An Examination of Temporal and Spatial Water Quality Variations in Lakes, with Emphasis on the Limnology and Palaeolimnology of Lough Currane, Co. Kerry, Ireland

Elaine Treacy

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Declaration

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Thesis Summary

An aim of the WFD is that all waters achieve good water status by 2015 and includes the chemical and ecological status of rivers, lakes, groundwater estuarine and coastal waters. If member states of the EU are to meet the requirements of the WFD, good evidence-based understanding of the linkages between pollutant sources and their specific ecological impacts is needed. Within lakes, a number of factors can influence the extent of nutrient enrichment. These factors include individual catchment characteristics, sources of nutrients, pathways of nutrient transfer and the physical structure of a lake. Separating different anthropogenic signals in the palaeolimnological record from each other and from natural and climatically induced variations is difficult, but is necessary if palaeolimnological approaches are to be used to assist in interventions aimed at mitigating against further ecosystem deterioration. In addition, establishing the variability of both the pressure (nutrient enrichment) and the effects both spatially within a lake and temporally is important to understanding the ranges of responses within a lake to eutrophication.

The current research examines the parameters that can influence eutrophication in lakes. Lough Currane in south-west Ireland was chosen as a test site for the current research and the research places an emphasis on the Irish Ecoregion. The location of the test site aided the study of climatic fluctuations and their effect on lake water quality. Limnological and palaeolimnological methods can provide important information on the response of aquatic ecosystems to variations in nutrient inputs, while the analysis of historical records can maximise the information potential of palaeolimnological investigations. The use of documentary sources, in combination with palaeoecological data can provide otherwise unobtainable explanations for long term phenomena and can be used to test competing hypotheses about environmental change.

A within-lake multi-site approach was deployed in the collection of surface water, surface sediment and core samples at the test site. A range of palaeolimnological methods were used to determine the extent to which recent eutrophication is caused by anthropogenic factors. Chronological control was provided by ^{210}Pb, ^{137}CS, SCP and ^{14}C analyses and the results of these analyses indicated that the time period recorded by the sediment cores

spanned c.2000 years. Diatom analyses and reconstructions of DI-TP were used as proxies for temporal and spatial variations in water quality at the test site, while analyses of pollen, % organic content, PSA as well as historical documentary climate records aided in the interpretation of the historical records of eutrophication provided by the sediment cores. The findings of this research indicate that recent eutrophication is primarily anthropogenically induced. Increasing livestock numbers related to both point and diffuse sources appeared to be primarily responsible for the recent nutrient enrichment (c.1970s) of the test site. However, climatic fluctuations enhanced the effects of nutrient enrichment. Fluctuations in precipitation associated with the NAO were deemed to have had an effect on the delivery of nutrients to the test site. Periods of low precipitation combined with increased levels of P from a point source led appear to have led to rapid diatom assemblage change at two out of the three coring sites. Moreover, high precipitation events associated with highly positive NAO index values were deemed to have been important in delivering nutrients from diffuse and intermediate sources to the test site

Both limnological and palaeolimnological methods as well as G.I.S. were deployed to determine the extent to which the response to increased nutrient loads varied spatially within a lake basin. Analyses of TP and DI-TP in surface water and sediment samples indicated that water quality can vary within a lake basin. The coring sites displayed similar responses to increased nutrient loads and the analysis of pollen and diatom concentrations, % organic content and PSA indicated that, in general, the deepest point is representative of overall limnological conditions. However, the timing and extent of the response to increased nutrient loads was spatially variable within the test site. Proximity to nutrient source was deemed to be important in influencing variability in current and past water quality. In addition, water depth was deemed to be important in dictating the within-lake response to increased nutrient loads. The coring site located at the shallowest water depth appeared to be more sensitive to changing nutrient levels than the coring sites located in the profundal zones of the lake. The findings from this research indicate that a within-lake multi-site sampling approach allows the effects of individual nutrient sources to the nutrient enrichment of both an entire lake and individual areas within a lake to be determined. The strategy also allowed for an examination of the influence of morphometric parameters, such as water depth, to nutrient enrichment.

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List of Abbreviations and Acronyms

%	Percent or percentage
$(NaPO_3)6$	Sodium hexametaphosphate
$<$	Less than
$>$	Greater than
$\leq$	Less than or equal to
µg	microgram
µm	micrometre
^{12}C	Carbon – 12
^{131}I	Iodine – 131
^{134}CS	Cesium – 134
^{137}Cs	Caesium – 137
^{13}C	Carbon - 13
^{14}C	Carbon -14
$^{14}CO_2$	Carbon dioxide – 14
^{206}Pb	Lead - 206
^{210}Pb	Lead – 210
^{210}Po	Polonium – 210
^{214}Bi	Bismuth - 214
^{214}Pb	Lead - 214
^{214}Po	Polonium - 214
^{222}Rn	Radon - 222
^{226}Ra	Radium - 226
^{230}Th	Thorium - 230
^{238}U	Uranium - 238
$^{239, 240, 241}$ Pu	Plutonium – 239, 240, 241
^{90}Sr	Strontium – 90

AD	Anno Domini
Al	Aluminium
AMS	Accelerator mass spectrometry
BC	Before Christ
BP	Before present
C	Carbon
Ca	Calcium
CA	Correspondence analysis
CAP	Common Agricultural Policy
CCA	Caconical correspondence analysis
CIC	Constant initial concentration
cm	Centimetre
CO_2	Carbon dioxide
CONISS	Constrained cluster analysis by sum of squares
CORINE	CO-oRdination of INformation on the Environment
CRL	Candidate reference lake
CRS	Constant rate of supply
CSA	Critical source area
CSO	Central Statistics Office
DAZ	Diatom assemblage zone
DCA	Detrended correspondence analysis
DED	District Electoral Division
DI-pH	Diatom inferred pH
DI-TP	Diatom inferred total phosphorus
DKIT	Dundalk Institute of Technology
DM	Dry matter
DO	Dissolved Oxygen
DOC	Dissolved organic carbon

DPM	Disintegrations per minute
EDDI	European Diatom Database
EPA	Environmental Protection Agency
EU	European Union
Fe	Iron
FOI	Freedom of information
g	Gram
G.I.S	Geographical Information System
GPS	Global Positioning System
H_2O_2	Hydrogen peroxide
Ha	Hectare
HCl	Hydrochloric acid
HF	Hydrpfluoric acid
HPGe	High purity germanium
HPGe	High purity germanium
IGM	Inclusive graphical mean
IGSD	Inclusive graphical standard deviation
IN-SIGHT	Identification of reference-Status for Irish lake typoloGies using palaeolimnological metHods and Techniques
IPCC	Intergovernmental panel on climate change
kg	Kilogram
km	Kilometre
l	litre
LLAS	Low angle laser light scattering
LOI	Loss on Ignition
LU	Livestock Unit
m	Metre
MAT	Modern Analogue Technique

MinDC	Coefficient of minimum dissimilarity
ml	Millilitre
mm	Millimetre
MRP	Molybdate reactive phosphorus
N	Nitrogen
Na	Sodium
$Na_5P_3O_{10}$	Sodium tripolyphosphate
NAO	North-Atlantic Oscillation
NaOH	Sodium hydroxide
NH_3	Ammonia
NPPR	Non principal private residence
ø	phi
O	Oxygen
^oC	Degrees Celsius
^oC	Degrees Celsius
OECD	Organisation for Economic Co-operation and Development
^oF	Degrees Fahrenheit
P	Phosphorus
p	Probability coefficient
PAST	PAlaeontological STatistics
PCA	Principle components analysis
PO_4^{3-}	Orthophosphate
PP	Particulate phosphorus
PROTECH	Phytoplankton RespOnses To Environmental Change
PSA	Particle size analysis
R	Correlation coefficient
R^2	Coefficient of Determination
RDA	Redundancy analysis

RI	Refractive index
RMSE	Root mean square error of prediction
RPM	Revolutions per minute
s	Second
SAPS	Small Area Population Statistics
SCD	Squared Chord Distance
SCP	Spheroidal Carbonaceous Particle
SD	Standard deviation
SRP	Soluble reactive phosphorus
SWAP	Surface Water Acidification Project
TCD	Trinity College Dublin
TP	Total Phosphorus
U.K.	United Kingdom
USA	United States of America
WA Inv	Weighted averaging – inverse rescaling
WA	Weighted averaging
WAPLS	Weighted averaging partial least squares
WAT_Inv	Weighted averaging with tolerance down weighting and inverse rescaling
WFD	Water Framework Directive
yr	Year
β	Beta
λ	Eigenvalue (Sample or species score)

Chapter One: Introduction

1.1 Water quality

Humans have been impacting upon the environment for millennia (Jackson and Hobbs, 2009). However, since the advent of industrialisation, urbanisation and agricultural intensification over 300 years ago, the human impact on the environment, including lake ecosystems, has grown significantly (Crutzen, 2002; Steffen et al., 2007). With industrialisation, water quality problems began to emerge on a large scale (Steffen et al., 2007; Smol, 2008). These problems have ranged from low level contamination by long-distance transported air pollutants in remote areas to complete ecosystem transformation in agricultural and heavily populated areas (Bennion et al., 2011). In an effort to improve ecological quality in European surface waters, the WFD (2000/60/EC) was established in order to provide a regulatory means of ensuring good water quality, once achieved, into the future (Anon, 2000). Under the WFD, good water status should be achieved in fresh, transitional and coastal waters by 2015 (Arnscheidt et al., 2007). Good water status is defined as at most a slight deviation from reference or undisturbed conditions (Bennion et al., 2004). Eutrophication is the most common water quality problem worldwide (Mason, 2002) and in Ireland, 18% of lakes are classified as being eutrophic (Environmental Protection Agency, 2009). This research focuses on the eutrophication of lakes with an emphasis on the Irish Ecoregion.

