.B. (1972) Numerical methods in Quaternary Palaeoecology. 1. Zonation of Pollen Diagrams. *New Phytologist*, **71**, 961-979.
- Gorham, E. (1998) Acid deposition and its ecological effects: a brief history of research. *Environmental Science and Policy*, **1**, 153-166.
- Greene, S., Taylor, D., McElarney, Y., 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.
- Grimm, E.C. (1987) CONISS: a fortran 77 programme for stratigraphically constrained cluster analysis by the method of incremental sum of squares. *Computational Geoscience*, **13**, 13-35.
- Guiry, M.D. & Guiry, G.M. (2012) *AlgaeBase*. World-wide electronic publication, National University of Ireland, Galway. <http://www.algaebase.org>; 01.07.2010
- Haasnoot, M., Middelkoop, H., van Beek, E. & van Deursen, W.P.A. (2011) A method to develop sustainable water management strategies for an uncertain future. *Sustainable Development*, **19**, 369-381.
- Hadjikakou, M., Whitehead, P.G., Jin, L., Futter, L.J.M., Hadjinicolaou, P. & Shahgedanova, M. (2011) Modelling nitrogen in the Yeşilirmak River catchment in Northern Turkey: Impacts of future climate and environmental change and implications for nutrient management. *Science of the Total Environment*, **409**, 2404-2418.
- Haith, D.A., Mandel, R. & Wu, R.S. (1992) *Generalized Watershed Loading Functions Version 2.0 User's Manual*. Cornell University, Ithaca, New York.
- Haith, D.A. & Shoemaker, L.L. (1987) Generalized watershed loading functions for stream flow nutrients. *Water Resources Bulletin*, **23**, 471-478.

- Haith, D.A. & Tubbs, L.J. (1981) Watershed loading functions for nonpoint sources. *Proceedings of the American Society of Civil Engineers, Journal of the Environmental Engineering Division*, **107**, 121-37.
- Håkanson, L.H. (1997) Determinations of clusters, functional groups and variants among lake and catchment area variables. *International Review of Hydrobiology*, **82**, 247-275.
- Håkanson, L.H. & Jansson, M. (1983) *Principles of lake sedimentology*. pp. 322. Springer, Berlin.
- Håkanson, L.H., & Peters, R.H. (1995) *Predictive Limnology. Methods for Predictive Modelling*. SPB Academic Publishing, Amsterdam.
- Hall, R., Leavitt, P., Smol, J. & Zirnhelt, N. (1997) Comparison of diatoms, fossil pigments and historical records as measures of lake eutrophication. *Freshwater Biology*, **38**, 401-417.
- Hamilton, D.P. (1999) Numerical modelling and reservoir management: Applications of the DYRESM model. *Theoretical Reservoir Ecology and Its Applications* (eds J.G. Tundisi & M. Straskraba) pp.153-173. Backhuys, Leiden.
- Hamilton, D.P. & Landman, M.J. (2011) Lake restoration: an experimental ecosystem approach for eutrophication control. *Hydrobiologia*, **661**, 1-3.
- Hamilton, A.T., Barbour, M.T. & Bierwagen, B.G. (2010) Implications of global change for the maintenance of water quality and ecological integrity in the context of current water laws and environmental policies. *Hydrobiologia*, **657**, 263-278.
- Hammer, Ø., Harper, D.A.T. & Ryan, P.D. (2001) Past: Paleontological statistic software package for education and data analysis. *Palaeontologica Electronica*, **4**, 1-9.
- Harding, R. (1846) *Report on the drainage navigation and mill-power on Loughs Corrib, Mask & Carra on the value of the lands improved and a schedule of the apportionment of the cost of navigation*. 1846 Svo.
- Harris, G.P. (1986) *Phytoplankton ecology: structure, function, and fluctuations*. pp. 384. Chapman and Hall, London.
- Hartley, B. (1986). A check-list of the freshwater, brackish and marine diatoms of the British Isles and adjoining coastal waters. *Journal of Marine Biology Association of the United Kingdom*, **66**, 531-610.
- Hayhoe, K., Jones, B. & Gross, J. (2011) Peering into the Future: Climate and Ecological Models. *Scanning the Conservation Horizon: A Guide to Climate Change*

- Vulnerability Assessment* (eds P. Glick, B.A. Stein & N.A. Edelson) pp. 51-67. U.S. Fish and Wildlife Service.
- Hecky, R.E. & Kilham, P. (1988) Nutrient Limitation of Phytoplankton in Freshwater and Marine Environments: A Review of Recent Evidence on the Effects of Enrichment. *Limnology and Oceanography*, **33**, 796-822.
- Heiri, O., Lotter, A.F. & Lemcke, G. (2001) Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology*, **25**, 101-110.
- Heiskanen, A.S. & Solimini, A.G. (2005) *Relationships between pressures, chemical status and biological quality elements. Analysis of the current knowledge gaps for the implementation of the Water Framework Directive # EUR 21497 EN*. Report to the European Union Joint Research Centre. European Commission, Brussels.
- Helama, S., Fauria, M.M., Mielikäinen, K., Timonen, M. & Eronen, M. (2010) Sub-Milankovitch solar forcing of past climates: Mid and late Holocene perspectives. *Geological Society of America Bulletin*, **122**, 1981-1988.
- Hering, D., Borja, A., Carstensen, J., Carvalho, L., Carvalho, L., Elliott, M., Feld, C.K., Heiskanen, A., Johnson, R.K., Moe, J., Pont, D., Lyche Solheim, A. & Van de Bund, W. (2010) The European Water Framework Directive at the age of 10: A critical review of the achievements with recommendations for the future. *Science of the Total Environment*, **408**, 4007-4019.
- Hession, W.E. & Storm, D.E. (2000) Watershed-level uncertainties: implications for phosphorus management and eutrophication. *Journal of Environmental Quality*, **29**, 1172-1179.
- Hipsey, M.R., Romero, J.R., Antenucci, J.P. & Hamilton, D. (2006) *Computational Aquatic Ecosystem Dynamics Model. v. 2.3 Science Manual*. Centre for Water Research. University of Western Australia (online). <http://www.cwr.uwa.edu.au/services/models/legacy/model/dyresmcaedym/>
- Hobæk, A., Løvik, J.E., Rohrlack, T., Moe, S.J., Grung, M., Bennion, H., Clarke, G. & Piliposyan, G.T. (2012) Eutrophication, recovery and temperature in Lake Mjøsa: detecting trends with monitoring data and sediment records. *Freshwater Biology*, doi: 10.1111/j.1365-2427.2012.02832.x

- Hobbs, W., Irvine, K. & Donohue, I. (2005) Using sediments to assess the resistance of a calcareous lake to diffuse nutrient loading. *Archiv Fur Hydrobiologie*, **164**, 109-125.
- Hobbs, W.O., Ramstack Hobbs, J.M., LaFrançois, T., Zimmer, K.D., Theissen, K.M., Edlund, M.B., Michelutti, N., Butler, M.G., Hanson, M.A. & Carlson, T.J. (2012) A 200-year perspective on alternative stable state theory and lake management from a biomanipulated shallow lake. *Ecological Applications*, **22**, 1483-1496.
- Hoffland, E., Giesler, R., Jongmans, A.G. & Van Breemen, N. (2003) Feldspar tunneling by fungi along natural productivity gradients. *Ecosystems*, **6**, 739-746.
- Højberg, A.L., Refsgaard, J.C., van Geer, F., Flindt Jørgensen, L. & Zsuffa, I. (2007) Use of Models to Support the Monitoring Requirements in the Water Framework Directive. *Water Resources Management*, **21**, 1649-1672.
- Holland, C.H. (2009) *The geology of Ireland* (2nd edition) pp. 59. Dunedin Academic, Edinburgh.
- Holmes, J., Arrowsmith, C., Austin, W., Boyle, J., Fisher, E., Holme, R., Marshall, J., Oldfield, F. & van der Post, K. (2010) Climate and atmospheric circulation changes over the past 1000 years reconstructed from oxygen isotopes in lake-sediment carbonate from Ireland. *Holocene*, **20**, 1105-1111.
- Holmes, J., Jones, R., Haasc, J.N., McDermott, F., Molloy, K. & O'Connell, M. (2007) Multi-proxy evidence for Holocene lake-level and salinity changes at An Loch Mór, a coastal lake on the Aran Islands, Western Ireland. *Quaternary Science Reviews*, **26**, 2438-2462.
- Howarth, R.W., Fruci, J.R. & Sherman, D. (1991) Inputs of Sediment and Carbon to an Estuarine Ecosystem: Influence of Land Use. *Ecological Applications*, **1**, 27-39.
- Howarth, W. (2011) Diffuse Water Pollution and Diffuse Environmental Laws. Tackling Diffuse Water Pollution in England. *Journal of Environmental Law*, **23**, 129-141.
- Howley, P., Donnellan, T. & Hanrahan, K. (2010) Potential impact of CAP reform post-2013 on the cereal and livestock sectors: an Irish case study. *Journal of Farm Management*, **13**, 731-746.
- Huang, C.C. & O'Connell, M. (2000) Recent land-use and soil-erosion history within a small catchment in Connemara, western Ireland: evidence from lake sediments and documentary sources. *Catena*, **41**, 293-335.
- Hurrell, J.W. (1995) Decadal trends in the North Atlantic Oscillation, regional temperatures and precipitation. *Science*, **269**, 676-679.

- Hurrell, J.W. & Van Loon, H. (1997) Decadal variations in climate associated with the North Atlantic Oscillation. *Climatic Change*, **36**, 301-326.
- Hyde, B. & Carton, O. (2005) Manure management facilities on farms and their relevance to efficient nutrient use. *Proceedings of the Fertiliser Association of Ireland no. 42*. <http://www.fertilizer-assoc.ie/publications.htm>.
- Ibelings, B.W., Portielje, R., Lammens, E.H.R.R., Noordhuis, R., van den Berg, M.S., Joosse, W. & Meijer, M.L. (2007) Resilience of Alternative Stable States during the Recovery of Shallow Lakes from Eutrophication: Lake Veluwe as a Case Study. *Ecosystems*, **10**, 4-16.
- Inland Fisheries Ireland (IFI) (2010) *Inland Fisheries Ireland Inaugural Report 1st July 2010 to 31st July 2010*. pp. 108. IFI, Dublin.
- Imberger, J. & Patterson, J.C. (1981) A dynamic reservoir simulation model-DYRESM: 5. *Transport Models for Inland and Coastal Waters* (ed H.B. Fischer) pp. 310-361. Academic Press, New York.
- Imberger, J. & Patterson, J.C. (1989) Physical limnology. *Advances in applied mechanics*, vol. 27. pp. 303-475. Academic Press, London.
- Imerito, A. (2007) *DYRESM v4.0 Science Manual*. Centre for Water Research, University of Western Australia, Perth.
- Institute of Public Administration (2009) *EU Policy Review Analysis of recent EU legislation and policy for local and regional government*, 6/09. Institute of Public Administration and Irish Regions Brussels Office.
- IPCC (Intergovernmental Panel on Climate Change) (2007) *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. pp.104. IPCC, Geneva.
- Irvine, K., Donohue, I., Wemaëre, A., Styles, D. & Hobbs, W. (2003) Connecting land-use with water quality: sources, sinks and time-bombs. *Diffuse pollution and basin management* (ed M. Bruen) pp.56-60. Proceedings of the 7th IWA International Conference, Dublin.
- Irvine, K., Mills, P., Bruen, M., Walley, W., Hartnett, M., Black, A., Tynan, S., Duck, R., Bragg, O., Rowen, J., Wilson, J., Johnston, P. & O'Toole, C. (2004) *The use of mathematical models to support the implementation of the Water Framework*

Directive in Ireland. National Hydrology Seminar 2004, Office of Public Works, Ireland.

- Irvine, K., Mills, P., Bruen, M., Walley, W., Hartnett, M., Black, A., Tynan, S., Duck, R., Bragg, O., Rowen, J., Wilson, J., Johnston, P. & O'Toole, C. (2005) *Water Framework Directive – The Application of Mathematical Models as Decision-Support Tools (2002-W-DS-11) Synthesis report*. pp. 532. Environmental Protection Agency (Ireland), Wexford.
- Jakeman, A.J., Letcher, R.A. & Norton, J.P. (2006) Ten iterative steps in development and evaluation of environmental models. *Environmental Modelling and Software*, **21**, 602-614.
- Jennings, E. & Allott, N. (2006) Influence of the Gulf Stream influences lake nitrate concentrations in SW Ireland. *Aquatic Sciences*, **68**, 482-489.
- Jennings, E., Allott, N., McGinnity, P., Poole, R., Quirke, W., Twomey, H. & George, G. (2000) The North Atlantic Oscillation: implications for freshwater systems in Ireland. *Biology and Environment: Proceedings of the Royal Irish Academy B*, **100**, 149-158.
- Jennings, E., Allott, N., Pierson, D., Schneiderman, E.M., Lenihan, D., Samuelsson, P. & Taylor, D. (2009). Impacts of climate change on phosphorus loading from a grassland catchment – implications for future management. *Water Research*, **43**, 4316-4326.
- Jennings, E., Dalton, C., Olas, M., de Eyto, E., Allott, N. Bosch, K., Murnaghan, S. & Taylor, D. (2008). Reconstruction of the recent past in a west of Ireland catchment. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, **30**, 512-514.
- Jennings, E., Mills, P., Jordan, P., Jensen, J., Søndergaard, M., Barr, A., Glasgow, G. & Irvine K. (2003) *Eutrophication from Agricultural Sources: Seasonal Patterns and Effects of Phosphorus (2000-LS-2.1.7-M2) Final Report*. Environmental Protection Agency (Ireland), Dublin.
- Jensen, H.S., Kristensen, P., Jeppesen, E. & Skytthe, A. (1992) Iron:phosphorus ratio in surface sediment as an indicator of phosphorus release from aerobic sediments in shallow lakes. *Hydrobiologia*, **235/236**, 731-743.
- Jeppesen E., Jensen J.P., Jensen C., Faafeng B., Brettum P., Hessen D., Søndergaard M., Lauridsen T. & Christoffersen K. (2003) The impact of nutrient state and lake depth

on top-down control in the pelagic zone of lakes: study of 466 lakes from the temperate zone to the Arctic. *Ecosystems*, **6**, 313-325.

Jeppesen, E., Moss, B., Bennion, H., Carvalho, L., De Meester, L., Friberg, N., Gessner, M.O., Lauridsen, T.L., May, L., Meerhoff, M., Olafsson, J.S., Soons, M.B. & Verhoeven, J.T.A. (2010) Interaction of climate change and eutrophication. *Climate change impacts on freshwater ecosystems* (eds M. Kernan, R.W. Battarbee & B. Moss), pp. 119-152. Wiley-Blackwell, Chichester.

Jeppesen, E., Søndergaard, M., Jensen, J.P., Havens, K.E., Anneville, O., Carvalho, L., Coveney, M.F. & Deneke, R. (2005) Lake responses to reduced nutrient loading – an analysis of contemporary long-term data from 35 case studies. *Freshwater Biology*, **50**, 1747-1771.

Jewson D.H., Rippey B. & Gilmore K. (1981) Loss rates from sedimentation, parasitism and grazing during the growth, nutrient limitation and dormancy of a diatom crop. *Limnology and Oceanography*, **26**, 1045-1054.

Jiang, S., Liu, X., Sun, J., Yuan, L., Sun, L. & Wang, Y. (2011) A multi-proxy sediment record of late Holocene and recent climate change from a lake near Ny-Alesund, Svalbard. *Boreas*, **40**, 468-480.

Johnes, P.J. (1996) Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. *Journal of Hydrology*, **183**, 323-349.

Johnes P.J. & Heathwaite A.L. (1997) Modelling the impact of land use changes on water quality in agricultural catchments. *Hydrological Processes*, **11**, 269-286.

Jöhnk, K.D., Huisman, J., Sharples, J., Sommeijer, B., Viser, P.M. & Stroom, M. (2007) Summer heatwaves promote blooms of harmful cyanobacteria. *Global Change Biology*, **14**, 495-512.

Johnson, R.K. & Angeler, D.G. (2010) Tracing recovery under changing climate: response of phytoplankton and invertebrate assemblages to decreased acidification. *Journal of the North American Benthological Society*, **29**, 1472-1490.