1.2 Lake eutrophication

The term eutrophication refers to the enrichment of waters by inorganic plant nutrients, mainly P and N (Brönmark and Hansson, 2005). An increase in P and N can stimulate the growth of algae, cyanobacteria and macrophytes in lakes leading to algal blooms (Khan and Ansari, 2005; Smol, 2008). The current research examines the factors that influence eutrophication in lakes. These factors include individual catchment characteristics, sources of nutrients, pathways of nutrient transfer and the morphometry of a lake basin.

Nutrients enter water bodies, including lakes, mainly via runoff water and inlet streams (Khan and Ansari, 2005) and reach surface waters either directly via point sources such as sewage and wastewater treatment (Ongley, 1996;

Mason, 2002) or indirectly from diffuse sources such as those associated with agricultural activities including fertiliser application and livestock grazing (Toner et al., 2004). Diffuse sources of nutrients are increasingly important to the eutrophication of lakes both worldwide (Smol, 2008) and within the Irish ecoregion (Toner et al., 2004). In Ireland, increases in nutrients from diffuse sources associated with fertiliser application (McGarrigle and Champ, 1999; Jordan et al., 2002), livestock density (Donohue et al., 2010) and afforestation (Taylor et al., 2006a) were deemed to be responsible for the increased nutrient enrichment of a number of lakes. These lakes include Lough Conn (McGarrigle and Champ, 1999), Lower Lough Erne (Zhou et al., 2000), Loughs Ballybeg, Crans, Egish, Mullagh and Sillan in Northern Ireland (Taylor et al., 2006a), Lough Carra (Donohue et al., 2010), Lough Leane, Bunaveela Lough, Lough Feeagh and Lough Mask (Dalton et al., 2010). Lough Neagh, the Irish Ecoregions largest lake, has experienced eutrophication since 1880 AD (Foy et al., 2003). Since the early 1980s, after P reduction from point sources associated with sewage, a gradual increase in P from diffuse sources became apparent at Lough Neagh and exceeded the lake P concentrations before sewage P reduction (Gibson et al., 2001).

Catchment characteristics, such as hydrology, topography, geology and soils, influence the capacity of a lake catchment to transport nutrients to surface water and are therefore important to the nutrient loading of lakes (Fraterrigo and Downing, 2008). The influence of these factors will be outlined in more detail in chapter two. The hydrological cycle also influences the degree to which point and diffuse sources impact upon a lake (Edwards and Withers, 2007). Point sources deliver relatively constant concentrations of nutrients to lakes (Greene et al., 2011) and are influential during drier conditions and low flows (Withers and Jarvie, 2008). Diffuse sources are highly dependent on flow (Greene et al., 2011) and on rainfall duration, seasonality and intensity (Jennings et al., 2009). There has been a clear increase in precipitation over northern Europe throughout the 20th century, associated with global warming (Eisenreich, 2005) and if no further action is taken to reduce greenhouse gas emissions further, runoff is projected to increase by 10 % to 40% by the mid 21st century in northern Europe (IPCC, 2007). In Ireland, mean annual temperatures have risen by 0.7°C over the past century and are predicted to rise by 1.4°C to 1.8°C by 2050, while winter rainfall in Ireland is predicted to increase by c.10% by 2050 (Sweeney et al., 2008). These increases in precipitation and runoff have clear implications for the quality of lake water. High levels of rainfall have already been associated with an increase in nutrient loading from diffuse sources in a number of studies (e.g. Donohue et al., 2005; Jordan et al., 2005; Douglas et al., 2007; Jordan et al.,2007).

The within-lake response to increased nutrient loads can be site specific and is associated with the morphometry of a lake basin as well as the characteristics of the catchment. Morphometry refers to the size and form of a lake (Hakanson, 2005). A number of studies have shown that the morphological features of lakes, such as lake depth and volume, are significantly related to nutrient concentration or trophic status (e.g. Hakanson, 2005; Søndergaard et al., 2005; Taranu and Gregory-Eaves, 2008; Liu et al., 2010b). Deep lakes are far less responsive to an increase in nutrient concentrations than small shallow lakes. The differences in response between deep and shallow lakes are associated with differences in thermal stratification between the two lake types (Lampert and Sommer, 2007). Biological productivity is generally greater in cases where the photic zone extends to the lake bed and is in contact with the sediment (Wetzel, 2001). While there are important differences in the response to eutrophication between lakes according to morphometry, responses to increased nutrient concentrations can vary spatially within a single lake basin. For example, the distribution of phytoplankton assemblages in lakes is affected by distance to nutrient source (Pla et al., 2005), water depth (Anderson, 1998; Adler and Hübener, 2007; Selby and Brown, 2007), distance to shore and the availability of light for photosynthesis within a lake (Anderson, 1998; Moos et al., 2005). Macrophyte abundance, a symptom of increased nutrient loads, is also affected by light availability in lakes, with large abundances of macrophytes preferentially growing in near shore areas (Havens and Walker, 2002).

1.3 Limnology and palaeolimnology

Limnological and palaeolimnological approaches can provide important information on the response of aquatic ecosystems to variations in nutrient inputs (Battarbee et al., 2005; Dalton et al., 2010). Limnology refers to the study of inland waters and is a diverse science including the disciplines of physics, chemistry, biology, geology and geography, amongst others (Wetzel, 2001). Limnological methods are used in the monitoring of lake water quality and include direct measurements of water chemistry and biological assemblages. These methods can be used to identify the current nutrient status of a lake (Battarbee et al., 2005). Palaeolimnology refers to changes over time to lakes and their catchments (watersheds and airsheds), and generally involves the examination of sediment-based evidence. Historical perspectives on variations in water quality allow us to determine what an ecosystem was like before its initial anthropogenic disturbance and to ascertain how far and quickly a system has changed as a result of human activities (Smol, 2008). In many parts of the world, including the developed world, instrumental records of water quality are either very recent or unavailable (Cohen, 2003). In the absence of long-term monitoring records, palaeolimnological methods can provide a means of reconstructing historical variations in water quality and can indicate the timing, rate and direction of water quality changes (Simpson et al., 2005).

Knowledge of pre-disturbance conditions is important for setting realistic restoration targets for lakes and is a requirement of the WFD (Bennion and Simpson, 2011). Palaeolimnological methods have been widely used in order to define pre-disturbance or reference conditions in lakes including reconstructions of DI-pH and DI-TP in Scottish freshwater lochs (Bennion et al., 2004), the reconstruction of DI-TP and water colour in Finnish lakes (Miettinen et al., 2005) and the reconstruction of DI-TP, submerged macrophytes and benthi-planktivorous fish in Danish lakes (Bjerring et al., 2008).The EPA IN-SIGHT project (Taylor et al., 2006b), aimed to test the ecological status of a representative selection of CRLs in Ireland using palaeolimnology. Reconstructions of temporal variations in DI-pH and DI-TP as well as the floristic composition of samples indicated that 68% of the lakes studied displayed biologically important deviations from reference conditions with the main drivers of change identified as nutrient enrichment and increased acidity (Taylor et al., 2006b).

In eutrophication research, biological proxy indicators have been widely used to reconstruct changes in the catchment of a lake and variations in the water quality of a lake through time. Lake sediments contain proxy data from both autochonous and allochthonous sources (Smol et al., 2001) and so different proxies reflect different environmental factors at a range of spatial scales (Birks and Birks, 2006). Changes in a lake's catchment can be recorded in the lake sediment, for example, through the remains of plants transported to the lake and deposited (Cohen, 2003), while changes within the water column can be recorded by organisms living within the lake. One of the most widely used biological groups in eutrophication studies are diatoms (Bacillariophyceae), which are unicellular siliceous algae (Bennion and Simpson, 2011). Diatoms are sensitive to changes in lake water quality (Battarbee et al., 2001) and are good indicators of lake trophic status (Bennion and Simpson, 2011).

The use of biological proxies in palaeolimnological research can rely heavily upon contemporary ecological studies (ter Braak and van Dam, 1989; Anderson, 1995) and the identification of modern analogues for fossil assemblages. If an assemblage of taxa resembles a modern community that lives in a defined ecological range today, that assemblage may be used to infer past conditions (Birks and Birks, 2006). Reference conditions and deviations from reference conditions can be determined both qualitatively and quantitatively (Dalton et al., 2009). Shifts in assemblages over time have been coupled with ecological information to provide a record of ecological change in lakes. Moreover, transfer functions have been developed to model the relationship between diatom assemblage composition and water chemistry in a training set of lakes (Bennion and Simpson, 2011). The primary aim of a transfer function in ecological research is to express the value of an environmental variable, for example TP, as a function of biological or environmental proxy data, for example diatom assemblages (Birks, 1995). Transfer functions that reconstruct pH and TP have been widely used in palaeolimnology to track the history of water quality variations at lake sites where long term water quality measurements have been unavailable (e.g. Renberg and Hellberg, 1982; Birks et al., 1990; Bennion et al., 1996; Reavie and Smol, 2001; Bennion et al., 2004; Bigler et al., 2007; Chen et al., 2008).

Determining the causes of deviations from reference conditions, be they anthropogenic, natural or a combination of both, necessitates the consultation of secondary sources of information. The analysis of historical records can maximise the information potential of palaeolimnological investigations. The use of documentary sources in combination with palaeoecological data can provide otherwise unobtainable explanations for long term phenomena and can be used to test competing hypotheses about environmental change (Tibby, 2003). The importance of anthropogenic factors can be assessed and sources of nutrients and causes of periods of eutrophication or oligotrophication determined (Hall and Leavitt, 1999).

1.4 Research rationale and research questions

Tackling the various sources of water pollution within catchments is a key theme of the WFD and in order to achieve good ecological status in water body types, including lakes, good evidenced-based understanding of the linkages between pollutant sources and their specific ecological impacts is needed (Edwards and Withers, 2007). Separating different anthropogenic signals in the palaeolimnological record from each other and from naturally induced and climatically induced variability is difficult (Bennion et al., 2011) but is necessary if palaeolimnological approaches are to be used to assist in interventions aimed at mitigating against further ecosystem deterioration. While the WFD does not explicitly refer to climate change, existing problems associated with eutrophication can be exacerbated by, for example, warming (Douglas et al., 2007). As mentioned previously, increased precipitation can lead to a greater delivery of nutrients to lakes (Douglas et al., 2007; Nõges et al., 2007) while increases in temperature can lead to raised levels of phytoplankton biomass and productivity in lakes, especially in shallower zones (Winder and Schlindler, 2004). One of the assumptions in palaeolimnology is that a single core, usually taken from the deepest point of a lake, provides a representative record of lake history (Anderson, 1998). However, phytoplankton assemblages and the response to increased nutrient loads can be spatially variable within lakes (Pla et al., 2005) and so the stratigraphic record of eutrophication may also be spatially variable. Establishing the variability of both the pressure (nutrient enrichment) and the effects both spatially within a lake and temporally is important to understanding the range of responses within a lake to eutrophication. Such understanding should enable the parts of a lake that are vulnerable to change, and possibly relatively resistant to efforts aimed at restoration, to be identified, and is therefore likely to be of value to those involved in the management of lakes and their catchments.

This research analyses the factors that influence eutrophication in lakes and seeks to answer the following research questions:

1. To what extent is recent eutrophication caused by anthropogenic factors?

This research question will assess the contribution of various point and diffuse sources of nutrients and the contribution of climatic and catchment characteristics to the long term eutrophication of a lake in the Irish Ecoregion. Palaeolimnological techniques, in addition to the use of historical documentary and climate records are used to separate the natural variability in lakes from anthropogenically induced change.

2. To what extent does the response to increased nutrient loads vary spatially within a lake basin?

Using a within-lake multi-site approach and a combination of limnological and palaeolimnological methods, this research question assesses the contribution of lake morphometry as well as catchment characteristics to the within-lake response to increased nutrient levels. The study of multiple sites within a lake will aid in identifying the most prominent sources responsible for lake eutrophication and the whole lake response to increased nutrient input.

1.5 Thesis structure

Chapter two provides an overview of the factors that influence eutrophication in lakes. Nutrients in freshwater and the trophic status of lakes are first outlined, followed by a synopsis of natural and cultural eutrophication. The sources of P, divided into point, intermediate and diffuse sources, are then outlined along with their respective delivery mechanisms to surface water. An overview of the within-lake controls on eutrophication is provided, including the importance of thermal stratification, sedimentary stores of P and the influence of morphometric parameters on lake P concentrations and phytoplankton biomass.

Chapter three provides a detailed description of the test site that was chosen for this research. The criteria for selecting the test site are first outlined followed by a description of the chosen site. The existing water quality records for the site are then described in detail. The potential anthropogenic nutrient sources to the lake and their associated histories are outlined, and the climate records that were available for the study area are described.

Chapter four outlines the methodological framework used in the current research. The field based techniques utilised in the study are first outlined, followed by the laboratory based techniques. Finally, the numerical methods used in the research are outlined and described.

Chapter five details the results obtained from the limnological and palaeolimnological analyses carried out on both surface and core samples at the test site. The preliminary analyses of the proxies used for assessing variations in sedimentary components and catchment change are first outlined followed by the chronological control for the current study. The results of the pollen analysis carried out on subsamples from the sediment cores, in order to determine variations in land use change are then described. The results of the analysis of the spatial variability of TP in the test site are outlined followed by the analysis of the diatom assemblages identified for the current study. The numerical methods used to address the two research questions are then outlined. The results of the numerical methods used to assess the spatial variability of the diatom assemblages in the surface and core samples are first described followed by the statistical analysis of the drivers of the ecological change in the lake.

Chapter six provides a synthesis and discussion of the results presented in chapter five. The historical record of eutrophication at the test site is first addressed followed by a discussion of the relative importance of the various point, intermediate and diffuse sources within its catchment to the eutrophication of the lake. The influence of climatic fluctuations associated with variations in oceanic circulation patterns to the nutrient enrichment of the lake is then discussed. The results of the palaeolimnological methods utilised in the study are analysed in relation to the historical, documentary and climate records collected for the catchment of the lake. The second research question is then addressed and the within-lake variability in the response to increased nutrient loads is examined. Current within-lake variability in water quality is first discussed followed by the within-lake variability of the historical record of eutrophication. The sedimentary patterns are discussed in relation to the assumption that the deepest point is representative of an entire lake basin. The historical records of eutrophication are then compared at each of the coring sites

Chapter seven provides a summary of the current research. The main conclusions are presented and the limitations of the research are described. Suggestions for future research are then provided.

Chapter Two: Eutrophication in Lakes

This research analyses the factors that influence eutrophication in lakes and this chapter provides a background to lake eutrophication in relation to those influencing factors. Nutrients in freshwater and the trophic status of lakes are first outlined, followed by a synopsis of natural and cultural eutrophication. The sources of P, divided into point, intermediate and diffuse sources, are then outlined along with their respective delivery mechanisms to surface water. An overview of the within-lake controls on eutrophication is provided, including the importance of thermal stratification, sedimentary stores of P and the influence of morphometric parameters on lake P concentrations and phytoplankton biomass.

2.1 Eutrophication

2.1.1 Plant nutrients in freshwater

Nutrients are chemical elements that organisms require as raw materials for cell growth. The quantity of nutrients in lake water is determined by bedrock, climate, vegetation cover, lake size and human activities both within and without the catchment area for a lake (Lampert and Sommer, 2007). When nutrients enter a lake system they may be dissolved in the water, where they are absorbed by bacteria, algae and other primary producers. These organisms then provide nutrients for herbivores, which are consumed by larger predatory organisms such as fish. In this way nutrients are transported upwards through the food web and are recycled through the ecosystem via decomposition of organic material and excretion by organisms (Brönmark and Hansson, 2005).

All organisms are composed of chemical elements including O, Fe, Na, C, N and P. Of these C, N and P are major constituents of organisms. N, and especially, P are often limiting for growth. The Redfield ratio (Redfield, 1958), or the relative amounts of C, N and P in planktonic organisms compared with the surrounding water, is 106:16:1 (Smol, 2008). Liebig's Law of the Minimum states that whatever element is in shortest supply in relation to demand, will limit growth (Brönmark and Hansson, 2005). For example, if algae are provided with ten times more N and C than they need but not enough P, growth will stop. Since N and P are often in short supply in lake water, they usually limit productivity. Limitations on productivity are relaxed when supplies of N and P are increased, leading to eutrophication (Smol, 2008). Primary producers can become N limited in eutrophic lakes where P concentrations are already high. However, N is not the main limiting nutrient for organisms in freshwaters and is less strongly connected to lake nutrient status than P (Brönmark and Hansson, 2005), the chemical element which forms the focus of this research.

P is essential for growth in organisms as it is used in processes such as the storage and transfer of genetic information, cell metabolism and in the energy system of cells (Brönmark and Hansson, 2005). P is also one of the least abundant elements in the hydrosphere which causes it to limit biological activity and makes it the main determinant for primary production (Wetzel, 2001). P in water may exist in one of four broadly defined states: dissolved as an inorganic molecule readily available for biotic uptake, incorporated through sorption onto solids, incorporated with biological material or dissolved within organic molecules of varying complexity, which may or may not be readily available for biotic use (Reynolds and Davies, 2001). Most P (80% to 90%) in freshwater occurs as organic P where it is incorporated into organisms (Brönmark and Hansson, 2005). However, the most bioavailable forms of P are in solution as inorganic PO_4^{3-} ions or are readily soluble from loose combinations of PO_4^{3-} ions (Reynolds and Davies, 2001). P is a highly particle-reactive element and is often involved in a series of sorption/desorption reactions with particulate material in the water column. When particulates enter a water body, adsorbed PO_4^{3-} equilibrates with the PO_4^{3-} in the water such that, if the P content of the water is low, P will be released from particulates to the water and vice-versa. Thus PP, both in suspension and in the sediment, represents a potentially large reservoir of P in excess of the P dissolved in the water column (Froelich, 1988; Jennings et al., 2003). Chemical analyses of P centre on the reactivity of P with molybdate (Wetzel, 2001) and the bioavailable form of P is measured as MRP or SRP (Reynolds and Davies, 2001). Measurements of P in freshwaters include the dissolved inorganic fraction (MRP or SRP) and the PP fraction. However, TP is widely used as an estimate of lake water quality and refers to the sum of all P fractions present in the water column (Wetzel, 2001).