Johnson, R.K., Battarbee, R.W., Bennion, H., Hering, D., Soons, M.B. & Verhoeven, J.T.A. (2010) Climate change: defining reference conditions and restoring freshwater ecosystems. *Climate change impacts on freshwater ecosystems* (eds M. Kernan, R.W. Battarbee & B. Moss), pp. 203-236. Wiley-Blackwell, Chichester.

- Jongmans, A.G., Van Breemen, N., Lundstrom, U.S., Van Hees, P.A.W., Finlay, R.D., Srinivasan, M., Unestam, T., Giesler, R., Melkerud, P.-A. & Olsson, M. (1997) Rock-eating fungi. *Nature*, **389**, 682-683.
- Jordan, P., Arnscheidt, J., McGrogan, H. & McCormick, S. (2007) Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser. *Hydrology and Earth System Sciences*, **11**, 372-381.
- Jordan, P., Melland, A.R., Mellander, P.-E., Shortle, G. & Wall, D. (2012) The seasonality of phosphorus transfers from land to water: Implications for trophic impacts and policy evaluation. *Science of The Total Environment*, **434**, 101-109.
- Jordan, P., Rippey, B. & Anderson, N.J. (2002) The 20th century whole-basin trophic history of an inter-drumlin lake in an agricultural catchment. *The Science of the Total Environment*, **297**, 161-173.
- Juggins, S. (2001) *The European Diatom Database. User Guide Version 1.0.* pp. 72. University of Newcastle, Newcastle-upon-Tyne.
- Juggins, S. (2003) *C2 User Guide. Software for Ecological and Palaeoecological Data Analysis and Visualisation.* University of Newcastle, Newcastle-upon-Tyne.
- Kämäri, J., Alcamo, J., Bärlund, I., Duel, H., Farquharson, F., Flörke, M., Fry, M., Houghton-Carr, H., Kabat, P., Kaljonen, M., Kok, K., Meijer, K.S., Rekolainen, S., Sendzimir, J., Varjopuro, R. & Villars, N. (2008) *Envisioning the future of water in Europe – the SCENES Project.* European Water Association.
- Kavanagh, P. & Bree, T. (2009) Water Framework Directive programme of measures: protection of high-status sites, forest, water and on-site wastewater treatment systems. *Biology and Environment: Proceedings of the Royal Irish Academy B*, **109**, 345-364.
- Keatley, B.E., Bennett, E.M., MacDonald, G.K., Taranu, Z.E. & Gregory-Eaves, I. (2011) Land-Use Legacies Are Important Determinants of Lake Eutrophication in the Anthropocene. *PLoS ONE*, **6** doi:10.1371/journal.pone.0015913
- Kelly, M.G. (2000). Identification of Common Benthic Diatoms in Rivers. *Field Studies*, **9**, 583-700.
- Kelly-Quinn, M., Tierney, D. & McGarrigle, M. (2009) Progress and challenges in the selection of type-specific reference conditions for Irish rivers and lakes. *Biology and Environment: Proceedings of the Royal Irish Academy B*, **109**, 151-160.
- Kernan, M., Battarbee, R.W., Curtis, C.J., Monteith, D.T. & Shilland, E.M. (2010) *20 Year Interpretative Report Recovery of lakes and streams in the UK from acid rain. The*

- United Kingdom Acid Waters Monitoring Network 20 year interpretative report. ECRC Research Report #141. Report to the Department for Environment, Food and Rural Affairs (Contract EPG 1/3/160) (UK).*
- Khan, F.A. & Ansari, A.A. (2005) Eutrophication: An Ecological Vision. *The Botanical Review*, **71**, 449-482.
- Kirilova, E., Heiri, O., Enters, D., Cremer, H., Lotter, A.F., Zolitschka, B. & Hübener, T. (2009) Climate-induced changes in the trophic status of a Central European lake. *Journal of Limnology*, **68**, 71-82.
- Kirk McClure Morton (2003) *A catchment based approach for reducing nutrient inputs from all sources to the Lakes of Killarney - final report*. Kerry County Council, Tralee.
- Kleinman, P.J.A. & Sharpley, A.N. (2003) Effect of broadcast manure on runoff phosphorus concentrations over successive rainfall events. *Journal of Environmental Quality*, **32**, 1072-1081.
- Knie, M. & Hübener, T. (2007) Morphopological variability of the *Cyclotella ocellata-krammeri-rossi* complex in field samples and cultures. *Proceedings of the 1st Central European Diatom Meeting 2007* (eds W.H. Kusber & R. Jahn) 2007 Botanic Garden and Botanical Museum Berlin-Dahlem. Freie Universität Berlin, Berlin.
- Kovach, W.L. (1995) Multivariate Data Analysis. *Statistical Modelling of Quaternary Science Data. Technical Guide 5*. (eds D. Maddy & J.S. Brew) pp. 1-37. Quaternary Research Association, Cambridge.
- Krammer, K. & Lange-Bertalot, H. (1986) Bacillariophyceae. 1. Teil: Naviculaceae *Süßwasserflora von Mitteleuropa, Vol. 2/1* (eds H. Ettl, J. Gerloff, H. Heynig & D. Mollenhauer) pp. 876. Fischer-Verlag, Stuttgart.
- Krammer, K. & Lange-Bertalot, H. (1988) Bacillariophyceae. 2. Teil: Bacillariaceae, Epithemiaceae, Surirellaceae. *Süßwasserflora von Mitteleuropa, Vol. 2/2* (eds H. Ettl, J. Gerloff, H. Heynig & D. Mollenhauer) pp. 596. Fischer-Verlag, Stuttgart.
- Krammer, K. & Lange-Bertalot, H. (1991a) Bacillariophyceae. 3. Teil: Centrales, Fragilariaceae, Eunotiaceae. *Süßwasserflora von Mitteleuropa Vol. 2/3* (eds H. Ettl, J. Gerloff, H. Heynig & D. Mollenhauer) pp. 576. Fischer-Verlag, Stuttgart.
- Krammer, K. & Lange-Bertalot, H. (1991b) Bacillariophyceae. 4. Teil: Achnanthaceae. Kritische Ergänzungen zu *Navicula* (Lineolatae) und *Gomphonema*. *Süßwasserflora von Mitteleuropa, Vol. 2/4* (eds H. Ettl, J. Gerloff, H. Heynig & D. Mollenhauer) pp. 437. Fischer-Verlag, Stuttgart.

- Krause, W. & King, J.J. (1994) The ecological status of Lough Corrib, Ireland, as indicated by physiographic factors, water chemistry and macrophytic flora. *Vegetatio*, **110**, 149-161.
- Krichak, S.O. & Alpert, P. (2005) Decadal trends in the east Atlantic - west Russia pattern and Mediterranean precipitation. *International Journal of Climatology*, **25**, 183-192.
- Kronvang, B., Rubæk, G.H. & Heckrath, G. (2009) International Phosphorus Workshop: Diffuse Phosphorus Loss to Surface Water Bodies - Risk Assessment, Mitigation Options, and Ecological Effects in River Basins. *Journal of Environmental Quality*, **38**, 1924-1929.
- Kundzewicz, Z.W., Becker, A. & Hattermann, F.F. (2010) Introduction. *Water Framework Directive: model supported implementation – a water manager's guide*. (eds F.F.Hattermann & Z.W. Kundzewicz), pp. 11-53. IWA, London.
- Lange-Bertalot, H. & Metzeltin, D. (1996) *Indicators of oligotrophy: 800 taxa representative of three ecologically distinct lake types: carbonate buffered-oligodystrophic-weakly buffered soft water (Vol. 2)*. Koeltz Scientific Books, Königstein.
- Larssen, T. & Holmes J. (2006) Afforestation, seasalt episodes and acidification – A paired catchment study in western Norway. *Environmental Pollution*, **139**, 440-450.
- Last, W.M. (2001) Textural Analysis of Lake Sediments. *Tracking Environmental Change Using Lake Sediments. Vol 2: Physical and Geochemical Methods* (eds W.M. Last & J. P. Smol) pp. 41-81. Kluwer Academic Publishers, Dordrecht.
- Leavesley, G.H. (1999) Overview of models for use in the evaluation of the impacts of climate change on hydrology. *Impacts of climate Change and Climate Variability on Hydrologic Regimes* (eds J.C. van Dam) pp. 160. Cambridge University Press, Cambridge.
- Leavitt, P.R. & Hodgson, D.A. (2001) Sediment Pigments. *Tracking Environmental Change Using Lake Sediments. Vol. 3: Terrestrial, Algal and Siliceous Indicators* (eds J.P. Smol, H.J.B. Birks & W.M. Last) pp. 1-32. Kluwer Academic Publishers, Amsterdam.
- Lee, K.Y., Fisher, T.R., Jordan, T.E., Correll, D.L. & Weller, D.E. (2000) Modeling the Hydrochemistry of the Choptank River Basin Using GWLF and Arc/Info: 1. Model Calibration and Validation. *Biogeochemistry*, **49**, 143-173.

- Legendre, P. & Birks, H.J.B. (2012) From classical to canonical ordination. Chapter 7 In: *Tracking Environmental Change using Lake Sediments. Vol. 5: Data handling and numerical techniques* (eds H.J.B. Birks, S. Juggins, A.F. Lotter & J.P. Smol) Springer, Dordrecht.
- Leira, M., Jordan, P., Taylor, D., Dalton, C., Bennion, H. & Irvine, K. (2006) Recent histories of the main types of candidate reference lakes in Ireland: a palaeolimnological approach. *Journal of Applied Ecology*, **43**, 816-827.
- Leng, M.J., Swann, G.E.A., Hodson, M.J., Tyler, J.J., Patwardhan, S.V. & Sloane H.J. (2009) The Potential use of Silicon Isotope Composition of Biogenic Silica as a Proxy for Environmental Change. *Silicon*, **1**, 65-77.
- Lepš, J. & Šmilauer, P. (2003) *Multivariate Analysis of Ecological Data using CANOCO*. pp. 269. Cambridge University Press, Cambridge.
- Leslie, C. & Hancock, G.J. (2008) Estimating the date corresponding to the horizon of the first detection of ^{137}Cs and $^{239+240}\text{Pu}$ in sediment cores. *Journal of Environmental Radioactivity*, **99**, 483-490.
- Likens, G.E. & Davis, M.B. (1975) Post-glacial history of Mirror Lake and its watershed in New Hampshire USA: an initial report. *Verhandlungen der Internationalen Vereinigung der Limnologie*, **19**, 982-993.
- Linstead, C., Maltby, E., Neilson, H.O., Horlitz, T., Koundouri, P., Birol, E., Remoundou, K., Janssen, R. & Jones, P. (2010) Tools for better decision making: bridges from science to policy. *Climate Change Impacts on Freshwater Ecosystems* (eds M. Kernan, R.W. Battarbee & B. Moss) pp. 262-285. Wiley-Blackwell, Chichester.
- Littell, J.S., McKenzie, D., Kerns, B.K. Cushman, S. & Shaw C.G. (2000) Managing uncertainty in climate-driven ecological models to inform adaptation to climate change. *Ecosphere*, **2**, 1-19.
- Livingstone, D.M., Lotter, A.F. & Kettle, H. (2005) Altitude-dependent differences in the primary physical response of mountain lakes to climatic forcing. *Limnology and Oceanography*, **50**, 1313-1325.
- Ljung, L. (1999). *System identification - theory for the user* (2nd edition). Prentice-Hall, New Jersey.
- Lotter, A.F., Birks, H.J.B., Hofmann, W. & Marchetto, A. (1997) Modern diatom, cladocera, chironomid, and chrysophyte cyst assemblages as quantitative indicators for the

- reconstruction of past environmental conditions in the Alps. I. Climate. *Journal of Paleolimnology*, **18**, 395-420.
- Lowe, J.J. & Walker, M.J.C. (1997) Dating Methods. *Reconstructing Quaternary Environments*. Longman, London.
- Lowe, R. (2010) *Epithemia adnata*. *Diatoms of the United States*. Retrieved July 01, 2008, from http://westerndiatoms.colorado.edu/taxa/species/epithemia_adnata
- Luettich, R.A. Jr., Harlemann, D.R.F. & Somlyódy, L. (1990) Dynamic behaviour of suspended sediment concentrations in a shallow lake perturbed by episodic wind events. *Limnology and Oceanography*, **35**, 1050-1067.
- Lund J.W.G. (1950) Studies on *Asterionella formosa* Hass. II. Nutrient depletion and the spring maximum. *Journal of Ecology*, **38**, 1-5.
- Lund J.W.G. (1954) The seasonal cycle of the planktonic diatom *Melosira italica* (Ehr.). *Kutz. subsp. subarctica* O. Mull. *Journal of Ecology*, **42**, 151-179.
- Luoto, T.P. & Raunio, J.A (2011) comparison of chironomid-based training sets developed from pupal exuviae and larval head capsules to infer lake trophic history. *Archiv für Hydrobiologie*, **179**, 93-102.
- Lyche-Solheim, A., Rekolainen, S., Moe, S.J., Carvalho, L., Phillips, G., Ptacnik, R., Penning, W.E., Toth, L.G., O'Toole, C., Schartau, A.L. & Hesthagen, T. (2008) Ecological threshold responses in European lakes and their applicability for the Water Framework Directive (WFD) implementation: synthesis of lakes results from the REBECCA project. *Aquatic Ecology*, **42**, 317-334.
- Mackay, A.W., Flower, R.J., Kuzmina, A.E., Granina, L.Z., Rose, N.L., Appleby, P.G., Boyle, J.F. & Battarbee, R.W. (1998) Diatom succession trends in recent sediments from Lake Baikal and their relation to atmospheric pollution and to climate change. *Philosophical Transactions of the Royal Society of London B*, **353**, 1011-1055.
- Macintosh, K., Jordan, P., Cassidy, R., Arnscheidt, J. & Ward, C. (2011) Low flow water quality in rivers; septic tank systems and high-resolution phosphorus signals. *Science of the Total Environment*, **412**, 58-65.
- Mackereth, F.J.H. (1966) Some chemical observations on post-glacial lake sediments. *Philosophical Transactions of the Royal Society of London B*, **250**, 165-213.
- Magny, M. (2007) Early Holocene climate oscillations - causes and consequences - Early Holocene climate oscillations - causes and consequences. *Quaternary Science Reviews*, **26**, 1951-1964.

- Magny, M., Peyron, O., Gauthier, E., Rouèche, Y., Bordon, A., Billaud, Y., Chapron, E., Marguet, A., Pétrequin, P. & Vannière, B. (2009) Quantitative reconstruction of climatic variations during the Bronze and early Iron ages based on pollen and lake-level data in the NW Alps, France. *Quaternary International*, **200**, 112-110.
- Maguire, R.O., Crouse, D.A. & Hodges, S.C. (2007) Diet modification to reduce phosphorus surpluses: a mass balance approach. *Journal of Environmental Quality*, **36**, 1235-1240.
- Maguire, R.O., Rubæk, G.H., Haggard, B.E. & Foy, B.H. (2009) Critical Evaluation of the Implementation of Mitigation Options for Phosphorus from Field to Catchment Scales. *Journal of Environmental Quality*, **38**, 1989-1997.
- Maher, L.J. (1972) Absolute pollen diagram of Redrock Lake, Boulder County, Colorado. *Quaternary Research*, **2**, 531-533.
- Maitland, P.S. & Campbell, R.N. (1992) *Freshwater fishes of the British Isles*. 368 pp. Harper Collins, London.
- Maitland, P.S., Winfield, I.J., McCarthy, I.D. & Igoe, F. (2007) The status of Arctic charr *Salvelinus alpinus* in Britain and Ireland. *Ecology of Freshwater Fish*, **16**, 6-19.
- Mance, G., Raven, P.J., & Bramley, M.E. (2002) Integrated river basin management in England and Wales: a policy perspective. *Aquatic Conservation: Marine And Freshwater Ecosystems*, **12**, 339-346.
- Manly, B.F.J. (2005) *Multivariate Statistical Methods: a primer* 3rd Edition. pp.214. Chapman and Hall, Florida.
- Marshall, P.A. & Randhir, T. (2008) Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic Geochemistry*, **34**, 261-289.
- Mason, C. (2002) *Biology of Freshwater Pollution*. Pearson Education Limited, Edinburgh.
- Mathieu, G.G., Biscaye, P.E., Lupton, R.A. & Hammond, D.E. (1988) System for measurement of ²²²Rn at low levels in natural waters. *Health Physics*, **55**, 989-992.
- Mauquoy, D. & van Geel, B. (2007) Plant macrofossil methods and studies: Mire and peat macros. *Encyclopedia of Quaternary Science* (eds S.A. Elias) Elsevier, Amsterdam.
- Mayewski, P.A., Rohling, E.E., Stager, J.C., Karlén, W., Maasch, K.A., Meeker, L.D., Meyerson, E.A., Gasse, F., van Kreveld, S., Holmgren, K., Lee-Thorp, J., Rosqvist, G., Racki, F., Staubwasser, M., Schneider, R.R. & Steig, E.J. (2004) Holocene climate variability. *Quaternary Research*, **62**, 243-255.