2.1.2 Lake trophic status

The trophic component of water quality is most commonly assessed using a classification scheme proposed by the OECD (1982). The OECD scheme establishes the level of nutrient enrichment, or eutrophication, in a water body using measured values of TP, chlorophyll *a* and secchi disc readings (water transparency). Low levels of TP are associated with low levels of algae (chlorophyll *a*) which in turn are associated with high secchi disc readings or high levels of transparency in the water (Shaw et al., 2004; Toner et al., 2005). The parameters on which the OECD scheme is based are shown in Table 2.1. According to this classification, lakes that display low levels of TP (< 10 μg l^{-1}) are termed oligotrophic and are also generally clear, deep and free of a large algal biomass. Conversely, eutrophic lakes display high levels of TP (> 35 μg l^{-1}), support a large biomass and are usually subject to frequent algal blooms (OECD, 1982). Mesotrophic lakes have intermediate levels of productivity and nutrients and lie in the middle of the trophic range, between oligotrophic and eutrophic states (Shaw et al., 2004).

The OECD scheme has been modified for different countries and for different types of lakes (Smol, 2008). For example, in countries with a large proportion of nutrient poor oligotrophic lakes, such as Canada, a lake with TP levels of 35 μg l^{-1} would be considered eutrophic (Smol, 2008); while in Denmark, a country with many naturally nutrient rich lakes, a lake with TP levels of 35 μg l^{-1} would be considered oligotrophic (Søndergaard et al., 2005; Rasanan et al., 2006). In Ireland, the usual frequency of sampling in lakes does not generate sufficient data to permit the calculation of annual mean TP values specified by the OECD scheme. For example sampling for chemical data in Irish lakes can range from 1 to 9 times $year^{-1}$ (Chen, 2006). The classification in Ireland is thus partly based on the annual maximum chlorophyll concentration (Toner et al., 2005). Chlorophyll is a constituent of all plants, algae and cyanobacteria (Brönmark and Hansson, 2005) and so is a direct indicator of the increase in primary productivity associated with eutrophication. Due to the wide limits set for the eutrophic category by the OECD, sub divisions of moderately eutrophic, strongly eutrophic and highly eutrophic were made for the Irish scheme (Toner et al., 2005). The parameters for the modified Irish OECD scheme are shown in Table 2.2.

Lake Category	TP ($\mu g\ l^{-1}$) Mean	Chlorophyll ($\mu g\ l^{-1}$) Mean	Chlorophyll ($\mu g\ l^{-1}$) Max.	Transparency (m) Mean	Transparency (m) Max
Ultra - Oligotrophic	< 4	< 1.0	< 2.5	> 12	> 6
Oligotrophic	< 10	< 2.5	< 8.0	> 6	> 3
Mesotrophic	10 - 35	2.5 - 8	8 - 25	6 - 3	3 - 1.5
Eutrophic	35 - 100	8 - 25	25 - 75	3 - 1.5	1.5 - 0.7
Hypertrophic	> 100	> 25	> 75	< 1.5	< 0.7

Table 2.1: Trophic classification scheme for lake waters proposed by the OECD (OECD, 1982)

Lake Category		Annual Chlorophyll ($\mu g\ l^{-1}$) Max
Oligotrophic		< 8
Mesotrophic		8 - 25
Eutrophic	Moderately Eutrophic	25 - 35
	Strongly Eutrophic	35 - 55
	Highly Eutrophic	55 - 75
Hypertrophic		> 75

Table 2.2: Modified Irish version of the OECD trophic classification scheme based on values of chlorophyll concentration. Adapted from Toner et al. (2005)

2.1.3 Natural eutrophication

Natural eutrophication in lakes is largely governed by the characteristics of the drainage basin. Lakes situated on P rich bedrock usually have high P concentrations (Rasanan et al., 2006). In rocks, P exists in the minerals of the apatite group (Smithson et al., 2008). During weathering the P in apatite is released to the soil and eventually to water bodies (Stevenson and Cole, 1999). Naturally eutrophic lakes are usually associated with underlying deposits that are rich in apatite, for example, rock PO_4^{3-}. Lakes with naturally high P concentrations have been studied in British Columbia (Canada), where the main source of P was from the weathering of volcanic rocks (Murphy et al., 1983). The geographic distribution of confirmed naturally eutrophic lakes in Finland was also related to the presence of bedrock characterised by high levels of P (Miettinen et al., 2005; Rasanan et al., 2006). In addition, several meres in the west Midlands of Britain have been described as naturally eutrophic and this is mainly due to the drift-derived soils characteristic of the area that are particularly rich in P (Moss et al., 1994).

The process of eutrophication is also part of the successional development or ontogeny of a lake basin (Smol, 2008). Lake ecosystems are constantly evolving (Wetzel, 2001) and over time will normally fill with soil and other materials carried by inflowing rivers, eventually becoming a marsh and ultimately a terrestrial system through the process of succession (Rest and Holland, 1988). Sedimentation of lakes is generally quite slow and so, under undisturbed conditions, the process of eutrophication occurs over geological time periods. Generally the eutrophication or ontogeny of lakes is from low to high productivity where lakes gradually change from an oligotrophic to eutrophic state (Wetzel, 2001).

Oligotrophic lakes are characterised by low inputs of inorganic nutrients from external sources and low production of organic matter, which results in low rates of decomposition and a relatively low rate of nutrient release from the sediment. An increased input of organic matter is important in changing the trophic state of lakes, as it accelerates the cyclic regeneration of nutrients through bacterial metabolism. This in turn both accelerates the decomposition of organic matter and increases the availability of inorganic nutrients required for photosynthesis (Wetzel, 2001). Lakes undergoing natural eutrophication generally have water quality that is adequate for most human uses and support a healthy and diverse biological community (Rest and Holland, 1988).

2.1.4 Cultural eutrophication

The classification of some lakes as naturally eutrophic is difficult, due to the degree and longevity of human impacts on ecosystems (Rasanan et al., 2006). Human-induced alterations to a lake catchment, for example due to changing farming practices, can lead to an increased supply of nutrients to a lake. This increased supply of nutrients can accelerate the natural eutrophication process and lead to water quality and management problems. Humans have been exerting an influence on ecosystems from simple hunting and harvesting to fire management and direct vegetation alteration for many millennia (Jackson and Hobbs, 2009) and this long-term influence is likely to have had both direct and indirect effects on lakes. For example, a rapid expansion of submerged macrophyte vegetation at Gundsømagle Sø in Denmark, in response to shallowing of water, was caused by a combination of reduced precipitation and enhanced sedimentation due to intensified agricultural activities in the catchment (Rasmussen and Anderson, 2005). The advent of agriculture at Kassjön, a forested lake catchment in northern Sweden, also led to increased phytoplankton abundance and an increase in taxa favouring mesotrophic to eutrophic water (Anderson et al., 1995). In addition, at Crawford lake, Canada, nutrient input caused by horticultural activity, dated between 1268 and 1486, elevated lake productivity, caused bottom water anoxia and irreversibly altered phytoplankton community structure (Ekdahl et al., 2004).

While it is evident that very few regions have escaped human influence and that human activities have impacted the environment for thousands of years at local, regional and even continental scales, the human impact on the landscape increased substantially with the onset of industrialisation (Steffen et al., 2007). Crutzen and Stoermer (2002) coined the term Anthropocene as a departure from the Holocene into a new human–dominated geological epoch marked by the beginning of the industrial era. The beginning of the Anthropocene coincides with James Watts' design of the steam engine in 1784 (Crutzen, 2002; Crutzen and Stoermer, 2002). The invention of the fossil fuel-fired steam engine heralded an era where there were far looser constraints on energy supply, on human numbers and upon the global economy. During the Anthropocene the global human population has increased by more than six-fold, the global economy by about 50-fold and energy use by about 40-fold (Steffen et al., 2007). The onset of industrialisation occurred quickly and by 1850 had transformed England and was beginning to transform the rest of the world. In the last 250 years about 30% to 50% of the planet's land surface has been exploited by humans (Crutzen, 2002), while the environmental impacts of industrialisation have become increasingly evident.

Culturally eutrophic lakes are characterised by an increase in primary productivity and the development of large algal and cyanobacterial blooms (Ferguson et al., 1996). Blooms form where nutrient loading is high, where the ratio of N to P is low and where conditions in the water are warm and still. Bloom forming cyanobacteria will influence their surrounding environment physically, chemically and biologically and can sometimes produce toxins that may be harmful to human and animal health (Mason, 2002). An increase in nutrient levels can also lead to the excessive growth of aquatic macrophytes, especially non-rooted taxa (Khan and Ansari, 2005). As a result, there is usually a decline in submerged rooted macrophytes due to lower light availability (Matthews et al., 2002; Smol, 2008). This decline in light availability and thus submerged rooted macrophytes may in turn adversely affect zooplankton, phytoplankton and fish populations. An overabundance of algae and macrophytes can cause difficulties in water treatment by blocking filters. Some algal cells may pass through the filters and begin to decompose in distribution pipes causing taste and odour problems (Mason, 2002). As a result, the cost of producing drinking water from eutrophic water bodies can be far higher than from unpolluted sources (Toner et al., 2004). High densities of algae and macrophytes can also affect the recreational value of lakes by rendering water unfit for swimming and can make boating difficult (Mason, 2002; Khan and Ansari, 2005).

2.2 Sources of nutrients

The main anthropogenic sources of P and N entering lakes are those associated with wastewater treatment plants, sewage, organic waste, fertiliser application and animal slurries. The sources of nutrients can be divided into point, intermediate and diffuse sources.

2.2.1 Point sources of nutrients

A point source of pollution is one that can be traced back to a single known source. In relation to eutrophication, point sources provide a continuous discharge of nutrients to freshwaters (Withers and Jarvie, 2008). Point sources are primarily considered to consist of sewage treatment and industrial effluent discharges (Bowes et al., 2010). In the 1940s, detergents were developed containing $Na_5P_3O_{10}$, which softens water by neutralising Ca and keeps dirt in suspension once it is washed off clothes. Between 1950 and 1970 detergent consumption increased more than five times in the USA and more than seven times in Britain. Detergents are now an important source of P in domestic sewage, often making up more than half of the P in effluents (Mason, 2002). In the 1950s, with increased urbanisation and the use of detergents containing P, point sources associated with sewage and wastewater treatment plants became important (Mason, 2002; Smol, 2008). Studies carried out at Lough Leane in southern Ireland (Kirk McClure Morton and Pettit, 2003; Dalton et al., 2010); Lough Neagh in Northern Ireland (Foy et al., 2003); Lago Grange di Avigliana, northern Italy (Finsinger et al., 2006); and in the Mogan lakes in Turkey (Karakoc et al., 2003), have shown that inputs of P from sewage treatment works have caused increased nutrient loading to and eutrophication in their respective lake catchments.

Agricultural point sources are generally from direct slurry input to streams causing organic pollution (Mason, 2002). Intensive livestock farms can act as agricultural point sources. The production and excessive spreading of organic fertilisers (manure) from these farms can pose major problems (Ongley, 1996). This is especially the case with pigs and poultry where there is usually no direct relationship between the number of animals and the availability of land for grazing on the farm. Feedstuffs are frequently imported from elsewhere, adding to the natural P budget (Toner et al., 2004). Manure from the animals is the main agent acting as a nutrient source, mostly during storage and application on the land (de Haan et al., 1997).

Point transfers are highly concentrated in soluble P forms and are largely storm independent. Streams receiving wastewater effluent from point sources typically show a characteristic pattern of high P concentrations during summer low flows and more diluted concentrations during winter storm events (Withers and Jarvie, 2008). While improvements in wastewater treatment facilities and the introduction of P-free detergents have lead to a marked reduction in nutrient loadings from point sources (Heathwaite, 2010), discharges from point sources can be significant, especially during summer when the eutrophication risk is higher (Bowes et al., 2010). During spring and summer biological activity in surface waters is greatest, so increases in SRP concentrations at this time represent a larger ecological risk (Jarvie et al., 2006). Both Arnscheidt et al. (2007) and Jordan et al. (2007) found that storm independent P transfers associated with rural point and intermediate sources, such as individual farmyards and septic tanks, maintained rivers in subcatchments of the Lough Neagh basin in a eutrophic state between high flows. In addition, Bowes et al. (2010), in a study of British rivers, discovered that while 80% of the annual P loads originated from diffuse sources, during low flows point sources were dominant in the majority of the studied river catchments.

2.2.2 Intermediate sources of nutrients

Growing evidence suggests that a mixed group of smaller sources having properties intermediate to those of point and diffuse sources also contribute significantly to P concentrations and loads, especially in rural catchments (Edwards and Withers, 2007). These sources are largely storm dependent (Edwards and Withers, 2008) and include road and track runoff, septic tank discharges and farmyard runoff (Withers and Jarvie, 2008). The low permeability of hardstanding areas, associated with impervious surfaces in farmyards and road and track runoff, increases their susceptibility and capacity for generating large volumes of rapid runoff during storm events (Edwards and Hooda, 2008). Edwards et al. (2008), in a comparison of water upstream and downstream of a farmyard, found that the farmyards acted as a source of multiple contaminants during hydrologically active storm events. Contamination pathways included a combination of both point (e.g. septic tanks) and non-point (e.g. from livestock housing) sources. In addition, Withers et al. (2009) reported that nutrient sources associated with impervious surfaces, such as farmyards, and wastewater from septic tank discharge in a series of microwatersheds of the River Wye in the U.K. delivered highly concentrated P during both low and high flow conditions.

Domestic septic tank systems can act as both point and intermediate sources. Systems that discharge directly to a stream through a pipe are point sources, however, storm overflow from a septic tank system that discharges to a soakaway is an intermediate source (Edwards and Withers, 2008). In rural catchments, particularly in Ireland, a substantial proportion of the population (27%) (Central Statistics Office, 2009) use septic tank systems for waste disposal (Arnscheidt et al., 2007). Many older septic tank systems either discharge directly to a stream, are not emptied frequently or do not have adequate soakaway facilities, and therefore can make a substantial contribution to stream P concentrations (Arnscheidt et al., 2007; Withers and Jarvie, 2008). In a study of three sets of paired catchments in Britain, Jarvie et al. (2010) reported that even in sparsely populated rural headwater catchments, small settlements and isolated groups of houses are sufficient to cause significant nutrient pollution. They maintained that septic tank systems serving rural communities operate as multiple point sources rather than as a diffuse source.

2.2.3 Diffuse sources of nutrients

Diffuse sources of pollutants originate from various activities and are often difficult to monitor and control (Heathwaite, 2010). Diffuse sources of nutrients usually consist of atmospheric deposition, commercial forestry, agricultural fertilisers and animal manure runoff from soils (Jennings et al., 2003). Where improvements in wastewater treatment have been effective, the impacts of point sources of nutrients have been diminished. However reduced inputs from point sources have tended to highlight the effects of diffuse sources of nutrients, with eutrophication persisting in many water bodies after inputs from point sources have been controlled (Jennings et al., 2003). For example, an 80% to 86% decrease in wastewater loading from point sources in Lake Lappajarvi, Finland, did not lead to aquatic recovery, because of the continued effects of diffuse loading (Merilainen et al., 2000). Moreover, Räike et al. (2003) highlight the extent of the problem of pollution of rivers and lakes in Finland from diffuse agricultural sources during the 25 years to 2000. At Lough Neagh in Northern Ireland, improvements in water quality following a reduction in point sources were temporary and by the end of the 20th century, diffuse P contributed more than 80% of the TP entering the lake (Foy et al., 2003). In addition, at Lough Leane, in the south-west of Ireland, point sources of nutrients, associated with untreated sewage, were prominent up until the 1980s when sewage treatment facilities were completed. After this date diffuse agricultural sources of P became more prominent (Dalton et al., 2010).

Atmospheric deposition may be an important source of P in some lake ecosystems. Most P from atmospheric sources occurs through rain and snowfall (Jennings et al., 2003), while dry atmospheric deposition arises from gaseous and particulate transport from the air to the surface of aquatic and terrestrial landscapes (Anderson and Downing, 2006). Sources of atmospheric P include wind erosion of soil and crustal material, pollen and plant exudates and urban and industrial contaminants. In heavily fertilised agricultural regions, the P content in precipitation is much higher during the active growing season, when compared with winter (Wetzel, 2001). The importance of atmospheric P loading varies with lake trophic status. In oligotrophic lakes with few areal sources of nutrients, atmospheric deposition may account for a significant proportion of the annual P load. Whereas in lakes with large point source loading and/or a catchment that includes a high proportion of agricultural land, atmospheric deposition may constitute a small proportion of the annual TP load (Jennings et al., 2003).

The application of fertilisers in agriculture constitutes an important diffuse source of nutrients to freshwaters (Mason, 2002). Towards the end of the 19th century, in response to increased demand for fertiliser, P rich fertilisers were developed by extracting P from iron ore (Aftalion, 2001; Kjeldsen-Kragh, 2007). In addition, in the early 20th century the Haber-Bosch synthesis was developed by Fritz Haber and Carl Bosch, which allowed

NH_3 to be synthesised from atmospheric N. The development of P and N fertilisers revolutionised agriculture and sharply increased crop yields all over the world (Kjeldsen-Kragh, 2007; Steffen et al., 2007). The use of fertilisers increased dramatically after World War Two due to food shortages. With the development and widespread use of fertilisers, significantly more nutrients were delivered to water bodies (Sharpley et al., 2003). In Ireland, fertilisers were used intensively from the 1960s to the 1990s and there is still a soil surplus input of 8 kg ha^{-1} $year^{-1}$ of P in Ireland (Ulén et al., 2007). As a consequence, a large amount of lake eutrophication in Ireland has been attributed to diffuse nutrient loading from inputs of agricultural fertilisers (e.g. McGarrigle and Champ, 1999; Foy et al., 2003; Jennings et al., 2003; Jordan and Rippey, 2003). Many agricultural soils in developed countries, including Ireland, are now considered to be P saturated and require little or no further P fertilisation (Jennings et al., 2003). This soil surplus of P continues to act as a diffuse source of nutrients to surface water.

Another major source of nutrients from the agricultural industry is livestock farming (Toner et al., 2004) and changes in livestock farming practices are directly related to agricultural policies. In Europe, the CAP emerged out of a shortage of food in most European countries after World War Two and was implemented to safeguard food supplies and protect farming communities (Gardner, 1996; Routledge, 1999). The main objective of the original CAP was to support farmers through market rather than by direct subsidisation, with prices that were aimed to be high enough to maintain incomes of even the least efficient areas. Subsidies were paid to traders to sell surpluses of the main commodities on the generally lower priced international markets. As a response to these subsidies and high prices paid for surpluses, EU farmers began to produce more than the domestic market could absorb (Gardner, 1996). In addition, in the 1980s and 1990s direct payments were introduced to beef and sheep producers based on their flock and herd numbers. This resulted in more intensive farming and increased stocking ratios of breeding ewe sheep, beef cattle and dairy cows (Routledge, 1999).