- McCarthy, T.K., Barbiero, R., Doherty, D., Cullen, P., Ashe, P., O'Connell, M., Guiry, M., Sheehy-Skeffington, M., King, M. & O'Connor, B. (2001) *Investigations of Eutrophication Processes in the Littoral Zones of Western Irish Lakes*. Environmental Protection Agency (Ireland), Wexford.
- McCarthy, T.K., Barbiero, R.P., King, J., Doherty, B., O'Connor, B. & Cullen, P. (2000). Water quality monitoring in larger western Irish lakes. *Verhandlungen der Internationalen Vereinigung der Limnologie*, **27**, 1816-1821.
- McDermott, F., Frisia, S., Huang, Y., Longinelli, A., Spiro, B., Heaton, T.H.E., Hawkesworth, C.J., Borsato A., Keppens, E., Fairchild, I.J., van der Borg, K., Verheyden, S. & Selmo, E. (1999) Holocene climate variability in Europe: Evidence from $d^{18}O$, textural and extension-rate variations in three speleothems. *Quaternary Science Reviews*, **18**, 1021-1038.
- McGarrigle, M.L. & Champ, W.S.T. (1999) Keeping pristine lakes clean: Loughs Conn and Mask. *Hydrobiologia*, **395/396**, 455-469.
- McGarrigle, M.L., Lucey, J. & Ó Cinnéide, M. (2010) *Water Quality in Ireland 2007-2009*. Aquatic Environment Office of Environmental Assessment, Environmental Protection Agency (Ireland), Wexford.
- McGechan, M.B., Lewis, D.R. & Hooda, P.S. (2005) Modelling through-soil transport of phosphorous to surface waters from livestock agriculture at the field and catchment scale. *Science of the Total Environment*, **344**, 185-199.
- McGowan, S., Barker, P., Haworth, E.Y., Leavitt, P.R., Maberly, S.C. & Pates, J. (2012) Humans and climate as drivers of algal community change in Windermere since 1850. *Freshwater Biology*, **57**, 260-277.
- McNally, T. (2009) Overview of the EU Water Framework Directive and its implementation in Ireland. *Biology and Environment: Proceedings of the Royal Irish Academy B*, **109**, 131-138.
- Meybeck, M. (1980) Pathways of major elements from land to ocean through rivers. *Proceedings of the Review and Workshop on River Inputs to Ocean-Systems*. (eds J.M. Martin, J.D. Burton & D. Eisma) pp. 18-30.
- Meyers, P.A. (2003). Applications of organic geochemistry to paleolimnological reconstruction: A summary of examples from the Laurentian Great Lakes. *Organic Geochemistry*, **34**, 261-289.

- Meyers, P.A. (2006) An overview of sediment organic matter records of human eutrophication in the Laurentian Great Lakes Region. *Water, Air and Soil Pollution: Focus*, **6**, 453-463.
- Millard, S.P. & Neerchal, N.K. (2001) *Environmental statistics with S-Plus*. CRC Press, London.
- Miller, A.W. (2011) Monitoring and Classifying Trophic States of Selected Lakes in Yellowstone Park, USA. *International Journal of Sustainable Water and Environmental Systems*, **2**, 49-56.
- Mirchi, A., Watkins, D. & Madani, K. (2009) Modeling for watershed planning, management, and decision making. *Watersheds: Management, Restoration and Environmental Impacts* (Ed J.C. Vaughn) Nova Science Publishers.
- Monteith, D.T., Evans, C.D. & Reynolds, B. (2000) Are temporal variations in the nitrate content of UK upland freshwaters linked to the North Atlantic Oscillation? *Hydrological Processes*, **14**, 1745-1749.
- Monteith, D.T. & Shilland, E.M. (2007) *The United Kingdom acid waters monitoring network assessment of the first 18 years of data: data summary annex accompanying research project final report*. ENSIS Ltd, London.
- Mooij, W.M., Hulsmann, S., De Senerpont, L.N., Nolet, B.A., Bodelier, P.L.E., Boers, P.C.M., Pires, L.M.D., Gons, H.J., Ibelings, B.W., Noordhuis, R., Portielje, R., Wolfstein, K. & Lammens, E.H.R.R. (2005) The impact of climate change on lakes in the Netherlands: a review. *Aquatic Ecology*, **39**, 381-400.
- Moore, K., Jennings, E., May, L., Jarvinen, M., Allott, N., Arvola, L., Tamm, T., Jarvet, A., Nõges, T., Pierson D. & Schneiderman, E. (2010) Modelling the effects of climate change on the supply of inorganic nitrogen. *The Impact of Climate Change on European Lakes. Aquatic Ecology Series, Vol. 4.* (eds D.G. George) pp. 179-198. Springer.
- Moss, B. (1999) Ecological challenges for lake management. *Hydrobiologia*, **395/396**, 3-11.
- Moss, B. (2010) What of the future? *Climate Change Impacts on Freshwater Ecosystems* (eds M. Kernan, R.W. Battarbee & B. Moss) pp. 285-300. Wiley-Blackwell, Chichester.
- Moss, B., Kosten, S., Meerhoff, M., Battarbee, R.W., Jeppesen, E., Mazzeo, N., Havens, K., Lacerot, G., Liu, Z., De Meester, L., Paerl, H. & Scheffer, M. (2011) Allied attack: climate change and eutrophication. *Inland Waters*, **1**, 101-105.

- Murnaghan, S., Taylor, D., Jennings, E., Dalton, C., Olaya-Bosch, K. & O'Dwyer, B. (2012) Middle to late Holocene environmental changes in western Ireland inferred from fluctuations in preservation of biological variables in lake sediment. *Journal of Paleolimnology*, **48**, 433-448.
- Murphy, T.P., Hall, K.J. & Yesaki, I. (1983) Coprecipitation of phosphate with calcite in a naturally eutrophic lake. *Limnology and Oceanography*, **28**, 58-69.
- Murray, M.R. (2002) Is laser particle size determination possible for carbonate-rich lake sediments? *Journal of Paleolimnology*, **27**, 173-183.
- Naden, P.S., Allott, N., Arvola, L., Järvinen, M., Jennings, E., Moore, K., Nic Aongusa, C., Pierson, D. & Schneiderman, E. (2010) Modelling the impacts of climate change on dissolved organic carbon. *The Impact of Climate Change on European Lakes. Aquatic Ecology Series, Vol. 4.* (eds D.G. George) pp. 221-252. Springer.
- Naiman, R.J. & Dudgeon, D. (2011) Global alteration of freshwaters: influences on human and environmental well-being. *Ecological Research*, **26**, 865-873.
- Nash, J.E. & Sutcliffe, J.V. (1970) River flow forecasting through conceptual models. Part 1: A discussion of principles. *Journal of Hydrology*, **10**, 282-290.
- Neal, M., Reynolds, B., Maberly, S.C., May, L., Ferriere, R.C., Smith, J. & Parker J.E. (2005) Silicon concentrations in UK surface waters. *Journal of Hydrology*, **304**, 75-93.
- Nesje, A., Bakke, J., Dahl, S.O., Lie, Ø. & Bøe, A. (2007) A continuous, high-resolution 8500-yr snow-avalanche record from western Norway. *Holocene*, **17**, 269-277.
- Nickus, U., Bishop, K., Erlandsson, M., Evans, C.D., Forsius, M., Laudon, H., Livingstone, D.M., Monteith, D. & Thies, H. (2010) Direct impacts of climate change on freshwater ecosystems. *Climate Change Impacts on Freshwater Ecosystems* (eds M. Kernan, R.W. Battarbee & B. Moss) pp. 38-65. Wiley-Blackwell, Chichester.
- Nixon, S.W. (1995) Coastal marine eutrophication, a definition, social causes and future concerns. *Ophelia*, **41**, 199-219.
- Nöges, P., Adrian, R., Orlane, A., Arvola, L., Blenckner, T., George, G., Jankowski, T., Järvinen, M., Jarvine, M., Maberly, S., Padisak, J., Straile, D., Teubner, K. & Weyhenmeyer, G. (2010) The impacts of variations in the climate on seasonal dynamics of phytoplankton. *The impact of climate change on European lakes.* (eds D.G. George), Aquatic Ecology Series 4, pp. 253-274. Springer.

- Nõges, P., Nõges, T., Adrian, R. & Weyhenmeyer, G. (2008) Silicon load and the development of diatoms in three river-lake systems in countries surrounding the Baltic Sea. *Hydrobiologia*, **599**, 67-76.
- Northern Ireland Environment Agency (2008) *Neagh Bann Draft River Basin Management Plan*. Northern Ireland Environment Agency, Belfast.
- O'Brien, S.R., Mayewski, P.A., Meeker, L.D., Messe, D.A., Twickler, M.S. & Whitlow, S.I. (1995) Complexity of Holocene climate as reconstructed from a Greenland ice core. *Science*, **270**, 1962-1964.
- O'Connell, M. (1986) Reconstruction of local landscape development in the post-Atlantic based on palaeoecological investigations at Carrownaglogh prehistoric field system, County Mayo, Ireland. *Review of Palaeobotany and Palynology*, **49**, 117-176.
- Odgaard, B.V. (1994) Holocene vegetation history of norther West Jutland, Denmark. *Opera Botanica*, **123**, 1-171.
- O'Dwyer, B. & Taylor, D. (2010) Variations in levels of depositions of atmosphere-borne industrial pollutants at three oligotrophic lakes in Ireland over the last 50-150 years: sediment-based archives of sources, levels and ecological sensitivity. *Journal of Paleolimnology*, **44**, 123-142.
- OECD (Organisation of Economic Co-operation and Development) (1982) *Eutrophication of Waters: Monitoring and Assessment*. pp. 154. OECD, Paris.
- Ó Gráda, C. (1995) *The Great Irish famine*. pp. 80. University press, Cambridge.
- Ohmann, J.L. & Spies, T.A. (1998) Regional gradient analysis and spatial pattern of woody plant communities of Oregon forests. *Ecological Monographs*, **68**, 151-182.
- Økland, R.H. (1999) On the variation explained by ordination and constrained ordination axes. *Journal of Vegetation Science*, **10**, 131-136.
- Økland, R.H. & Eilertsen, O. (1994) Canonical correspondence analysis with variation partitioning: some comments and an application. *Journal of Vegetation Science*, **5**, 117-26.
- Økland, T. (1996) Vegetation-environment relationships of boreal spruce forests in ten monitoring reference areas in Norway. *Sommerfeltia*, **22**, 1-349.
- Oldfield, F. (2005) *Environmental change: key issues and alternative perspectives*. University Press, Cambridge.
- Oldfield, F., Battarbee, R.W., Boyle, J.F., Cameron, N.G., Davis, B., Evershed, R.P., McGovern, A.D., Jones, V., Thompson, R. & Walker (née Wake), R. (2010)

- Terrestrial and aquatic ecosystem responses to late Holocene climate change recorded in the sediments of Lochan Uaine, Cairngorms, Scotland. *Quaternary Science Reviews*, **29**, 1040-1054.
- Oldfield, F., Barnosky, C., Leopold, E.B. & Smith J.P. (1983) Mineral magnetic studies of lake sedi- ments. *Hydrobiologia*, **103**, 37-44.
- O'Mealoin, P. (2005) *5-Year Review: 2000-2005*. Carra Mask Corrib Water Protection Group Ltd., Headford, Co.Galway, Ireland.
- Oreskes, N., Shrader-Frechette, K. & Belitz, K. (1994) Verification, Validation, and Confirmation of Numerical Models in the Earth Sciences. *Science*, **263**, 641-646.
- Ormerod, S. J. & Durance, I. (2009) Restoration and recovery from acidification in upland Welsh streams over 25 years. *Journal of Applied Ecology*, **46**, 164-174.
- Ormerod, S.J., Dobson, M., Hildrew, A.G. & Townsend, C.R. (2010) Multiple stressors in freshwater ecosystems. *Freshwater Biology*, **55**, 1-4.
- O'Sullivan, P.E. & Reynolds, C.S. (2004) *The Lakes Handbook, Volume 1. Limnology and Limnetic Ecology*. pp.699. Blackwell, Malden.
- Otsuki, A. & Wetzel, R.G. (1972) Coprecipitation of phosphate with carbonates in a marl lake. *Limnology and Oceanography*, **17**, 763-767.
- Overland, A. & O'Connell, M. (2008) Fine-spatial paleoecological investigations towards reconstructing late Holocene environmental change, landscape evolution and farming activity in Barrees, Beara peninsula, southwestern Ireland. *Journal of the North Atlantic*, **1**, 37-73.
- Paerl, H.W., Xu, H., McCarthy, M.J., Zhu, G., Qin, B., Li, Y. & Gardner, W.S. (2010) Controlling harmful cyanobacterial blooms in a hyper-eutrophic lake (Lake Taihu, China): The need for a dual nutrient (N & P) management strategy. *Water Research*, **45**, 1973-1983.
- Palmer, M.W. (1993) Putting things in even better order: the advantages of canonical correspondence analysis. *Ecology*, **74**, 2215-30.
- Parajka, J., Merz, R. & Blöschl, G. (2005) A comparison of regionalisation methods for catchment model parameters. *Hydrology and Earth Systems Sciences*, **9**, 157-171.
- Patrick, S.T. (1988) Septic tanks as sources of phosphorus to Lough Erne, Ireland. *Journal of Environmental Management*, **26**, 239-248.

- Peng, C., Guiot, J., Wu, H., Jiang, H. & Luo, Y. (2011) Integrating models with data in ecology and palaeoecology: advances towards a model-data fusion approach. *Ecology Letters*, **14**, 522-536.
- Pennington, W., Haworth, E.Y., Bonny, A.P. & Lishman, J.P. (1972) Lake sediments in northern Scotland. *Philosophical Transactions of the Royal Society of London B*, **264**, 191-294.
- Perrin, C., Michel, C. & Andréassian, V. (2001) Does a large number of parameters enhance model performance? Comparative assessment of common catchment model structures on 429 catchments. *Journal of Hydrology*, **242**, 275-301.
- Pierson, D.C., Arvola, L., Allott, N., Järvinen, M., Jennings, E., May, L., Moore, K., Naden, P. & Schneiderman, E. (2010) Modelling the effects of climate change on the supply of phosphate-phosphorus. *The Impact of Climate Change on European Lakes*. Aquatic Ecology Series, 4. (eds D.G. George) pp. 139-159. Springer.
- Podriska, B. & Gajewski, K. (2007) Diatom community response to multiple scales of Holocene climate variability in a small lake on Victoria Island, NWT, Canada. *Quaternary Science Reviews*, **26**, 3179-3196.
- Pollard, P., Devlin, M. & Holloway, D. (2001) Managing a complex river catchment: a case study on the River Almond. *Science of the Total Environment*, **265**, 343-357.
- Potapova, M. & Hamilton, P.B. (2007) Morphological and ecological variation within the *Achnantheidium minutissimum* (Bacillariophyceae) species complex. *Journal of Phycology*, **43**, 561-575.
- Press, W.H., Teukolsky, S.A., Vetterling, W.T. & Flannery, B.P. (1992) *Numerical recipes in C: the art of scientific computing* (2nd edition). Cambridge University Press, Cambridge
- Raadgever, G.T., Dieperink, C., Driessen, P.P.J., Smith, A.A.H. & Van Rijswijk, H.F.M.W. (2011) Uncertainty management strategies: Lessons from the regional implementation of the Water Framework Directive in the Netherlands. *Environmental Science & Policy*, **14**, 64-75.
- Racca, J.M.J., Philbert, A., Racca, R. & Prairie, Y.T. (2001) A comparison between diatom based pH inference models using Artificial Neural Networks(ANN), Weighted Averaging (WA) and Weighted Averaging Partial Least Squares (WA-PLS) regressions. *Journal of Paleolimnology*, **26**, 411-422.

- Rasanan, J., Kauppila, T. & Salonen, V. (2006) Sediment based investigation of naturally or historically eutrophic lakes - implications for lake management. *Journal of Environmental Management*, **79**, 253-265.
- Rast, W. & Holland, M. (1988) Eutrophication of lakes and Reservoirs: A Framework for Making Management Decisions. *Ambio*, **17**, 2-12.
- Reavie, E.D. & Smol, J.P. (2001) Diatom–environmental relationships in 64 alkaline southeastern Ontario (Canada) lakes: a diatom-based model for water quality reconstructions. *Journal of Paleolimnology*, **25**, 25-42.
- Reckhow, K.H. & Chapra, S.C. (1998) Modelling excessive nutrient loading in the catchment. *Environmental Pollution*, **100**, 197-207.
- Reed, J.M. (1998) Diatom preservation in the recent sediment record of Spanish saline lakes: implications for palaeoclimate study. *Journal of Paleolimnology*, **19**, 129-137.
- Reimer, P.J., Baillie, M.G.L., Bard, E., Bayliss, A., Bertrand, B.J.W., Chanda, J.H., Blackwell, P. G., Buck, C.E., Burr, G.S., Cutler, K.B., Damon, P.E., Edwards, R.L., Fairbanks, R.G., Friedrich, M., Guilderson, T.P., Hogg, A.G., Hughen, K.A., Kromer, B., McCormac, G., Manning, S., Ramsey, C.B., Reimer, R.W., Remmele, S., Southon, J.R., Stuiver, M., Talamo, S., Taylor, F.W., van der Plicht, J. & Weyhenmeyer, C.E. (2004) IntCal04 terrestrial radiocarbon age calibration, 26–0 ka BP. *Radiocarbon*, **46**, 1029-1058.
- Rekolainen, S., Kämäri, J. & Hiltunen, M. (2003) A conceptual framework for identifying the need and role of models in the implementation of the Water Framework Directive. *International Journal of River Basin Management*, **1**, 347-352.
- Renberg, I. & Hansson, H. (2008) The HTH sediment corer. *Journal of Paleolimnology*, **40**, 655-659.
- Reynolds, C.S. & Petersen, A.C. (2000) The distribution of planktonic cyanobacteria in Irish lakes in relation to their trophic status. *Hydrobiologia*, **424**, 91-99.
- Richter, T.O., Peeters, F.J.C. & van Weering, T.C.E. (2009) Late Holocene (0–2.4 ka BP) surface water temperature and salinity variability, Feni Drift, NE Atlantic Ocean. *Quaternary Science Reviews*, **28**, 1941-1955.
- Rippey, B. & Anderson, N.J. (1996) Reconstruction of lake phosphorus loading and dynamics using the sedimentary record. *Environmental Science and Technology*, **30**, 1786-88.

- Robbins, J.A. (1978) Geochemical and geophysical applications of radioactive lead. *Biogeochemistry of lead in the environment* (ed J.O. Nriagu) pp.285-293. Elsevier Scientific Publishers, Amsterdam.
- Rooney, N. & Kalff, J. (2000) Inter-annual variation in submerged macrophyte community biomass and distribution: the influence of temperature and lake morphometry. *Aquatic Botany*, **68**, 321-335.
- Rose, N.L. (1994) A note on further refinements to a procedure for the extraction of carbonaceous fly-ash particles from sediments. *Journal of Paleolimnology*, **11**, 201-204.
- Rose, N.L. (2001) Fly-Ash Particles. *Tracking Environmental Change Using lake Sediments. Vol 2: Physical and Geochemical Methods* (eds W.M. Last & J.P. Smol) pp. 319-350. Kluwer Academic Publishers, Dordrecht.
- Rose, N.L. (2008) Quality control in the analysis of lake sediments for spheroidal carbonaceous particles. *Limnology and Oceanography: Methods*, **6**, 172-179.
- Rose, N.L., Harlock, S. & Appleby, P.G. (1999) Within-basin profile variability and cross correlation of lake sediment cores using the spheroidal carbonaceous particle record. *Journal of Paleolimnology*, **21**, 85-96.
- Rose, N.L., Harlock, S., Appleby, P.G. & Battarbee, R.W. (1995) Dating of recent lake sediments in the United Kingdom and Ireland using spheroidal carbonaceous particle (SCP) concentration profiles. *The Holocene*, **5**, 328-335.
- Rose, N.L., Rose, C.L., Boyle, J.F. & Appleby, P.G. (2004) Lake-sediment evidence for local and remote sources of atmospherically deposited pollutants on Svalbard. *Journal of Paleolimnology*, **31**, 499-513.
- Rosenzweig, C., Major, D.C., Demong, K., Stanton, C., Horton, R. & Stults, M. (2007) Managing climate change risks in New York City's water system: Assessment and adaptation planning. *Mitigation and Adaptation Strategies for Global Change*, **12**, 1391-1409.
- Russell, J.M. & Johnson, T.C. (2005) A high-resolution geochemical record from Lake Edward, Uganda Congo and the timing and causes of tropical African drought during the late Holocene. *Quaternary Science Reviews*, **24**, 1375-1389.
- Ryves, D.B., Battarbee, R.W. & Fritz, S.C. (2009) The Dilemma of Disappearing Diatoms: Incorporating Diatom Dissolution Data into Paleoenvironmental Modeling and Reconstruction. *Quaternary Science Reviews*, **28**, 120-136.

- Ryves, D.B., Battarbee, R.W., Juggins, S., Fritz, S.C. & Anderson, N.J. (2006) Physical and Chemical Predictors of Diatom Dissolution in Freshwater and Saline Lake Sediments in North America and West Greenland. *Limnology and Oceanography*, **51**, 1355-1368.
- Ryves, D.B., Juggins, S., Fritz, C. & Battarbee, R.W. (2001) Experimental diatom dissolution and the quantification of microfossil preservation in sediments. *Palaeogeography Palaeoclimatology Palaeoecology*, **172**, 99-113.
- Salmaso, N. (2012) Influence of atmospheric modes of variability on a deep lake south of the Alps. *Inter-Research*, **51**, 125-133.
- Sayer, C.D. (2001) Problems with the application of diatom-total phosphorus transfer functions: examples from a shallow English lake. *Freshwater Biology*, **46**, 743-57.
- Scheffer, M. (2004) *Ecology of shallow lakes*. pp. 357. Kluwer Academic Publishers. Dordrecht.
- Scheffer, M. & Carpenter, S.R. (2003) Catastrophic regime shifts in ecosystems: linking theory to observation. *Trends in Ecology & Evolution*, **18**, 648-656.
- Scheffer, M. & Van Nes, E.H. (2007) Shallow lakes theory revisited: various alternative regimes driven by climate, nutrients, depth and lake size. *Hydrobiologia*, **584**, 455-466.
- Scheffer, M., Carpenter, S.R., Foley, J.A., Folke, C. & Walker, B. (2001a) Catastrophic shifts in ecosystems. *Nature*, **413**, 591-596.
- Scheffer, M., De Redelijkheid, M.R. & Noppert, F. (1992) Distribution and dynamics of submerged vegetation in a chain of shallow eutrophic lakes. *Aquatic Botany*, **42**, 199-216.
- Scheffer, M., Hosper, S.H., Meijer, M.L., Moss, B. & Jeppesen, E. (1993) Alternative equilibria in shallow lakes. *Trends in Ecology and Evolution*, **8**, 275-79.
- Scheffer, M., Straile, D., Van Nes, E.H. & Hosper, H. (2001b) Climatic warming causes regime shifts in lake food webs. *Limnology and Oceanography*, **46**, 1780-1783.
- Schelske, C.L., Stoermer, E.F., Fahnenstiel, G.L. & Haibach, M. (1986) Phosphorus Enrichment, Silica Utilization, and Biogeochemical Silica Depletion in the Great Lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, **43**, 407-415.
- Schettler, G., Romer, R.L., O'Connell, M. & Molloy, K. (2006) Holocene climatic variations and postglacial sea-level rise geochemically recorded in the sediments of the brackish karst lake An Loch Mor, western Ireland. *Boreas*, **34**, 674-693.

- Schindler, D.W., Hecky, R.E., Findlay, D.L., Stainton, M.P., Parker, B.R., Paterson, M.J., Beaty, K.G., Lyng, M. & Kasian, S.E.M. (2008) Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences*, **105**, 11254-58.
- Schneiderman, E.M., Pierson, D.C., Lounsbury D.G. & Zion, M.S. (2002) Modelling the hydrochemistry of the Cannonsville Watershed with the Generalized Watershed Loading Functions GWLF. *Journal of the American Water Resources Association*, **38**, 1323-47.
- Schneiderman, E.M., Järvinen, M., Jennings, E., May, L., Moore, K., Naden, P. & Pierson, D.C. (2010) Modeling the effects of climate change on catchment hydrology with the GWLF model. *The Impact of Climate Change on European Lakes. Aquatic Ecology Series, Vol. 4.* (eds D.G. George) pp 33-49. Springer.
- Schulte, R.P.O., Melland, A.R., Fenton, O., Herlihya, M., Richards, K. & Jordan, P. (2010) Modelling soil phosphorus decline: Expectations of Water Framework Directive policies. *Environmental Science and Policy*, **13**, 472-484.
- Sharpley, A., Herron, S., West, C. & Daniel, T. (2009) Outcomes of phosphorus-based nutrient management in the Eucha-Spavinaw Watershed. *Farming with Grass Achieving Sustainable Mixed Agricultural Landscapes* (eds A.J. Franzluebbers), pp. 192-204. Soil and Water Conservation Society, Ankeny, Iowa.
- Shimoda, Y., Azim, M.E., Perhar, G., Ramin, M., Kenney, M.A., Sadraddini, S., Gudimov, A. & Arhonditsis, G.B. (2011) Our current understanding of lake ecosystem response to climate change: What have we really learned from the north temperate deep lakes? *Journal of Great Lakes Research*, **37**, 173-193.
- Shrestha, S., Hennessy, T. & Hynes, S. (2007) The effect of decoupling on farming in Ireland: A regional analysis. *Irish Journal of Agricultural and Food Research*, **46**, 1-13.
- Shumway, R.H. & Stoffer, D.S. (2011) Time Series Regression and Exploratory Data Analysis. *Time Series Analysis and Its Applications: With R Examples*. Springer.
- S.I. 101 (2009) European Communities Good agricultural practice for protection of waters regulations. Government Publication Office, Dublin.
- S.I. 258 (1998) Local Government (Water Pollution) Act, 1977 (Water Standards for Phosphorus) Regulations. Government Publications Office, Dublin.

- S.I. 610 (2010) European Communities Good agricultural practice for protection of waters. Government Publication Office, Dublin.
- Simms, M.J. (2005). The Great Western Lakes. In: *The Quaternary of central western Ireland: Field Guide* (eds P. Coxon) pp. 71-78. Quaternary Research Association, London.
- Simpson, G.L. & Anderson, N.J. (2009) Deciphering the effect of climate change and separating the influence of confounding factors in sediment core records using additive models. *Limnology and Oceanography*, **54**, 2529-2541.
- Skjelkvåle, B.L., Stoddard, J.L., Jeffries, D.S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D.T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A. & Worsztynowicz, A. (2005) Regional scale evidence for improvements in surface water chemistry 1990–2001. *Environmental Pollution*, **137**, 165-176.
- Smart, R.P., Soulsby, C., Cresser, M.S., Wade, A.J., Townend, J., Billett, M.F. & Langan, S. (2001) Riparian zone influence on stream water chemistry at different spatial scales: a GIS-based modelling approach, an example for the Dee, NE Scotland. *Science of the Total Environment*, **280**, 173-193.
- Smith, B.N. & Epstein, S. (1971) Two categories of $^{13}\text{C}/^{12}\text{C}$ ratios for higher Plants. *Plant Physiology*, **47**, 380-384.
- Smith, I.R. (1975) Turbulence in lakes and rivers. *Freshwater Biological Association, Scientific Publications*, **29**, 1-79.
- Smith, I.R. (1979) Hydraulic Conditions in Isothermal Lakes. *Freshwater Biology*, **9**, 119-145.
- Smith, I.R. (2002) Diatom-based Holocene paleoenvironmental records from continental sites on northeastern Ellesmere Island, high Arctic, Canada. *Journal of Paleolimnology*, **27**, 9-28.
- Smith, V.H., Joye, S.B. & Howarth, R.W. (2006) Eutrophication of freshwater and marine ecosystems. *Limnology and Oceanography*, **51**, 351-355.
- Smith, V.H. & Schindler, D.W. (2009) Eutrophication science: Where do we go from here? *Trends in Ecology and Evolution*, **24**, 201-207.
- Smith, V.H., Tilman, G.D. & Nekola, J.C. (1999). Eutrophication: impacts of nutrient inputs to freshwater, marine and terrestrial ecosystems. *Environmental Pollution*, **100**, 179-196.

- Smol, J.P. (2008) *Pollution of lakes and rivers: a paleoenvironmental perspective*, pp. 383. Blackwell, Malden.
- Smol, J.P. (2010) The power of the past: using sediments to track multiple stressors on lake ecosystems. *Freshwater Biology*, **55**, 43-59.
- Smol, J.P. & Douglas, M.S.V. (2007) From Controversy to Consensus: Making the Case for Recent Climate Change in the Arctic Using Lake Sediments. *Frontiers in Ecology and the Environment*, **5**, 466-474.
- Smol, J.P., Wolfe, A.P., Birks, H.J.B., Douglas, M.S.V., Jones, V.J., Korhola, A., Pienitz, R., Ruhland, K., Sorvari, S., Antoniades, D., Brooks, S. J., Fallu, M., Hughes, M., Lain, T.E., Michelutti, N., Nazarov, L., Nyman, M., Paterson, A.M., Perren, B., Quinlan, R., Rautio, M., Saulnier-Talbot, E., Siitonen, S., Solovieva, N. & Weckstrome J. (2005) Climate-driven regime shifts in the biological communities of Arctic lakes. *Proceedings of the National. Academy of Sciences, USA*, **102**, 4397-4402.
- Søndergaard, M., Jensen, J.P. & Jeppesen, E. (2003) Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia*, **506-509**, 135-145.
- Sophocleous, M. (2002) Interactions between groundwater and surface water: the state of the science. *Hydrogeology Journal*, **10**, 52-67.
- Stefánsson, A., Gunnarsson, I. & Giroud, N. (2007) New methods for the direct determination of dissolved inorganic, organic and total carbon in natural waters by Reagent-Free Ion Chromatography and inductively coupled plasma atomic emission spectrometry. *Analytica Chimica Acta*, **582**, 69-74.
- Steffen, W., Grinevald, J., Crutzen, P. & McNeill J. (2011) The Anthropocene: conceptual and historical perspectives. *Philosophical Transactions of the Royal Society of London A*, **369**, 842-867.
- Steinberg, P.D., Brett, M.T., Bechtold, J.S., Richey, J.E., Porensky, L.M. & Smith, S.N. (2011) The influence of watershed characteristics on nitrogen export to and marine fate in Hood Canal, Washington, USA. *Biogeochemistry*, **106**, 415-433.
- Stendera, S. & Johnson, R.K. (2008) Tracking recovery trends of boreal lakes: use of multiple indicators and habitats. *Journal of the North American Benthological Society*, **27**, 529-540.