Livestock can improve soil and vegetation cover and plant and animal diversity. However, excessive livestock grazing can cause soil compaction and erosion, decreased soil fertility, water infiltration and a loss in organic matter content and water storage capacity (de Haan et al., 1997). For example, Heathwaite (1995) found that heavily grazed grassland showed consistently higher levels of export in N and P in comparison with lightly grazed and ungrazed land uses. May et al. (2005) found that sheep grazing contributed to the substantial erosion of blanket peat in the Burrishoole catchment in Co. Mayo, Ireland, while Garcia Rodriguez et al. (2002) argue that intensive cattle and sheep grazing led to gully formation and increased sedimentation rates at Lake Blanca in south-east Uruguay. In general, losses of P from soil increase with stocking density (Mason, 2002), due to a combination of increased inputs of faecal matter and a greater importance of overland flow because of reduced infiltration through soil compaction and vegetation removal (Jennings et al., 2003; Toner et al., 2004).

Forestry is a potentially important diffuse source of nutrients to freshwaters. P export from commercial forests may increase markedly during establishment and deforestation and following fertiliser application (Jennings et al., 2003). Studies in the UK have shown that 10 % of P from aerial applications was delivered to streams over the following three to five years, and mainly within six months (Nisbet, 2001). In addition, ground preparation techniques in the establishment of a plantation can cause drastic alterations to the original landscape (Neal et al., 2004). Existing vegetation is eliminated and deep drains are dug to remove surface water from soil often into nearby streams (Giller and Halloran, 2004). Clearfelling of plantations or parts of plantations can lead to an increase in the concentration of DOC, suspended solids and nutrients such as P and N to both surface and groundwater (Neal et al., 2004; Girvan and Foy, 2006). Highest losses of P from forestry occur from organic soils, which are characterised by low P-binding capacity (Jennings et al., 2003)

2.2.3.1 Nutrient transfer from diffuse sources

P losses from diffuse agricultural sources to surface waters are principally driven by soil biochemical processes, which control the form of soil P available for transport, and hillslope hydrology, which defines the mechanisms and pathways of P loss (Heathwaite and Dils, 2000). Land management practices also contribute to the potential P loss from agricultural land (Doody et al., 2006). P loss from agricultural land can occur via surface runoff, subsurface flow or via groundwater flow (Jennings et al., 2003). Surface runoff may be generated by infiltration excess where runoff occurs when rainfall intensity exceeds the infiltration capacity of the soil or by saturation excess where runoff occurs as a water-table rises to the soil surface, so that the soils water storage capacity is exceeded. Infiltration excess runoff is comprised predominantly of rain water while saturation excess runoff includes both rain and soil water (Kleinman et al., 2006). Surface runoff is considered to be the main pathway of P loss from agricultural grassland soils with saturation excess runoff being the dominant type of surface runoff generated under Irish conditions (Doody et al., 2006). P loss in surface runoff from grassland is generally in dissolved, or soluble, forms (Heathwaite and Dils, 2000; Doody et al., 2006) while P loss in surface runoff from cultivated land, with higher surface roughness, is predominantly linked with PP (Heathwaite and Dils, 2000; Jennings et al., 2003).

Subsurface flow includes the movement of water through the soil matrix through preferential flow pathways such as soil macropores and worm burrows and through artificial drainage networks. The importance of subsurface flow depends on soil and catchment characteristics (Jennings et al., 2003). Soil type is significant in buffering the impact of P surpluses on P release to the soil solution and runoff water (Withers and Haygarth, 2007). Subsurface flow tends to occur under natural conditions to a greater extent in fine textured soils than in coarser textured soils because of the higher clay content of the former and hence a greater likelihood of cracking during dry periods (Simard et al., 2000). In addition, sandy and organic soils generally have a lower capacity to bind P than those with a high clay or with higher Fe and Al contents (Jennings et al., 2003). Jordan et al. (2005b) found that agricultural areas with mineral soils and catchments with low Al content and highly flashy hydrology are at greatest risk of transferring reactive P (via desorption) and PP (via erosion or enrichment) to freshwater. Daly et al. (2001), in a study of 90 representative Irish soils, reported that peat soils had low sorption and desorption values, but high soil solution P concentrations compared with mineral soils. Therefore, peat soils are particularly at risk since they are normally located in high rainfall areas in Ireland. Where grassland peats receive P inputs in excess of crop demands, P remaining in the soil solution may be lost to water via overland flow.

Delivery of P in both surface runoff and subsurface flow is reliant upon the hydrological cycle and the timing and magnitude of precipitation (Edwards and Withers, 2007). Substantial temporal variability exists in the mobilisation and transport of P from diffuse sources (Withers and Jarvie, 2008), reflecting the frequency and distribution of high precipitation events (Bowes et al., 2008). High intensity/low frequency rainfall events or storm conditions account for a high proportion of the total losses of P from diffuse sources. Rapid hydrological flowpaths, including overland flow and preferential subsurface flow through macro-pore drains and natural pipes, are the main driver of P removal from soils via desorption/dissolution and erosion of adsorbed and precipitated P with fine soil particles (Douglas et al., 2007). Intense rainfall events are particularly important where artificial drainage systems and preferential pathways provide direct links to surface water (Jennings et al., 2003). Jordan et al. (2005a, 2007) discovered that storm dependant transfers delivered the majority of the TP load for an agricultural catchment in the Lough Neagh basin in Northern Ireland to surface waters. This load was seen to be particularly important for the eutrophic impacts of any receiving standing water body when integrated with the cumulative effects of all acute storm transfers from the wider drainage basin (Jordan et al., 2005a). In addition, Douglas et al. (2007) reported that storm transfers were responsible for the majority of P transfers in the Oona catchment in Northern Ireland.

Intense rainfall events are particularly significant if a prolonged dry period precedes the rainfall event, as there will have been a build up of P in the soil during dry weather (Jennings et al., 2003). For example, Simard et al. (2000) in a study of the St. Lawrence lowlands in Canada found that TP in drain water and its proportions as PP showed wide seasonal variations. Preferential flow pathways were shown to be most important following storm events after a period of drought. Donohue et al. (2005) reported similar results from the west of Ireland, with significantly higher nutrient concentrations, especially particulate forms of P and N, during high flows in summer and autumn than during winter owing to the retention of particulates during low flows and subsequent resuspension during flood events.

Transfers from non-point or diffuse sources are highly sensitive to changes in climate (Jennings et al., 2009). Subtle changes in climate can affect the hydrology of a lake, due to changes in the relative amounts of precipitation and evaporation (Bruchmann and Negendank, 2004). As hydrological conditions vary, the timing and magnitude of inflowing nutrients to a lake system will also change (Malmaeus et al., 2006). With continued greenhouse gas emissions at or above the current rate, the frequency of heavy precipitation events is predicted to increase in most areas globally (IPCC, 2007), including Europe (Eisenreich, 2005). Changes in precipitation have been observed in many parts of Europe, with wetter conditions reported in northern Europe and an increase in cyclonic activity in the north Atlantic (Jennings et al., 2009). In Ireland, winter precipitation is predicted to increase by 10% by 2050 (Sweeney et al., 2008) and by 15% in western areas (Sweeney and Fealy, 2002). Lengthier rainfall events are predicted in winter with more intense rainfall events predicted in summer leading to increased streamflows (Sweeney et al., 2008). The results of a forecasting model carried out on the Lough Leane catchment in southern Ireland have shown that the increase in annual TP loads which can be attributed to changes in climate is greater than that arising from population increase or potential land use changes (Jennings et al., 2009). These predictions have implications for the water quality of surface waters due to the significance of flow dependent diffuse sources in agricultural catchments.

2.3 Within-lake controls on eutrophication

Within riverine systems, lakes are recognised as natural traps for sediment and nutrients (Cook et al., 2010). The main feature of eutrophication within lake ecosystems is an increase in primary productivity, which is controlled by the concentration of bioavailable P in the water and by the morphometry of the lake (Jones and Elliott, 2007).

2.3.1 Thermal stratification and seasonality of P concentrations

The P concentration of a lake is dependent on complex equilibria between external and internal loading, together with the physical and biological processes occurring in the water column and in the sediment (Jennings et al., 2003). Thermal stratification is crucial for the physical, chemical and biological processes in lakes (Brönmark and Hansson, 2005). As water warms during the spring, warmer water remains near the surface while colder water stays near the bottom of the lake. Wind mixing determines the thickness of the warm surface water layer that usually extends to the first few metres (Shaw et al., 2004). Two layers of water are formed: a warm, less dense layer at the surface is known as the epilimnion; and an underlying layer of dense, cool water, known as the hypolimnion. The stratum between the two layers, characterised by a steep thermal gradient, is called the thermocline or the metalimnion (Brönmark and Hansson, 2005). Lakes with large open areas are more exposed to wind than small lakes. A larger wind-fetch supplies more energy to the water mass and causes a more efficient mixing of the epilimnion and a deeper thermocline than in smaller or more sheltered lakes (Kvarnäs, 2001).