- Stevens, R.J., Laughlin, R.J., O'Bric, C.J., Carton, O.T. & Lenehan, J.J. (1997) The efficiency of nitrogen in cattle slurry acidified with nitric acid for grass production. *Journal of Agricultural Science*, **129**, 335-342.
- Stoddard, J.L., Driscoll, C.T., Kahl, J.S. & Kellogg, J.H. (1998) Can site-specific trends be extrapolated to a region? An acidification example for the northeast. *Ecological Applications*, **8**, 288-299.
- Straile, D. (2002) North Atlantic Oscillation synchronizes food-web interactions in central European lakes. *Proceedings of the Royal Society of London B*, **269**, 391-395.
- Stuiver, M. & Reimer, P.J. (1993) Extended ^{14}C Data Base and Revised Calib 3.0 ^{14}C Age Calibration Program. *Radiocarbon*, **35**, 215-230.
- Stutter, M.I., Langan, S.J. & Lumsdon D.G. (2009) Vegetated Buffer Strips Can Lead to Increased Release of Phosphorus to Waters: A Biogeochemical Assessment of the Mechanisms. *Environmental Science and Technology*, **43**, 1858-1863.
- Styles, D., Donohue, I., Coxon, C. & Irvine, K. (2006) Linking soil phosphorus to water quality in the Mask catchment of western Ireland through the analysis of moist soil samples. *Agriculture, Ecosystems and Environment*, **112**, 300-312.
- Sutherland, W.J. (2006) Predicting the ecological consequences of environmental change: a review of the methods. *Journal of Applied Ecology*, **43**, 599-616.
- Sweeney, J. (2003) *Climate Change, Scenarios and Impacts for Ireland*. pp. 229. Environmental Protection Agency (Ireland), Wexford.
- Swindles, G.T., Plunkett, G. & Roe, H.M. (2007) A delayed climatic response to solar forcing at 2800 cal. BP: multiproxy evidence from three Irish peatlands. *Holocene*, **17**, 177-182.
- Taylor, D., Dalton, C., Leira, M., Jordan, P., Chen, G., León-Vintró, L., Irvine, K., Bennion, H. & Nolan, T. (2006) Recent histories of six productive lakes in the Irish Ecoregion based on multiproxy palaeolimnological evidence. *Hydrobiologia*, **571**, 237-259.
- Taylor, D., McElarney, Y., Greene, S., Barry, C., Foy, B., Jordan, P., Macintosh, K., Arnscheidt, J. & Murnaghan, S. (2012) *An Effective Framework For assessing aquatic ECosysTem responses to implementation of the Phosphorous Regulations (EFFECT) (# 2007-W-MS-3-SI)*. Environmental Protection Agency (Ireland), Wexford.
- Taylor, W. (2003) *Change-Point Analyzer 2.3 software package*. Taylor Enterprises, Illinois.

- Telford, R.J., Heegaard, E. & Birks, H.J.B. (2004) All age-depth models are wrong: but how badly? *Quaternary Science Reviews*, **23**, 1-5.
- ter Braak, C.F.G. & Prentice, I.C. (1988) A theory of gradient analysis. *Advances in Ecological Research*, **18**, 271-317.
- ter Braak, C.J.F. (1995) Ordination. *Data Analysis in Community and Landscape Ecology* (eds R.H.G. Jongman, C.J.F. Ter Braak & O.F.R. Van Tongeren) pp. 91-173. Cambridge University Press, Cambridge.
- ter Braak, C.J.F. & Juggins, S. (1993) Weighted averaging partial least squares regression (WA-PLS): an improved method for reconstructing environmental variables from species assemblages. *Hydrobiologia*, **269-270**, 485-502.
- ter Braak, C.J.F. & Šmilauer, P. (2002) *CANOCO reference manual and CanoDraw for Windows. User's guide: software for canonical community ordination (version 4.5)*. Microcomputer Power, Ithaca, New York.
- Thackeray, S.J., Jones, I.D. & Maberly, S.C. (2008) Long-term change in the phenology of spring phytoplankton: species-specific responses to nutrient enrichment and climatic change. *Journal of Ecology*, **96**, 523-535.
- Thomann, R.V. (1982) Verification of Water Quality Models. *Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers*, **108**, 923-940.
- Thompson, D.W. & Wallace, K.M. (1998) The Arctic Oscillation signature in the winter time geopotential high and temperature fields. *Geophysical Research Letters*, **25**, 1297-1300.
- Tilman, D., Kilham, S.S. & Kilham P. (1982) Phytoplankton Community Ecology: The Role of Limiting Nutrients. *Annual Review of Ecology and Systematics*, **13**, 349-372.
- Tinner, W., Lotter, A.F., Ammann, B., Conedera, M., Hubschmid, P., Van Leeuwena, J.F.N & Wehrli, M. (2003) Climatic change and contemporaneous land-use phases north and south of the Alps 2300 BC to 800 AD. *Quaternary Science Reviews*, **22**, 1447-1460.
- Toner, P., Bowman, J., Clabby, K., Lucey, J., McGarrigle, M., Concannon, C., Clenaghan, C., Cunningham, P., Delaney, J., O'Boyle, S., MacCárthaigh, M., Craig, M. & Quinn, R. (2005) *Water Quality in Ireland 2001-2003*. Environmental Protection Agency (Ireland), Wexford.

- Townsend, P.D., Parish, R. & Rowlands, A.P. (2002) A new interpretation of depth-age profiles. *Radiation Protection Dosimetry*, **101**, 315-319.
- Treacy, E. (2011) *An Examination of Temporal and Spatial Water Quality Variations in Lakes, with Emphasis on the Limnology and Palaeolimnology of Lough Currane, Co. Kerry, Ireland*. PhD thesis, Trinity College, Dublin.
- Troels-Smith, J. (1955) Characterisation of unconsolidated sediments. *Danmarks geologiske Undersøgelse IV*, **3**, 1-734.
- Trolle, D., Hamilton, D.P., Pilditch, C.A., Duggan, I.C. & Jeppesen, E. (2011) Predicting the effects of climate change on trophic status of three morphologically varying lakes: Implications for lake restoration and management. *Environmental Modelling and Software*, **26**, 354-370.
- Trolle, D., Skovgaard, H. & Jeppesen, E. (2008) The Water Framework Directive: setting the phosphorus loading target for a deep lake in Denmark using the 1D lake ecosystem model DYRESM-CAEDYM. *Ecological Modelling*, **219**, 138-152.
- Turner, M. (2002) *After the Famine: Irish Agriculture, 1850-1914*. pp. 317. University press, Cambridge.
- Turner, J.N., Macklin, M.G., Jones, A.F. & Lewis, H. (2010) New perspectives on Holocene flooding in Ireland using meta-analysis of fluvial radiocarbon dates. *Catena*, **82**, 183-190.
- Ulen, B. (1978) Seston and Sediment in Lake Norrviken. III Nutrient Release from Sediment. *Schweizerische Zeitschrift für Hydrologie*, **40**, 287-305.
- Vadas, P.A., Harmel, R.D. & Kleinman, P.J.A. (2007) Transformations of soil and manure phosphorus after surface application of manure to field plots. *Nutrient Cycling in Agroecosystems*, **77**, 83-99.
- Vagstad, N., French, H.K., Andersen, H.E., Behrendt, H., Grizzetti, B., Groenendijk, P., Lo Porto, A., Reisser, H., Siderius, C., Stromquist, J., Hejzlar, J. & Deelstra, J. (2009) Comparative study of model prediction of diffuse nutrient losses in response to changes in agricultural practices. *Journal of Environmental Monitoring*, **11**, 594-601.
- Van Breemen, N., Finlay, R.D., Lundstrom, U.S. & Jongmans, A.G., Giesler, R. & Melkerud, P.-A. (2000a) Mycorrhizal weathering: a true case of mineral plant nutrition? *Biogeochemistry*, **49**, 53-67.
- Van Breemen, N., Lundstrom, U.S., Jongmans, A.G. (2000b) Do plants drive podzolization via rock-eating mycorrhizal fungi? *Geoderma*, **94**, 163-171.

- van der Keur, P., Henriksen, H.J., Refsgaard, J.C., Brugnach, M., Pahl-Wost, C., Dewulf, A. & Buiteveld, H. (2008) Identification of Major Sources of Uncertainty in Current IWRM Practice. Illustrated for the Rhine Basin. *Water Resources Management*, **22**, 1677-1708.
- Vasseur, D.A. & McCann, K.S. (2007) *The Impact of Environmental Variability on Ecological Systems*. The Peter Yodzis Fundamental Ecology Series 2, pp. 231, Springer, Dordrecht.
- Volk, M., Lautenbach, S., van Delden, H., Newham, L.T.H. & Seppelt, R. (2009) How Can We Make Progress with Decision Support Systems in Landscape and River Basin Management? Lessons Learned from a Comparative Analysis of Four Different Decision Support Systems. *Environmental Management*, **46**, 834-849.
- Vollenweider, R.A. (1968) *Scientific fundamentals of the eutrophication of lakes and flowing waters with particular reference to nitrogen and phosphorus as factors in eutrophication*. OECD Technical Report No. DAS/DST/88. pp.182. OECD, Paris.
- Walling, D.E. & Qingping, H. (1992) Sediment and water movement in rivers and their catchments: Interpretation of caesium-137 profiles in lacustrine and other sediments: the role of catchment-derived inputs. *Hydrobiologia*, **235-236**, 219-230.
- Walsh, M. (1974) *Corrib Mask drainage scheme: soils of the Lough Mask and River Robe catchment area and estimation of increase in agricultural production from the damaged soils following arterial drainage and reclamation*. pp. 66. An Foras Taluntais, Belclare.
- Wassmann, P., Duarte, C.M., Agustí, S. & Sejr, M.K. (2011) Footprints of climate change in the Arctic marine ecosystem. *Global Change Biology*, **17**, 1235-1249.
- Wasylikowa, K. (1986) The analysis of fossil fruits and seeds. In: *Handbook of Holocene palaeoecology and palaeohydrology* (eds B.E. Berglund), pp. 571-590. John Wiley & Sons Ltd, Chichester.
- Webster, K.E., Soranno, P.A., Baines, S.B., Kratz, T.K., Bowser, C.J., Dillon, P.J., Campbell, P., Fee, F.J. & Hecky, R.E. (2000) Structuring features of lake districts: landscape controls on lake chemical responses to drought. *Freshwater Biology*, **43**, 499-515.
- Wetzel, R.G. (2001) *Limnology: Lake and River Ecosystems*. (3rd Edition), pp. 1006. Academic Press, San Diego, California.

- Weyhenmeyer, G.A. (2001) Warmer Winters: Are Planktonic Algal Populations in Sweden's Largest Lakes Affected? *Ambio*, **30**, 565-571.
- Weyhenmeyer, G.A., Blenchner, T. & Pettersson, K. (1999) Changes in the plankton spring outburst related to the North Atlantic Oscillation. *Limnology and Oceanography*, **44**, 1788-1792.
- Weyhenmeyer, G.A., Willen, E. & Sonesten, L. (2004) Effects of an extreme precipitation event on water chemistry and phytoplankton in the Swedish Lake Malaren. *Boreal Environment Research*, **9**, 409-420.
- White, A.F. & Blum, A.E. (1995) Climate effects on chemical weathering in watersheds: application of mass balance approaches. *Solute Modelling of Catchments* (eds S.T. Trudgill) pp. 100-131. Wiley, Chichester.
- Whitehead, P.G. , Wilby, R.L. , Battarbee, R.W. , Kernan, M. & Wade, A.J. (2009) A review of the potential impacts of climate change on surface water quality *Hydrological Sciences Journal*, **54**, 101-123.
- Whitmore, T.J., Brenner, M. & Schelske, C.L. (1996) Highly variable sediment distribution in shallow wind-stressed lakes: a case for sediment-mapping surveys in paleolimnological studies. *Journal of Paleolimnology*, **15**, 207-221.
- Wik, M. & Renberg, I. (1991) Spheroidal carbonaceous particles as a marker for recent sediment distribution. *Hydrobiologia*, **214**, 85-90.
- Wilhelm, S. & Adrian, R. (2008) Impact of summer warming on the thermal characteristics of a polymictic lake and consequences for oxygen nutrients and phytoplankton. *Freshwater Biology*, **53**, 226-237.
- Williams, D.M., Hartley, B., Ross, R., Munro, M.A.R., Juggins, S. & Battarbee, R.W. (1988). *A coded checklist of British Diatoms*. pp. 74. ENSIS Publishing, London.
- Winder, M. & Schindler, D.E. (2004) Climate Change Uncouples Trophic Interactions in an Aquatic Ecosystem. *Ecology*, **85**, 2100-2106.
- Wischmeier, W.H. & Smith, D. (1978) *Predicting rainfall erosion losses: a guide to conservation planning*. USDA-ARS Agriculture Handbook No. 537, pp. 58. Washington DC.
- Withers, P.J.A., Clay, S.D. & Breeze, V.G. (2001) Phosphorus transfer following application of fertilizer, manure and sewage sludge. *Journal of Environmental Quality*, **30**, 180-188.

- Wolfe, B.B., Edwards, T.W.D., Elgood, R.J. & Beuning K.R.M. (2001) Carbon and oxygen isotope analysis of lake sediment cellulose: methods and applications. In: *Tracking Environmental Change Using Lake Sediments. Vol. 2: Physical and Geochemical Methods* (eds J.P. Smol, H.J.B. Birks & W.M. Last) pp. 373-400. Kluwer Academic Publishers, Amsterdam.
- Woodward, C.A. & Shulmeister, J. (2005) A Holocene record of human induced and natural environmental change from Lake Forsyth (Te Wairewa), New Zealand. *Journal of Palaeolimnology*, **34**, 481-501.
- Wright, H.H. (1990) An improved Hongve sampler for surface sediments. *Journal of Palaeolimnology*, **5**, 91-92.
- Wright, R.F. (2007) The decreasing importance of acidification episodes with recovery from acidification: an analysis of the 30-year record from Birkenes, Norway. *Hydrology and Earth System Sciences*, **12**, 353-362.
- Wunsam, S. & Schmidt, R. (1995) A diatom-phosphorus transfer function for Alpine and pre-alpine lakes. *Memorie dell Istituto Italiano di Idrobiologia*, **53**, 85-99.
- Zhou, Q., Gibson, C.E. & Foy, R.H. (2000) Long-Term Changes of Nitrogen and Phosphorus Loadings to a Large Lake in North-West Ireland. *Water Research*, **34**, 922-926.
- Yang, X. & Griffiths, I.M. (2010) A Comparison of the Legal Frameworks Supporting Water Management in Europe and China. *Water Science and Technology*, **61**, 745-61.
- Zalasiewicz, J., Williams, M., Smith, A., Barry, T.L. & Coe, A.L. (2008) Are we now living in the Anthropocene. *GSA Today*, **18**, 4-8.
- Zhang, H.X. (2010) Water Quality Management in the Context of Climate Change: Importance for Adapting Critical Condition and Uncertainty Analysis in the Threshold or Scenario Approach. *Proceedings of the World Environmental and Water Resources Congress 2010*. American Society of Civil Engineers, Virginia.

Appendices

Appendix A Mean annual air temperature (°C) and total annual precipitation (mm) for the Blacksod weather station (from 1900-1952 AD) and Claremorris synoptic meteorological station (from 1950-2006 AD) (Figure 2.1) available from Met Éireann

Year	Air temperature (°C)	Precipitation (mm)
1900	9.6	1414.5
1901	9.5	1210.6
1902	9.8	1114.6
1903	9.6	1619.5
1904	9.6	1274.8
1905	9.9	1195.8
1906	9.6	1120.4
1907	9.5	1548.1
1908	10.1	1406.9
1909	9.5	1353.3
1910	9.4	1189.2
1911	10.0	1289.3
1912	9.5	1608.3
1913	9.8	1385.3
1914	-	-
1915	9.1	-
1916	9.1	1113.3
1917	8.6	1249.9
1918	9.3	1230.2
1919	8.7	1273.8
1920	-	-
1921	-	-
1922	-	-
1923	-	-
1924	9.3	1198.5
1925	-	-
1926	9.8	-
1927	9.9	1368.7
1928	10.4	1453.2
1929	10.2	1554.8
1930	9.8	1220.7
1931	10.4	1565.4
1932	9.9	1195.8
1933	10.5	1203.0
1934	10.3	1325.7
1935	10.0	1160.0
1936	10.0	1274.0
1937	9.3	1233.0

Appendix A (continued)

Year	Air temperature (°C)	Precipitation (mm)
1938	10.0	-
1939	10.1	-
1940	10.2	1060.3
1941	9.8	1113.7
1942	10.1	1502.9
1943	10.3	1510.0
1944	10.4	1160.4
1945	11.1	1192.0
1946	10.1	1330.3
1947	9.8	1312.6
1948	9.7	1272.7
1949	11.0	1387.8
1950	8.7	1305.3
1951	8.4	1188.6
1952	8.7	785.7
1953	9.3	975.2
1954	8.8	1378.1
1955	8.9	1062.5
1956	8.7	1140.5
1957	9.4	1057.6
1958	8.9	1204.5
1959	9.4	1212.0
1960	8.8	1304.2
1961	8.8	1165.2
1962	8.4	907.8
1963	8.0	1035.6
1964	9.1	1280.0
1965	8.3	1068.2
1966	8.9	1122.0
1967	8.8	1213.5
1968	8.8	1261.9
1969	8.6	882.6
1970	9.0	1159.2
1971	9.4	879.7
1972	8.5	1066.0
1973	9.2	1104.0
1974	8.8	1110.1
1975	9.5	1021.9
1976	9.2	972.7
1977	9.1	1216.1
1978	9.2	1025.7
1979	8.2	1249.1
1980	8.9	1272.4
1981	9.1	1258.5

Appendix A (continued)

Year	Air temperature (°C)	Precipitation (mm)
1982	9.2	1307.9
1983	9.7	1109.1
1984	9.1	908.2
1985	8.4	1397.4
1986	8.2	1284.1
1987	8.8	1128.6
1988	9.4	1274.4
1989	9.5	1300.2
1990	9.7	1258.8
1991	9.3	1119.1
1992	9.1	1389.7
1993	9.0	1109.6
1994	9.3	1402.3
1995	9.9	1006.6
1996	8.8	996.1
1997	9.9	1192.0
1998	9.6	1392.4
1999	9.7	1303.1
2000	9.3	1284.4
2001	9.1	1005.8
2002	9.7	1133.5
2003	9.7	912.2
2004	9.6	1262.6
2005	9.9	1047.6
2006	10.4	806.0

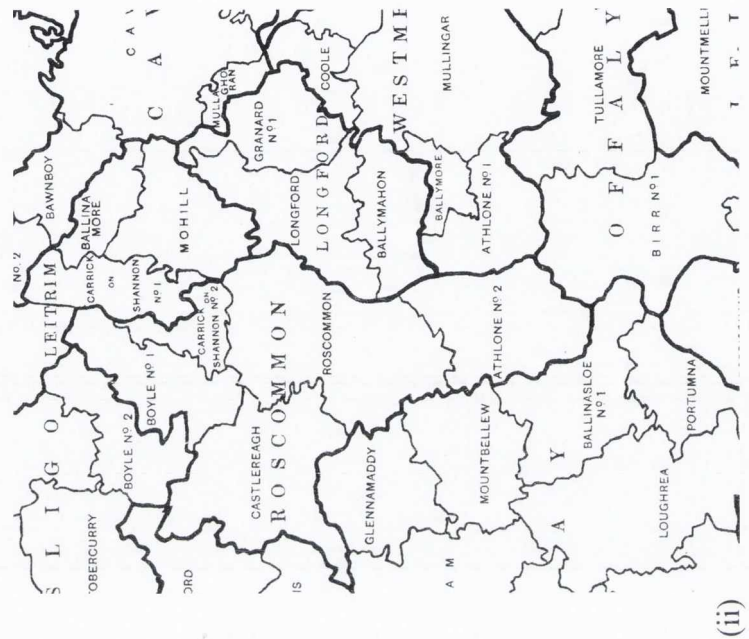
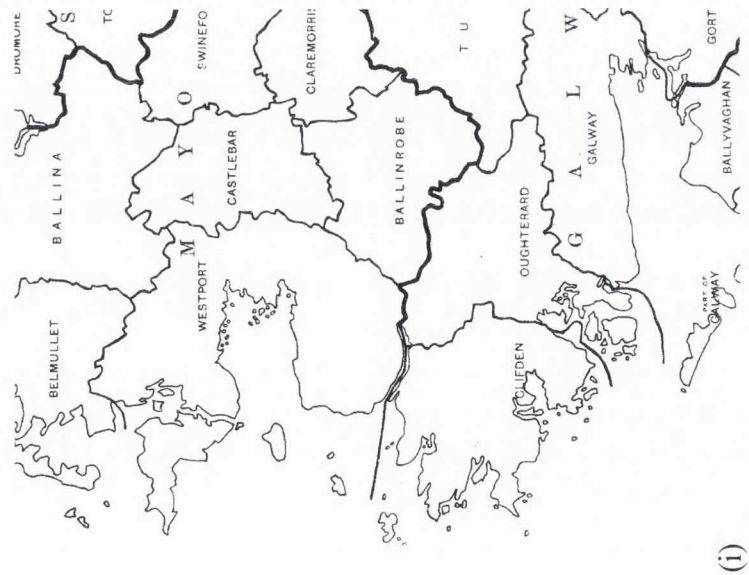
Appendix B List of District Electoral Divisions (DEDs) and Rural Districts in the Lough Mask catchment

County	Rural Districts	DEDs	% area in Mask catchment	subcatchment
Mayo	Westport	Aghagower-north	10%	Aille
		Aghagower-south	90%	Aille
		Ballinafad	1.5%	Carra
Galway	Oughterard	Ballinchalla	100%	Owenbrin
Mayo	Claremorris	Ballindine	87%	Robe
Mayo	Ballinrobe	Ballinrobe	100%	Robe
		Ballyhean	100%	Carra
		Ballyhowly	47%	Robe
		Ballyovey	96%	Srah
		Bekan	50%	Robe
Mayo	Castlebar	Breaghwy	20%	Carra
		Burriscarra	98%	Carra
		Cappaghduff	97%	Glensaul
		Caraun	100%	Robe
		Castlebar rural	8%	Carra
		Claremorris	98%	Robe
		Clogher	99%	Carra
		Cloghermore	55%	Robe
		Cloonbur	50%	Cong
		Cloonkeen	54%	Aille
		Cong	7%	Cong
		Coonard	100%	Robe
		Crossboyne	100%	Robe
		Culnacleha	50%	Robe
		Erriff	25%	Owenbrin
		Garrymore	50%	Robe
		Hollymount	100%	Robe
		Kilcolman	28%	Robe
		Kilcommon	30%	Robe
		Killavally	99%	Aille
		Kilmaine	40%	Robe
		Kilvine	10%	Robe
		Knock-south	25%	Robe
		Mayo	14%	Carra
Longford		Milltown	10%	Robe
Galway	Tuam	Murneen	6%	Robe
		Neale	60%	Robe
		Newbrook	77%	Carra/Robe
		Owenbrin	100%	Owenbrin
		Portroyal	100%	Carra
		Ross	94%	Srahnalong

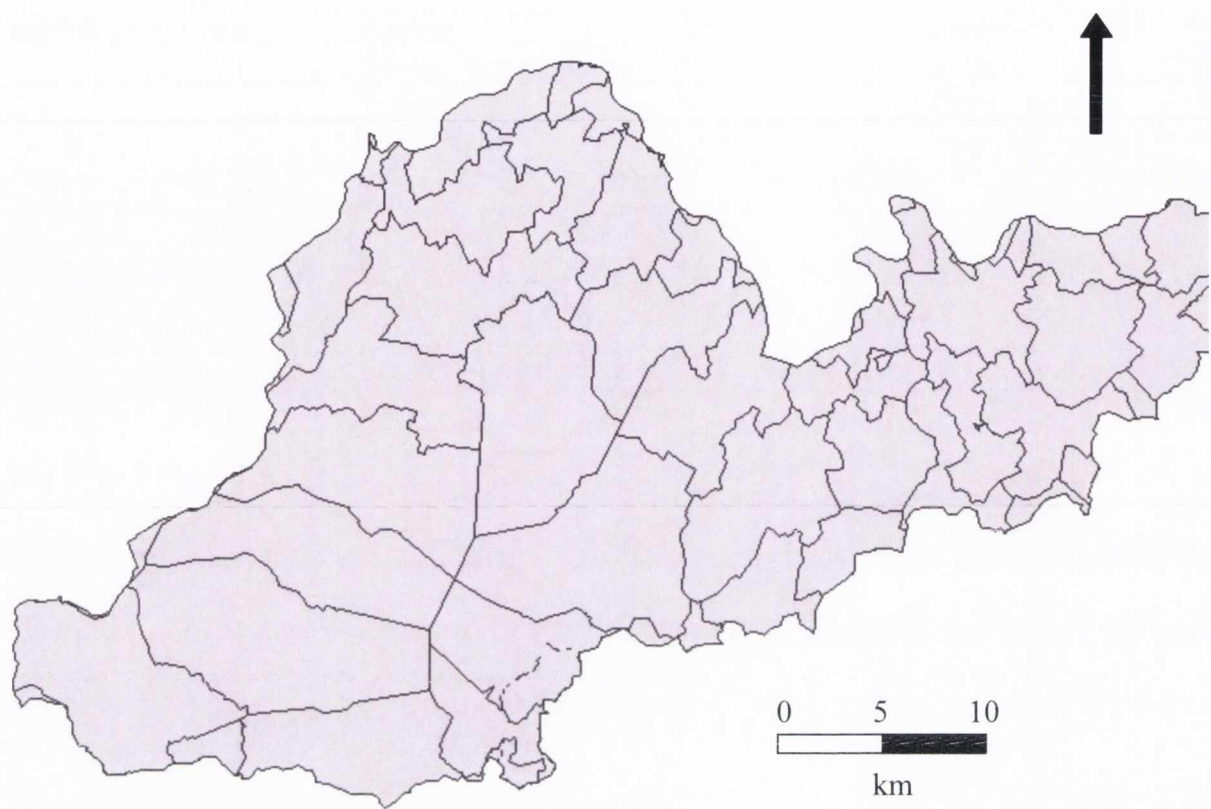
Appendix B (continued)

County	Rural Districts	DEDs	% area in Mask catchment	subcatchment
Galway	Tuam	Rosslie	50%	Carra
		Slieve Mahanagh	3%	Aille
		Tagheen	96%	Robe
		Tawnynagry	100%	Srah/Aille/Carra

Appendix C Map of Rural Districts that intersect the Lough Mask catchment: west (i) and east (ii), provided by Mr Simon Fernandez (Glucksman Map Library, Trinity College Dublin)



Appendix D Map showing the catchment boundary and DEDs in the Lough Mask catchment supplied by Dr Ian Donohue (Department of Zoology, Trinity College Dublin)



Appendix E Historical census data from 1880-2006 AD for the main Lough Mask subcatchments obtained from the CSO: (i) human population, (ii) cattle and sheep numbers

(i)

Year AD	number of people		
	Robe	West (total)	Carra
1881	22813	7492	5214
1891	19601	7458	4442
1901	16967	6733	3914
1911	16096	6272	3376
1926	14123	5423	2987
1936	13613	4651	2763
1946	12880	4164	2540
1951	12141	3805	2400
1956	11589	3394	2347
1961	10892	3043	2217
1966	10390	2843	2110
1971	10110	2708	1983
1979	10421	2801	2080
1981	10440	2836	2160
1986	10390	2856	2241
1991	10038	2641	2232
1996	9830	2592	2222
2002	10806	2430	2686
2005	10806	2430	2686

(ii)

Year AD	number of cattle			number of sheep		
	Robe	West (total)	Carra	Robe	West (total)	Carra
1880	17347	7987	2052	42656	24610	8441
1891	19803	10055	2330	62700	37439	10022
1901	21623	11019	2608	61447	34940	11604
1911	24891	11760	2949	52767	33186	11479
1926	16697	10736	3559	45476	31300	11576
1933	17794	11512	3872	47577	33151	12019
1955	22216	13937	4951	56198	35777	13267
1960	23480	13868	4992	72812	44481	16948
1965	25987	15255	5712	77209	46899	18667
1970	24149	16982	6445	11080	44671	17070
1975	38091	21455	8084	59650	40954	14756
1980	38432	21256	8304	35626	36194	12104
1991	29742	25087	7756	58004	94387	19981
2000	36094	18942	8613	61256	70407	16371
2005	36094	18942	8613	61256	70407	16371

Appendix F Historical landuse data available from the CSO for census years between 1841-1911 AD (i), on the basis of Rural Districts (acres), and recent (1981-2006 AD) landuse data from the EPA, on the basis of subcatchment (hectares). *includes meadow and clover

(i)

Rural district	Land use classification	1891	1901	1910	1926
		acres			
Ballinrobe	Crops*	20283	19398	11330	12129
	Grass	79806	80081	85119	90482
	Fallow	88	8	-	-
	Wood and plantations	4098	3453	3341	3355
	Turf bog	10665	6217	5374	5398
	Marsh	5375	2818	4648	4668
	Barren mountain land	19140	27068	23096	23195
	Water, roads, fences, etc.	5800	6307	7844	7878
Castlebar	Crops*	20693	20704	12347	10046
	Grass	61278	68764	102510	78053
	Fallow	42	41	40	-
	Wood and plantations	1500	1429	1453	2541
	Turf bog	13882	16473	10749	18805
	Marsh	9513	6805	3922	6861
	Barren mountain land	24850	16918	4648	8132
	Water, roads, fences, etc.	9500	9864	9587	16772
Claremorris	Crops*	22519	23120	20045	12428
	Grass	67117	67903	105160	86589
	Fallow	15	3	5	-
	Wood and plantations	844	484	872	1030
	Turf bog	9530	9507	7844	9268
	Marsh	4137	2997	4212	4977
	Barren mountain land	357	206	145	172
	Water, roads, fences, etc.	6500	6568	7408	8753
Oughterard	Crops*	10194	10282	5665	4878
	Grass	53395	56849	101764	26798
	Fallow	238	58	60	-
	Wood and plantations	1561	1680	1453	5452
	Turf bog	12479	15982	10894	40893
	Marsh	18950	7813	7263	27262
	Barren mountain land	66939	68890	7989	29988
	Water, roads, fences, etc.	8533	10735	10168	38167

Appendix F (continued)

Rural district	Land use classification	1891	1901	1910	1926
		acres			
Tuam	Crops*	27556	29945	15542	12129
	Grass	81030	123488	101794	90482
	Fallow	94	32	30	-
	Wood and plantations	2340	3231	2324	3708
	Turf bog	3835	14158	9442	15063
	Marsh	670	6139	6246	9965
	Barren mountain land	30	5486	436	695
	Water, roads, fences, etc.	3965	8170	9442	15063

(ii)