Some lakes show clear annual cycles of winter maxima and summer minima in TP concentrations and this seasonal pattern is most apparent in eutrophic lakes. Lake TP concentrations are controlled by the magnitude of the external load and the internal loading of P from the sediment (Jennings et al., 2003). The active growing season in lakes generally coincides with the stratification period. In spring, phytoplankton respond to increasing water stability, temperature, nutrient and light conditions through exponential growth (Winder and Schlindler, 2004). In general, low midsummer concentrations of P relate to biotic uptake of P and the sedimentation of algal biomass (Jennings et al., 2003). Due to the high heat capacity of water, aquatic ecosystems may be especially sensitive to temperature changes and increased water temperature may be as important in lake ecosystems as an altered hydrology (Winder and Schlindler, 2004; Malmaeus et al., 2006). Increases in temperature can extend the stratification period, and thus lead to increased growth of phytoplankton (Gerten and Adrian, 2000; Winder and Schlindler, 2004;

Elliott et al., 2006). Elliott et al. (2006), using the PROTECH model, found that an increase in temperature led to an increase in mean levels of phytoplankton biomass, including cyanobacteria. However this increase in phytoplankton biomass, due to warmer temperatures, was dependent on high nutrient loads. Wilhelm and Adrian (2008) reported that hypolimnetic water temperature and the intensity of stratification were determining factors in the decrease of hypolimnetic O concentration and the increase in SRP accumulation in the hypolimnion at Müggelsee in Germany. In addition, Ulén and Weyhenmeyer (2007) reported that prolonged summer periods led to increased P recycling in the sediments, counteracting P reduction at Lake Mälaren, Sweden.

2.3.2 P release from sediments

The external nutrient supply to a lake is the main determinant of the trophic status of a lake (Cardoso et al., 2007). Internal loading of P, however, can be significant in preventing improvements in water quality. Lake recovery following a reduction in external loading is often delayed due to internal loading of P (Søndergaard et al., 2001). In most lakes there is an apparent net movement of P into the sediments and the P content of sediments can be several orders of magnitude greater than that of the water (Wetzel, 2001). PP that enters a lake in inflowing waters will be generally sedimented rapidly and sedimenting planktonic material may make a significant contribution to sediment P loads during summer (Jennings et al., 2003). P exists in lake sediments in a variety of forms. P may be bound, for example, to Fe and Al oxides and it may exist in carbonates, apatite and organic matter. Some of the P forms are practically inert, whereas others may be potentially available to algae if they can be transformed to PO_4^{3-} via desorption (Krogerus and Ekholm, 2003). Once the P is within the sediment, exchanges across the sediment water interface are regulated by mechanisms associated with mineral-water equilibria, sorption processes and the physiological and behavioural activities of many of the biota associated with the sediment (Wetzel, 2001).

P release from sediments can be dependent on the extent of thermal stratification and the oxygen content of the hypolimnion. Oxic lake sediments retain P more efficiently than anoxic sediment (Köiv et al., 2011):

under oxic conditions at the sediment surface, P release rates from the sediment and hence P concentration in the water column are lower (Gächter and Müller, 2003). Anoxic sediment conditions have been demonstrated to increase P recycling from sediments, thus prolonging the eutrophication process (Ulén and Weyhenmeyer, 2007). Anoxia is a problem associated with eutrophication especially in late summer in stratified lakes (Smol, 2008). High levels of primary production, associated with eutrophication, result in high DO consumption in the hypolimnion and a low penetration depth of O to the sediment (Bowes et al., 2010). High levels of DO consumption by primary producers can lead to a depletion of O or anoxia (Khan and Ansari, 2005). As levels of O are depleted in a lake and deoxygenation sets in, bioavailable P may be released from the sediment through desorption (Matthews et al., 2002; Toner et al., 2004). Oxygenation may not be the only process driving P retention and release from sediments, however. For example, Gächter and Müller (2003) found that increased DO concentrations neither reduced the P release from sediments nor resulted in an increased permanent P retention in Lake Sempach in Switzerland. The proportion of Fe and Al oxides in the sediment is important to P retention. The presence of P binding mechanisms associated with these chemicals can enhance P retention and completely prevent P release even in the case of anoxic conditions (Hupfer and Lewandowski, 2008). Gibson et al. (2001) reported that the sediment P cycle in Lough Neagh, Northern Ireland, is dominated by Fe-P interactions and is sensitive to O concentrations in the sediment.

2.3.3 Lake morphometry and eutrophication

Lake morphometry refers to the size and form of a lake and can influence processes such as sedimentation, resuspension, diffusion, mixing, burial and outflow, which in turn influence abiotic state variables such as concentrations of P and water clarity. Both primary production and secondary production are then influenced by these processes (Hakanson, 2005). Vollenweider's research on the regulation of lake productivity by P inputs has been one of the most influential contributions in limnology. The family of models (Vollenweider, 1968, 1975, 1976) predict lake TP concentration as a function of lake morphometric and hydraulic characteristics such as areal P loading rate, mean lake depth and hydraulic retention time (Cheng et al., 2010). Essentially, the P concentration of a lake and the retention of P, largely within sediments, is influenced by the physical structure of a lake (Köiv et al., 2011).

2.3.3.1 Hydraulic retention time

The rate at which water moves through a lake can affect the supply and loss of nutrients in the lake (Elliott et al., 2009). The hydraulic retention time or water residence time of a lake is defined as the volume of the lake divided by the total water input to the lake (Kvarnäs, 2001). Phytoplankton dynamics depend on a range of factors such as limitation by nutrients, light availability and temperature (Jones and Elliott, 2007). Hydraulic retention time can affect phytoplankton abundance in lakes through determining the in-lake P concentration (Elliott et al., 2009). In general a longer residence time causes more extensive nutrient recycling and greater nutrient retention (Köiv et al., 2011). Cook et al. (2010) reported that annual TP retention rates could be predicted as a function of hydraulic retention time in the River Murray systems in Australia. Hydraulic retention time is dependent upon river discharge to a lake and so changes in the magnitude and timing of river discharges will affect P retention within lakes (Moore et al., 2008). Jones and Elliott (2007) reported that in simulations of short hydraulic retention time with a fixed load, chlorophyll concentrations were reduced, while longer retention times caused the spring bloom of phyotplankton to start earlier and the autumn bloom to persist longer. In addition, Nöges (2005) maintained that increased retention time in warm and dry years increases the retention of chemical constituents. In these years, lakes stratify earlier and tend to accumulate higher concentrations of decaying matter in the hypolimnion. In lakes with extremely long retention times, changes in river discharge are unlikely to have a major affect on lake ecology (Jones and Elliott, 2007).

2.3.3.2 Water depth

Lake morphometric parameters such as mean depth and volume, reflect the buffering capacity of a lake to nutrient inputs and are considered important factors affecting lake water quality (Liu et al., 2010b). Deep, large lakes were initially thought to be less productive than smaller and shallower lakes, in general (Lampert and Sommer, 2007). Based on a comprehensive review of TP retention models, Brett and Benjamin (2008) reported widespread acceptance of importance of the mean depth and the areal TP loading rate as controlling parameters for in-lake TP concentrations. In addition, negative relationships between water quality parameters, including P concentrations, and lake depth have been reported in many regions, including the USA (Taranu and Gregory-Eaves, 2008), Canada (Hamilton et al., 2001), Europe (Cardoso et al., 2007; Nöges et al., 2009) and China (Liu et al., 2010a). Deep lakes are more likely to undergo thermal stratification, with numerous nutrients and other pollutants settling out of the epilimnion (Liu et al., 2010a). As the depth of a lake increases, a greater proportion of nutrients are lost through sedimentation (Cardoso et al., 2007). For example, Nöges et al. (2007) reported that Lakes Peipsi and Võrtjärv, in Russia, showed positive relationships between the P content of the sediment and the lakes depth. Deep lakes also have a higher ratio of water volume to sediment surface and thus have more potential to dilute nutrients, such as P, than shallow lakes (Liu et al., 2010a). Deep lakes often contain large expanses of shallow water. Examples of such lakes in the Irish Ecoregion include Lough Leane in southern Ireland, Lough Feeagh in western Ireland (Dalton et al., 2010), Lough Cloonaghlin and Upper Killarney Lough in southern Ireland (Taylor et al., 2006b). Based on the premise that deep lakes are less productive than shallow lakes, the deeper areas of lakes should also be less productive compared to the shallower areas.

Shallow lakes and littoral parts of deep lakes are more prone to the release of P from sediment to surface water (Taranu and Gregory-Eaves, 2008). Wind induced resuspension of sediment can occur easily in shallow water (Krogerus and Ekholm, 2003), whereas nutrient exchange between the sediment and overlying water in deep water mainly depends on diffusion related processes (Liu et al., 2010a). P released from the sediment of shallow lakes can constitute a substantial part of the total P loading and sometimes exceeds external loading of P (Søndergaard et al., 2001). In shallow areas, the photic zone often extends to the lake bed and is in contact with the sediment, which increases sediment-water interactions (Wetzel, 2001). Resuspended sediments are a potential source of nutrients for phytoplankton growth in shallow areas (Liu et al., 2010a) and regular mixing by resuspension in shallow areas guarantees stable and near optimum conditions for primary production (Søndergaard et al., 2001), such that biological productivity is usually higher in the shallower zones of lakes (Wetzel, 2001).

In Ireland, deep lakes are classified as having a mean depth of over 4 m and a maximum depth greater than 12 m. Large lakes are classified as being greater than 50 ha in surface area (Free et al., 2006). This classification differs from other regions, for example Köiv et al. (2011) defined large lakes as having a surface area greater than 25 km^2. However the limits on water depth, surface area and alkalinity in the Irish classification system were deemed as important controlling variables on water quality parameters such as the development of littoral and profundal macroinvertabrates and macrophytes in Irish lakes (Free et al., 2006). Of the lakes that were studied as part of the IN-SIGHT project, large, deep, low-alkalinity lakes most consistently showed important biological deviations from reference conditions. These deviations were not deemed to be due to nutrient enrichment as increases in DI-TP were relatively minor (Taylor et al., 2006b). For example, Lough Cloonaghlin, in south-west Ireland, displayed one of the highest rates of floristic change in diatom assemblages between reference and the time of sampling (2003) and also displayed an increase in DI-TP. No obvious cause of these changes was found in Lough Cloonaghlin, although it was suggested that climate and local soluble inputs of P may be significant (Leira et al., 2006). As mentioned previously, changes in climate can have an impact on lake ecosystems. Increases in temperature can extend the stratification period in deeper lakes (Elliott et al., 2006) and increase the hydraulic retention time (Moore et al., 2008), leading to enhanced growth of phytoplankton (Gerten and Adrian, 2000).