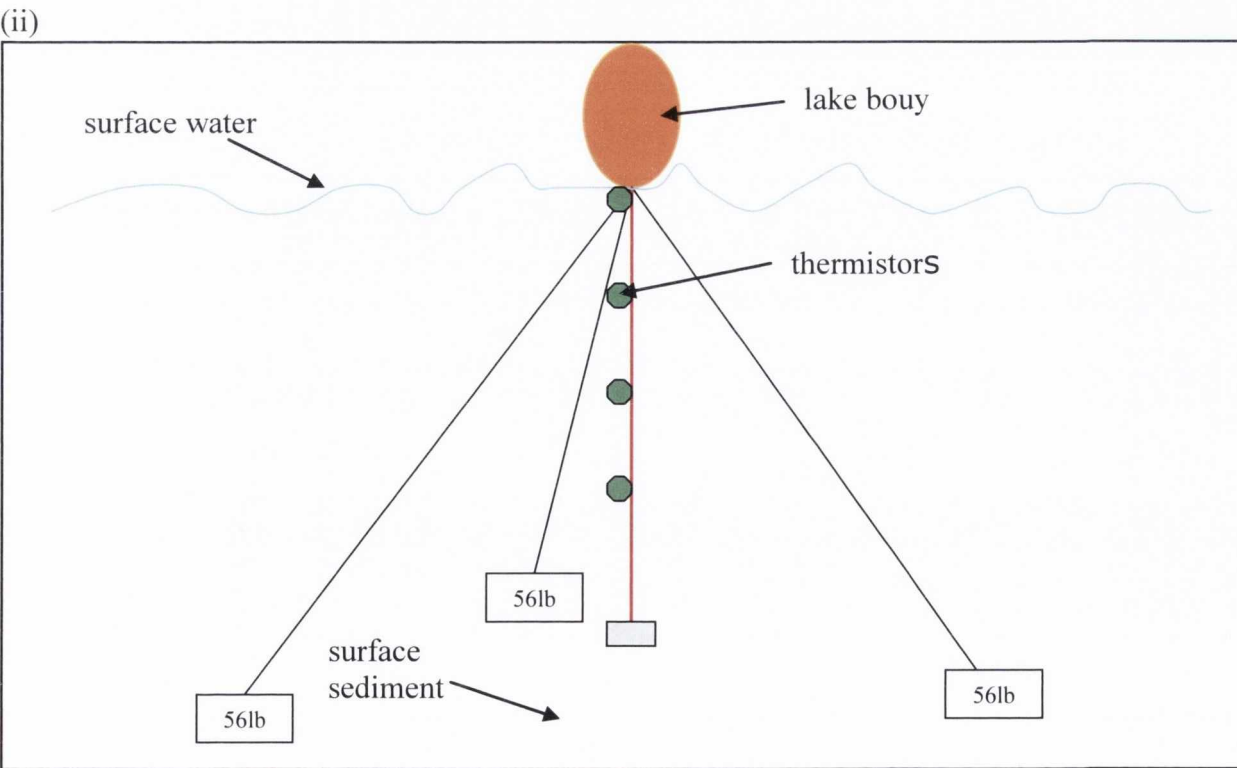
CORINE land cover	Robe	Carra hectares	Owenbrin
Continuous urban	0	0	0
Discontinuous urban	82	0	0
Road and rail networks	0	0	0
Construction sites	0	0	0
Sport and leisure facilities	51	0	0
High Productivity Pastures	8984	1013	138
Mixed Productivity Pastures	2800	5076	92
Low Productivity Pastures	1971	1258	0
Complex cultivation patterns	113	2294	0
principally agriculture	0	0	280
Broad leaved forest	9	43	0
Coniferous forest	263	94	52
Natural grasslands	4424	0	23
Moors and heathland	0	0	0
Transitional woodland shrub	140	212	53
Sparsely vegetated areas	0	0	0
Inland marshes	38	145	0
Exploited Peat bogs	40	1418	1610
Unexploited Peat bogs	3983	189	46
Non irrigated arable land	5460	0	0
Mixed forest	52	16	0
Mineral extraction sites	9	0	0

Appendix G Reclassification of historical land use classifications for comparison with contemporary land use categories. * including meadow and clover

Corine landuse category	Historical landuse category (equivalent)
Continuous urban	Crops*
Discontinuous urban	Water, roads, fences, etc.
Road and rail networks	Fallow
Construction sites	Wood and plantations
Sport and leisure facilities	Water, roads, fences, etc.
High Productivity Pastures	Grass
Mixed Productivity Pastures	Grass
Low Productivity Pastures	Grass
Complex cultivation patterns	Crops*
principally agriculture	Grass
Broad leaved forest	Wood and plantations
Coniferous forest	Wood and plantations
Natural grasslands	Barren mountain land
Moors and heathland	Barren mountain land
Transitional woodland shrub	Wood and plantations
Sparsely vegetated areas	Marsh
Inland marshes	Marsh
Exploited Peat bogs	Turf bog
Unexploited Peat bogs	Turf bog
Water bodies	Water, roads, fences, etc.
Non irrigated arable land	Crops*
Mixed forest	Wood and plantations

Appendix H Installation of a thermistor chain in Lough Mask: (i) description of the thermistor chain deployment, (ii) schematic diagram of the thermistor chain

(i) A thermistor chain with temperature loggers (StowAway TidbiT temperature data loggers obtained from Onset Computer Corporation, Bourne, USA) was installed at the deepest point of Lough Mask (Figure 2.1) on 16th March 2007 to collect water temperature data required for validation of the hydrodynamics model (Dynamic Reservoir Simulation Model, DYRESM). The thermistor chain apparatus consisted of a 3-point anchor design with 3 x 90 m lengths of rope positioned with large metal weights connected to a centred lake buoy at the water surface (see part (ii)). The thermistor chain was suspended vertically from the buoy with a lead weight. Deployment of the thermistor chain involved the use of 2 boats, ILLUMINATE project personnel, Mr. Padraig Hennigan and the Western Regional Fisheries Board. Temperature loggers were set to record hourly temperature and were placed at 15 different depths between the water surface and 50 m (0 m, 5 m, 10 m, 12 m, 15 m, 18 m, 21 m, 25 m, 30 m and 40m). Temperature data were downloaded from the loggers every 3-4 months between March 2007 and the end of the project. Six additional loggers were obtained from Dr Eleanor Jennings (Dundalk Institute of Technology) and were placed at more frequent intervals on the chain between 5-30m.



Appendix I[†] Lake water quality monitoring datasets available from the BUFFER (EU Fifth Framework Programme) project (I. Donohue, Trinity College Dublin, pers. comm.): pH, temperature (°C), conductivity ($\mu\text{S cm}^{-1}$), alkalinity ($\text{mg CaCO}_3 \text{ l}^{-1}$), turbidity (NTU), colour (PtCo), suspended solids (mg l^{-1}) and dissolved organic carbon (mg l^{-1}), soluble reactive phosphorus (SRP) ($\mu\text{g l}^{-1}$), particulate phosphorus (PP) ($\mu\text{g l}^{-1}$), total phosphorus (TP) ($\mu\text{g l}^{-1}$), nitrate (mg l^{-1}), total nitrogen (TN) (mg l^{-1}), secchi depth (m), chlorophyll *a* (mg l^{-1}), for four different sampling sites (A, B, C and D) in Lough Mask (see Figure 2.2 for sampling site locations)

[†] Appendix I is contained on the CR-ROM enclosed in this thesis

Appendix J Summary of available phytoplankton monitoring data (monthly single-point samples from the deepest point) from unpublished algal counts for the years 1975, 1983, 1984, 1985 and 1986 AD available from the Central Fisheries Board, CFB (now Inland Fisheries Ireland) (T. Champ & J. King, pers. comm.)

1975 AD												
No. ml ⁻¹	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	
Diatoms	254	138	259	32	0	53	76	76	37	24	1	
Chlorophytes	17	2	2	2	0	2	2	13	1	18	3	
Cyanophytes	246	336	560	96	0	88	160	600	20	56	9	
1983 AD												
No. ml ⁻¹	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	
Chlorophytes	0	0	0	0	0	115	0	0	0	0	0	
Cyanophytes	156	378	0	622	0	0	1117	4	0	163	0	
Diatoms	71	274	0	79	0	160	201	339	399	21	13	
1984 AD												
No. ml ⁻¹	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
Chlorophytes	0	0	0	375	0	0	0	0	0	0	39	0
Chrysophytes	0	0	0	39	3	0	0	1	1	0	0	0
Cyanophytes	0	0	0	192	121	114	96	57	0	114	949	472
Diatoms	40	102	163	262	64	210	237	28	68	334	169	52
Dinoflagellates	0	0	0	0	0	0	0	1	0	0	0	0

Appendix K[†] Monthly inflow water physico-chemical datasets (2001-2003) flow rate ($\text{m}^3 \text{s}^{-1}$), pH, temperature ($^{\circ}\text{C}$), conductivity ($\mu\text{S s}^{-1}$), alkalinity ($\text{mg CaCO}_3 \text{l}^{-1}$), turbidity (NTU), colour (PtCo), suspended solids (mg l^{-1}) and dissolved organic carbon (mg l^{-1}), and (ii) particulate phosphorus (PP) ($\mu\text{g l}^{-1}$), total phosphorus (TP) ($\mu\text{g l}^{-1}$), nitrate (mg l^{-1}), total nitrogen (TN) (mg l^{-1}), secchi depth (m), chlorophyll *a* (mg l^{-1}), for the main inflows to Lough Mask (river Robe, Keel canal and the Owenbrin river (see Figure 2.1 for locations)

[†] Appendix K is contained on the CR-ROM enclosed in this thesis

Appendix L Long term flow data availability for the main inflows to Lough Mask, from the Environmental Protection Agency (EPA) and the Office of Public Works (OPW), used to calibrate the catchment model (GWLF)

Sub-catchment	Station name	Water level data	Flow data	Time period (years AD)	Source
Robe	Foxhill	available	available	1955-2005	OPW
Carra	Keel weir	available	available	2001-2006	EPA
Owenbrin	Capanacreha	available	available	2000-2006	EPA
Glensaul	Tourmakeady	available	available	1997-2006	EPA
Aille	Cartronbower	not available	available	1972-2003	OPW

Appendix M LOI (%) and lithostratigraphic data for preliminary test sediment cores collected in November 2006 AD (see Figure 2.1 for test site locations) from the deepest point (MK-1) and the east Robe site (MK-2)

MK-1				MK-2			
Depth (cm)	Lithology	Brief description	LOI (%)	Depth (cm)	Lithology	Brief description	LOI (%)
0-0.5	organic silt & sand	some shells & plant macrofossils	7.1	0-0.5	organic silt, with sandy intervals	dark brown, abundant shell remains & plant macro-fossils	10.2
0.5-1			6.5	0.5-1			12.3
1-1.5			5.6	1-1.5			9.6
1.5-2			3.8	1.5-2			8.5
2-2.5			4.9	2-2.5			12.7
2.5-3			7.6	2.5-3			11.4
3-3.5			8.6	3-3.5			9.3
3.5-4			9.8	3.5-4			8.3
4-4.5			14.0	4-4.5			10.5
4.5-5			15.2	4.5-5			11.2
5-6	organic silt	plant macrofossils present	16.9	5-6	organic silt & some fine sand	green, some plant macro-fossils	13.2
6-7			17.8	6-7			12.2
7-8			16.4	7-8			14.5
8-9			19.3	8-9			14.8
9-10			16.3	9-10			9.4
10-11			14.7	10-11			10.5
11-12			17.8	11-12			9.3
12-13			24.0	12-13			8.7
13-14			25.1	13-14	organic silt & clay	brown/grey, occasional shells	9.9
14-15			23.8	14-15			10.5
15-16			22.0	15-16			11.2
16-17	organic silt	plant macrofossils present	24.6	16-17	fine clay	light grey	10.8
17-18			23.6	17-18			9.7
18-19			22.8	18-19			7.5
19-20			23.5	19-20			7.8
20-21			21.6	20-21			8.2
21-22			20.4	21-22			7.8
22-23			17.5	22-23			8.6
23-24			20.3	23-24			6.6
24-25			15.6				
25-26	fine clay & organic silt	some plant macrofossils	19.5				
26-27			21.0				
27-28			20.6				

Appendix N Diatom taxon names and authorities (based on the DIATCODE list; Hartley, 1986; Williams *et al.*, 1988)

DIATCODE	Taxon name	Authority
AC177A	<i>Achnanthes holsatica</i>	Hustedt in Schmidt et al.
AD009A	<i>Achnanthidium microcephalum</i>	Kutzing
AC006B	<i>Achnanthes clevei rostrata</i>	Hustedt
AC116A	<i>Achnanthes rossii</i>	Hustedt
AM007A	<i>Amphora commutata</i>	Grun. in Van Heurck
AM013A	<i>Amphora inariensis</i>	Krammer
AM084A	<i>Amphora montana</i>	Krasske
AM012A	<i>Amphora pediculus</i>	(Kutzing) Grunow
AM008A	<i>Amphora thumensis</i>	(Mayer) A. Cleve
AS001A	<i>Asterionella formosa formosa</i>	Hassall
AU002A	<i>Aulacoseira ambigua</i>	(Grun. in Van Heurck) Simonsen
AU005E	<i>Aulacoseira distans nivalis</i>	(W.Smith) E.Y.Haworth
AU003A	<i>Aulacoseira granulata</i>	(Ehrenberg) Simonson
BR006A	<i>Brachysira brebissonii brebissonii</i>	R. Ross in Hartley
BR001A	<i>Brachysira vitrea</i>	(Grunow) R. Ross in B. Hartley
BR004A	<i>Brachysira styriaca</i>	(Grunow in Van Heurck) R.(Grunow) Ross in Hartley
CO005A	<i>Cocconeis pediculus</i>	Ehrenberg
CO001A	<i>Cocconeis placentula placentula</i>	Ehrenberg
CO9999	<i>Cocconeis</i> sp.	-
CY022A	<i>Cyclotella bodanica</i>	(Eulenstein) Cleve-Euler
CY010A	<i>Cyclotella comensis</i>	Grunow in Van Heurck
CY028A	<i>Cyclotella distinguenda</i>	Hustedt
CY054A	<i>Cyclotella krammeri</i>	Håkansson
CY005A	<i>Cyclotella michiganiana</i>	Skvortzow
CY006B	<i>Cyclotella kuetzingiana planetophora</i>	Fricke in A. Schmidt
CY018A	<i>Cyclotella planctonica</i>	Brunnthaler
CY002A	<i>Cyclotella pseudostelligera</i>	Hust.
CY9999	<i>Cyclotella</i> sp.	-
CC9999	<i>Cyclostephanos</i> sp.	-
CL002A	<i>Cymatopleura elliptica elliptica</i>	(Breb. ex Kutz.) W. Sm.
CL005A	<i>Cymatopleura librile</i>	(Ehrenb.) Pant.
CM022A	<i>Cymbella affinis</i>	Kutzing
CM038A	<i>Cymbella delicatula</i>	Kutzing
CM013A	<i>Cymbella helvetica helvetica</i>	Kutzing
CM085A	<i>Cymbella lapponica</i>	Grunow ex Cleve
CM086A	<i>Cymbella leptoceros leptoceros</i>	(Ehrenb.) Kutz.
CM050A	<i>Cymbella subaequalis</i>	Grun. in Van Heurck
CM9999	<i>Cymbella</i> sp.	-
DE001A	<i>Denticula tenuis tenuis</i>	Kutzing

Appendix N (continued)

DIATCODE	Taxon name	Authority
DT004B	<i>Diatoma tenue elongatum</i>	Lyngb.
DE020A	<i>Denticula thermalis</i>	Kützing
DP009A	<i>Diploneis elliptica elliptica</i>	(Kützing) Cleve
DP007A	<i>Diploneis oblongella oblongella</i>	(Naegeli ex Kütz.) R. Ross
ENC01A	<i>Encyonopsis microcephala</i>	(Grunow) Krammer
EP007A	<i>Epithemia adnata adnata</i>	(Kütz.) Rabenh.
EP003A	<i>Epithemia argus argus</i>	(Ehrenberg) Kützing
EP021A	<i>Epithemia smithii</i>	Carruthers
EP9999	<i>Epithemia</i> sp.	-
EU013A	<i>Eunotia arcus arcus</i>	Ehrenberg
EU109A	<i>Eunotia circumborealis</i>	Norpel & LB
EU040A	<i>Eunotia paludosa</i>	Grunow in Van Heurck
EU040B	<i>Eunotia paludosa trinacria</i>	(Krasske) Nörpel et Alles
EU034A	<i>Eunotia parallela parallela</i>	Ehrenberg
EU002A	<i>Eunotia pectinalis pectinalis</i>	(O.F. Mull.) Rabenhorst
EU109A	<i>Eunotia circumborealis</i>	Norpel & LB
EU060A	<i>Eunotia pirla</i>	Carter et Flower
EU003A	<i>Eunotia praerupta praerupta</i>	Ehrenberg
PS001A	<i>Pseudostaurosira brevistriata</i>	(Grun. in Van Heurck) Williams & Round
FR009A	<i>Fragilaria capucina capucina</i>	Desmazières
FR002D	<i>Fragilaria construens exigua</i>	(W. Sm.) Schulz
FR008A	<i>Fragilaria crotonensis</i>	Kitton
FR057A	<i>Fragilaria fasciculata</i>	(Agardh) Lange-Bertalot sensu lato
FR042A	<i>Fragilaria nitzschoides</i>	Grun. in Van Heurck
FR061A	<i>Fragilaria zeilleri elliptica</i>	Heribaud
FU002A	<i>Frustulia rhomboides rhomboides</i>	(Ehrenberg) De Toni
FU002B	<i>Frustulia rhomboides saxonica</i>	(Rabenhorst) De Toni
FU9999	<i>Frustulia</i> sp.	-
GO073A	<i>Gomphonema angustum</i>	Agardh
GO030A	<i>Gomphonema auritum</i>	A.Braun ex Kützing
GO076A	<i>Gomphonema bavaricum</i>	Reichardt & Lange-Bertalot
GO029A	<i>Gomphonema clavatum</i>	Ehrenberg
GO024A	<i>Gomphonema clevei</i>	Fricke in A. Schmidt
GO036A	<i>Gomphonema dichotomum</i>	Kützing
GO9999	<i>Gomphonema</i> sp.	-
GO013A	<i>Gomphonema parvulum parvulum</i>	(Kütz.) Kütz.
GY005A	<i>Gyrosigma acuminatum</i>	(Kütz.) Rabenh.
GY001A	<i>Gyrosigma attenuatum</i>	(Kützing) Rabenhorst
GY9999	<i>Gyrosigma</i> sp.	-
LU003A	<i>Luticola goeppertiana</i>	(Bleisch in Rabenhorst) Mann
MA001B	<i>Mastogloia smithii lacustris</i>	Grunow
ME9999	<i>Melosira</i> sp.	-

Appendix N (continued)

DIATCODE	Taxon name	Authority
ME015A	<i>Melosira varians</i>	Agardh
NA156A	<i>Navicula leptostriata</i>	Jorgensen
NA9999	<i>Navicula</i> sp.	-
NA063A	<i>Navicula trivialis</i>	Lange-Bertalot
NI9999	<i>Nitzschia</i> sp.	-
NI042A	<i>Nitzschia acicularis</i>	(Kutz.) W. Sm. (W. Sm.) Grun. in Cleve & Grun.
NI020A	<i>Nitzschia angustata angustata</i>	(Kutzing) W.Smith
NI009A	<i>Nitzschia palea palea</i>	(Lange-Bertalot) Flower, Jones & Round
SF001A	<i>Stauroforma exiguiformis</i>	(Ehrenberg) Williams & Round
SS002A	<i>Staurosirella pinnata</i>	Hustedt in Huber-Pestalozzi
ST009A	<i>Stephanodiscus alpinus</i>	Grunow in Cleve & Grunow
ST001A	<i>Stephanodiscus hantzschii</i>	Hakansson & Hickel
ST022A	<i>Stephanodiscus neoastraea</i>	(Schum.) Kirchn.
SU002G	<i>Surirella ovata minuta</i>	(Roth) Kutz.
TA001A	<i>Tabellaria flocculosa flocculosa</i>	(Ehrenb.) Cleve
TH012A	<i>Thalassiosira eccentrica</i>	

Appendix O Values of TP($\mu\text{g l}^{-1}$) and pH (pH units) optima for key diatom taxa from different training sets

Species	TP ($\mu\text{g l}^{-1}$)	pH (pH units)	Source
<i>Achnantheidium microcephalum</i>	36.3	-	Anderson <i>et al.</i> (1993)
	66.0	-	Bennion (1994)
	145	-	Bennion <i>et al.</i> (1996)
	14.6	7.2	Chen <i>et al.</i> (2008)
	23.0	-	DeNicola <i>et al.</i> (2004)
	-	-	EDDI (2009)
	13.2		Wunsam & Schmidt (1995)
<i>Asterionella formosa</i>	54.9	-	Anderson <i>et al.</i> (1993)
	158.5	-	Bennion (1994)
	79.4	-	Bennion <i>et al.</i> (1996)
	36	7.7	Chen <i>et al.</i> (2008)
	21.9	-	DeNicola <i>et al.</i> (2004)
	43.6	6.9	EDDI (2009)
	16.6	-	Wunsam & Schmidt (1995)
<i>Aulacoseira granulata</i>	79.4	-	Anderson <i>et al.</i> (1993)
	-	-	Bennion (1994)
	-	-	Bennion <i>et al.</i> (1996)
	35.1	8	Chen <i>et al.</i> (2008)
	-	-	DeNicola <i>et al.</i> (2004)
	-	-	EDDI (2009)
	-	-	Wunsam & Schmidt (1995)
<i>Tabellaria flocculosa</i>	29.5	-	Anderson <i>et al.</i> (1993)
	50.1	-	Bennion (1994)
	-	-	Bennion <i>et al.</i> (1996)
	13.3	6.7	Chen <i>et al.</i> (2008)
	19.4	-	DeNicola <i>et al.</i> (2004)
	-	-	EDDI (2009)
	9.5	-	Wunsam & Schmidt (1995)
<i>Fragilaria capucina</i>	66.0	-	Anderson <i>et al.</i> (1993)
	177.8	-	Bennion (1994)
	97.7	-	Bennion <i>et al.</i> (1996)
	21.2	7.2	Chen <i>et al.</i> (2008)
	18.5	-	DeNicola <i>et al.</i> (2004)
	50.1	-	EDDI (2009)
	16.6	-	Wunsam & Schmidt (1995)
<i>Fragilaria crotonensis</i>	53.7		Anderson <i>et al.</i> (1993)
	-		Bennion (1994)
	-		Bennion <i>et al.</i> (1996)
	9.3	8.2	Chen <i>et al.</i> (2008)
	-	-	DeNicola <i>et al.</i> (2004)
	-	8.1	EDDI (2009)
	14.8	-	Wunsam & Schmidt (1995)

Appendix P Soil and runoff nutrient concentrations from different landuses used in the GWLF model based on published values for the Mask catchment, or a catchment with similar soil and landuse characteristics, from Daly (1999), Cummins & Farrell (2003), Daly *et al.* (2002), Styles *et al.* (2006) and Pierson *et al.* (2009)

CORINE land cover	Soil TP (mg kg ⁻¹)	Dissolved P (mg l ⁻¹)
High Productivity Pastures	1291	0.015
Low Productivity Pastures	1000	0.008
Complex cultivation patterns	798	0.008
Principally agriculture	1000	0.010
Farmyards	6000	1.828
Broad leaved forest	650	0.006
Coniferous forest	650	0.009
Natural grasslands	684	0.008
Transitional woodland shrub	650	0.008
Sparsely vegetated areas	684	0.008
Inland marshes	300	0.008
Unexploited Peat bogs	300	0.008
Sport and leisure facilities	1000	0.010
Continuous urban	1840	0.034
Discontinuous urban	1840	0.034

Appendix Q[†] Measured temperature profile data from the thermistor chain at the deepest point (see Appendix H)

[†] Appendix Q is contained on the CR-ROM enclosed in this thesis

Appendix R ^{210}Po (total and unsupported) and ^{137}Cs activity for MK-5, MK-8 and MK-11

Robe site (MK-5)				Deepest point (MK-8)				Southwest site (MK-11)			
Depth (cm)	^{210}Po total activity (DPM g ⁻¹)	^{210}Po unsupported activity (DPM g ⁻¹)	^{137}Cs (DPM g ⁻¹)	Depth (cm)	^{210}Po total activity (DPM g ⁻¹)	^{210}Po unsupported activity (DPM g ⁻¹)	^{137}Cs (DPM g ⁻¹)	Depth (cm)	^{210}Po total activity (DPM g ⁻¹)	^{210}Po unsupported activity (DPM g ⁻¹)	^{137}Cs (DPM g ⁻¹)
0.5-1	14.28	12.77	13.92	0-0.5	5.56	3.06	7.41	0-0.5	35.5	-	13.9
1-1.5	12.80	11.29	14.00	0.5-1	3.59	1.09	3.56	1.5-2	34.7	-	14.0
2-2.5	8.14	6.63	27.37	1-1.5	2.50	0.00	2.44	7-8	34.9	-	27.4
3-3.5	7.34	5.83	41.59	1.5-2	2.85	0.35	1.44	10-11	27.4	-	41.6
4-4.5	5.20	3.69	27.23	2-2.5	1.97	-0.53	1.46	13-14	27.4	-	27.2
6-7	3.37	1.86	31.46	2.5-3	2.82	0.32	1.38	16-17	22.0	-	31.5
8-9	1.80	0.29	30.06	3-3.5	2.84	0.34	0.80	19-20	16.5	-	30.1
10-11	1.95	0.44	12.45	3.5-4	2.66	0.17	1.19	22-23	12.2	-	12.5
15-16	2.17	0.66	6.27	4-4.5	2.71	0.21	0.67	25-26	9.6	-	6.3
20-21	2.90	1.39	3.83	4.5-5	2.67	0.17	1.17	28-29	8.4	-	3.8

Appendix R (continued)

Robe site				Deepest point				Southwest site			
Depth (cm)	²¹⁰ Po total activity (DPM g ⁻¹)	²¹⁰ Po unsupported activity (DPM g ⁻¹)	¹³⁷ Cs (DPM g ⁻¹)	Depth (cm)	²¹⁰ Po total activity (DPM g ⁻¹)	²¹⁰ Po unsupported activity (DPM g ⁻¹)	¹³⁷ Cs (DPM g ⁻¹)	Depth (cm)	²¹⁰ Po total activity (DPM g ⁻¹)	²¹⁰ Po unsupported activity (DPM g ⁻¹)	¹³⁷ Cs (DPM g ⁻¹)
24-25	2.33	0.82	1.62	8-9	2.10	-0.40	0.19	31-32	6.3	-	1.6
				12-13	3.15	0.65	0.45	34-35	4.8	-	0.6
				16-17	3.85	1.35	0.59	37-38	3.2	-	0.5
				20-21	3.37	0.87	0.53				
				24-25	2.58	0.08	0.73				
				28-29	2.73	0.23	0.36				
				32-33	2.81	0.31	0.21				
				36-37	2.32	-0.18	0.34				
				40-41	2.58	0.08	0.27				

Appendix S[†] Diatom count data for MK-4, MK-9 and MK-12

[†] Appendix S is contained on the CR-ROM enclosed in this thesis

Appendix T[†] Plant macrofossils count data for MK-5, MK-10 and MK-13

[†] Appendix T is contained on the CR-ROM enclosed in this thesis

Appendix U GWLF hindcast catchment TP loads (tonnes yr⁻¹) 1901-2006 AD by subcatchment. *West includes the Cloon, Srah, Glensaul, Cartron Bower, Owenbrin, Srahnaalong and Finny subcatchments

Year	Robe	Carra	West*
AD	TP load (tonnes yr ⁻¹)		
1900	4249.1	1329.4	13051.8
1901	3647.3	1189.2	9953.7
1902	3381.0	965.3	8802.3
1903	4700.5	1845.7	14469.1
1904	4055.9	1403.3	11454.9
1905	3756.8	1125.7	9567.0
1906	3682.8	1174.6	9540.1
1907	4255.5	1383.4	12379.7
1908	4521.6	1656.3	13403.6
1909	3898.6	1393.7	11557.0
1910	4048.1	1403.7	10910.5
1911	4020.1	1195.6	11252.8
1912	4530.0	1666.1	11948.4
1913	4542.5	2039.4	13402.7
1914	-	-	-
1915	-	-	-
1916	-	-	-
1917	3403.7	1064.8	7943.6
1918	3689.4	1181.0	8717.0
1919	3441.6	971.0	7729.9
1920	3634.8	1390.9	6463.5
1921	-	-	-
1922	-	-	-
1923	-	-	-
1924	-	-	-
1925	-	-	-
1926	-	-	-
1927	-	-	-
1928	-	-	-
1929	-	-	-
1930	3438.1	1099.7	8712.5
1931	4091.2	1654.7	10871.6
1932	4489.1	1481.1	9542.6
1933	3120.7	1118.2	7809.4
1934	4111.0	1476.4	10772.2

Appendix U (continued)

Year	Robe	Carra	West*
AD	TP load (tonnes yr ⁻¹)		
1935	3080.7	1154.9	7887.4
1936	3049.0	744.7	7463.9
1937	3881.5	1527.0	8924.8
1938	2873.9	913.6	6684.7
1939	2105.0	315.0	2952.0
1940	2964.8	814.0	7085.2
1941	2964.9	811.0	6743.1
1942	4395.1	1543.5	11559.3
1943	4932.5	2328.7	12608.0
1944	3093.0	1097.6	7808.4
1945	2686.5	828.5	7486.3
1946	3991.0	1470.3	10373.5
1947	3521.8	1434.9	9705.8
1948	3567.7	1294.0	9336.8
1949	3907.5	1695.6	10878.4
1950	4285.9	2011.8	12185.7
1951	4481.6	631.5	7572.3
1952	10829.3	1919.0	13830.4
1953	5670.6	1022.6	9546.1
1954	5349.8	760.9	8669.0
1955	6651.0	1373.1	10044.2
1956	6837.7	1171.6	11286.1
1957	7343.0	1132.8	10790.0
1958	7196.3	1568.8	11466.4
1959	7511.3	1500.9	11395.8
1960	5868.0	937.6	9618.3
1961	5406.8	848.5	8103.3
1962	7714.4	1114.1	11421.5
1963	6423.1	1203.0	10203.8
1964	5610.5	1269.9	10012.2
1965	6104.7	1176.1	10046.0
1966	9148.6	1550.2	12876.4
1967	5192.6	1131.3	8008.9
1968	6200.9	1338.8	10394.5
1969	3881.9	932.3	7053.3
1970	5332.7	1316.5	9505.1
1971	4793.2	1205.6	9052.0
1972	5990.5	1725.2	10103.5
1973	6191.0	1797.4	10246.2

Appendix U (continued)

Year	Robe	Year	Robe
AD	TP load (tonnes yr ⁻¹)		
1974	4842.9	1457.7	9252.0
1975	7166.2	2100.3	11853.0
1976	5951.3	1824.9	10281.3
1977	6720.1	2000.6	11607.0
1978	7916.8	2563.0	13644.8
1979	6243.4	2228.9	11986.9
1980	7179.3	2328.7	12650.1
1981	6135.1	1861.1	10522.4
1982	6393.0	1974.9	10255.8
1983	7749.4	2287.7	14413.9
1984	8899.6	2871.7	15519.8
1985	4375.5	1479.8	8679.2
1986	7852.1	2730.2	14286.7
1987	7959.4	2498.6	13484.4
1988	9563.2	3579.4	14898.4
1989	6801.1	2301.9	11638.2
1990	7873.9	2363.4	13785.7
1991	6398.8	2190.0	11683.7
1992	7593.1	2952.7	13932.0
1993	6633.1	2643.5	11227.6
1994	5672.3	1905.5	10724.9
1995	4972.2	1548.5	9527.8
1996	9313.5	2660.8	14778.3
1997	9456.3	2941.7	14845.1
1998	7657.5	2824.7	12590.8
1999	4978.1	1691.2	8666.8
2000	6495.6	2327.0	11343.3
2001	3621.7	1240.7	6618.1
2002	6667.0	2137.0	12094.2
2003	5997.7	1947.1	10443.0
2004	3621.7	1240.7	6618.1
2005	6667.0	2137.1	12094.2
2006	5997.7	1947.9	10443.1

Appendix V[†] DYRESM hindcast temperature data for periods between 1905-2009 AD

[†] Appendix V is contained on the CR-ROM enclosed in this thesis

Appendix W Modelled annual TP loads (kg yr⁻¹) for management scenarios 2, 6 and 10 for the Lough Mask subcatchments. *West includes the Cloon, Srah, Glensaul, Cartron Bower, Owenbrin, Srahnalong and Finny subcatchments

Year	Sc 2			kg yr ⁻¹			Sc 6			kg yr ⁻¹			Sc 10			kg yr ⁻¹		
	Robe	Carra	West*	Robe	Carra	West*	Robe	Carra	West*	Robe	Carra	West*	Robe	Carra	West*	Robe	Carra	West*
2000	9086.0	3212.8	16580.7	10719.6	3601.4	19781.3	13868.1	4119.8	16725.1									
2001	6743.3	3216.3	12867.1	8497.7	3600.2	16107.0	11453.3	4085.0	14134.3									
2002	4097.1	1360.8	8715.9	5804.5	1693.2	11052.4	8158.3	2121.1	9705.1									
2003	5594.2	1942.7	11573.2	8269.2	2472.5	15968.8	12615.4	3156.5	13095.4									
2004	2825.9	737.0	6620.9	4585.0	1065.6	9576.7	7287.0	1490.8	7670.0									
2005	5699.5	1889.1	12291.6	7904.4	2331.6	16055.1	11512.1	2901.5	13724.7									
2006	5089.9	1878.3	10597.6	6677.8	2205.7	13488.5	9402.8	2626.2	11739.5									