2.4 Summary

The current understanding of the historical record of eutrophication in freshwater lakes is often hampered owing to difficulty in separating the influence of various drivers of nutrient enrichment in the palaeolimnological record. These drivers of eutrophication include point, intermediate and diffuse sources of nutrients, climatic variability and catchment characteristics such as geology, topography and soils. A large number of nutrient sources can simultaneously influence nutrient levels in lakes while the transfer of nutrients from point, intermediate and diffuse sources within lakes is controlled by the hydrological cycle (Edwards and Withers, 2007). While the relative importance of nutrient sources, catchment characteristics and climate to nutrient levels in surface waters can be determined using current water measurements (e.g. Jordan et al. 2005; Jordan et al. 2007; Douglas et al., 2007; Jarvie et al., 2010), in lakes with limited historical water quality records, determining the combined importance of the above influencing factors to eutrophication is difficult (Bennion et al., 2011). In addition, the within-lake response to increased nutrient loads can be spatially variable owing to the morphometry of a lake basin (Pla et al., 2005). Shallow sites, owing to their increased potential for sedimentary P release (Taranu and Gregory-Eaves, 2008) and optimum conditions for phytoplankton growth (Søndergaard et al., 2001; Wetzel, 2001) should display higher levels of TP and should show an increased response to nutrient loads.

The current research, using data from a lake in the Ecoregion of Ireland as a case study and through a methodological framework that relies heavily (although not entirely) on palaeolimnological techniques, targets gaps in the understanding of eutrophication by using historical documentary and climate records to assess the extent to which recent eutrophication is caused by anthropogenic factors. Through the study of multiple locations within the test site, the research also attempts to assess the extent to which the response to increased nutrient loads varies spatially within a lake basin.

Chapter Three: Study Site

This chapter provides a detailed description of the test site that was chosen for the current research. The criteria for selecting the test site are first outlined followed by a description of the chosen site. The existing water quality records for the site are then described in detail. The potential anthropogenic nutrient sources to the lake and their associated histories are outlined and the climate records that were available for the study area are described.

3.1 Choice of the test site

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

- The lake should have a known problem of nutrient enrichment or eutrophication
- There should be a number of potential nutrient sources in the catchment including point and diffuse sources.
- The lake should be located close to a weather observing station so that detailed historical climate records for the catchment could be obtained.
- The lake should be large and relatively deep, based on the Irish classification system.

A number of large deep low alkalinity lakes were considered as test sites for the current research, including those sampled as part as the IN-SIGHT project. Lough Currane, Co. Kerry, Ireland was chosen for the current research as it fulfilled all of the criteria outlined above and is located within c.16 km of Valentia weather reporting station allowing detailed climate records for the catchment to be obtained. The lake is located on the south-west coast of Ireland which is an ideal location for the study of climatic fluctuations, particularly fluctuations in precipitation.

3.2 Lough Currane

3.2.1 Location and catchment

The location of Lough Currane, in south-west Ireland, is shown in Figure 3.1 while lake bathymetry is shown in Figure 3.2. Lough Currane is situated close to the town of Waterville, Co. Kerry, Ireland (51° 49' 40" north, 10° 07' 58" west). The two primary inflows to Lough Currane are the Cummeragh and Capall Rivers as shown in Figure 3.1. The Cummeragh River drains most of the lake's catchment and its river basin comprises Derriana Lough, Cloonaghlin Lough and Lough Namona.

Lough Cloonaghlin was sampled as part of the EPA IN-SIGHT project. The results from Lough Cloonaghlin were used to compare with the results from Lough Currane in order to assist in determining the causes of eutrophication in the lake. Lough Cloonaghlin has a relatively low TP content of 5 $\mu g\ l^{-1}$ indicating that oligotrophic conditions prevail, however the lake showed one of the highest degrees of floristic change between reference and c.2003 AD samples in the IN-SIGHT project (Leira et al., 2006). The physical characteristics of both Lough Currane and Cloonaghlin are shown in Table 3.1. Both lakes were classified as large, deep low alkalinity lakes by the EPA in Ireland (Free et al., 2006). Based on the bathymetric survey of Lough Currane, carried out by Dixon-Brosnan environmental consultants, the mean lake depth is 6 m. According to EPA measurements (http://hydronet.epa.ie), the average daily flow rate of the Cummeragh River from 2000 to 2010 AD is 3.2 $m^3\ s^{-1}$. Based on this value and a lake volume of 60,000,000 m^3, the hydraulic retention time of Lough Currane is calculated as approximately 1 year. The Capall River drains the south-west section of the catchment and also comprises Isknagihiny Lough. Lough Currane discharges to Ballinskelligs Bay, about 400m away, via the Currane River.

Lough Currane and all of the lakes in it's catchment are entirely underlain by Upper Devonian sandstones. The geology of the catchment is shown in Figure 3.3. The catchment of the lake is primarily underlain by the St. Finians sandstone formation which is medium grained, chloritic and is characterised by large scale cross stratification. In the north and north-west of the catchment there are some Upper Devonian medium grained sandstones of the Ballinskelligs Bay formation.

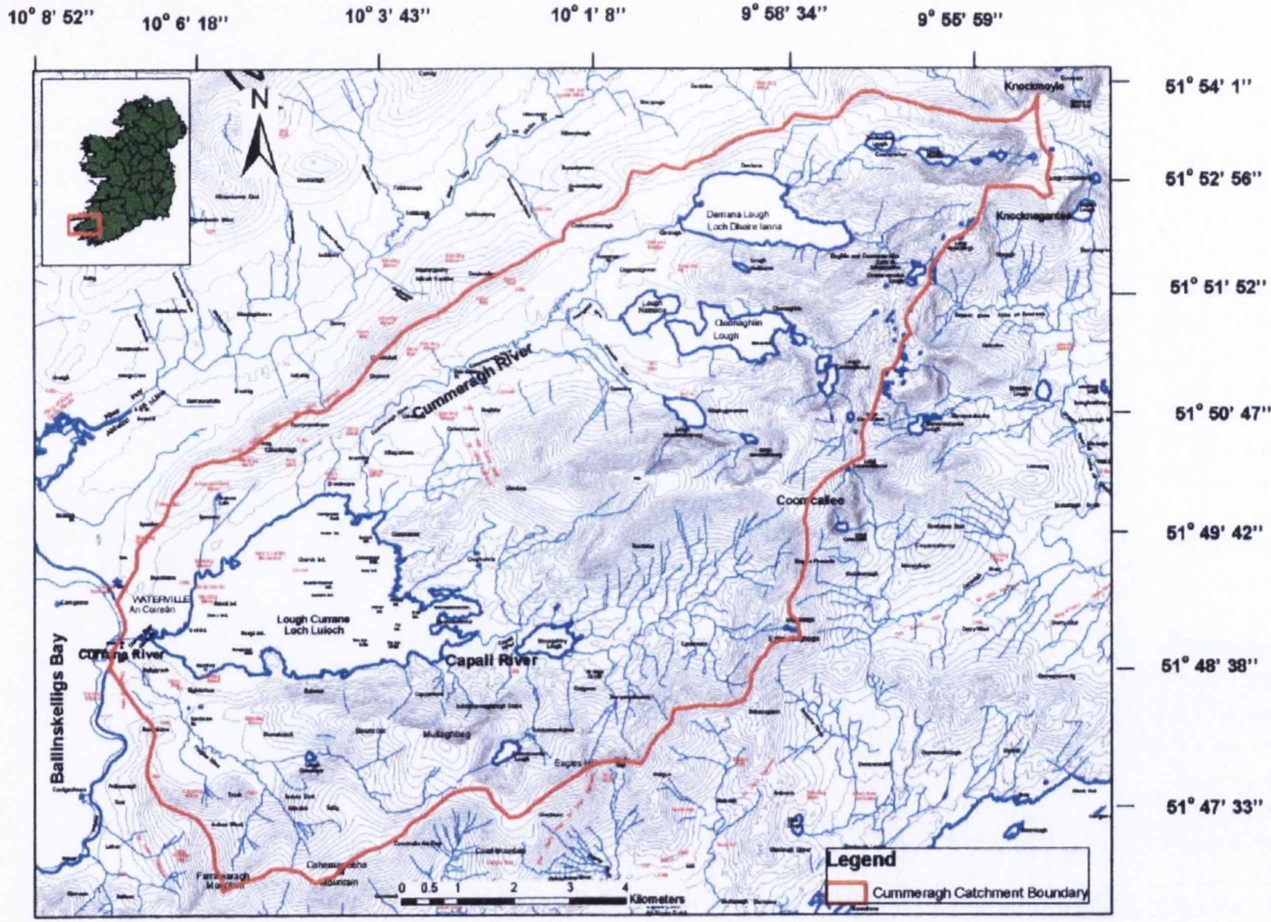


Figure 3.1: Location map of Lough Currane. The contour intervals are shown at 25m intervals

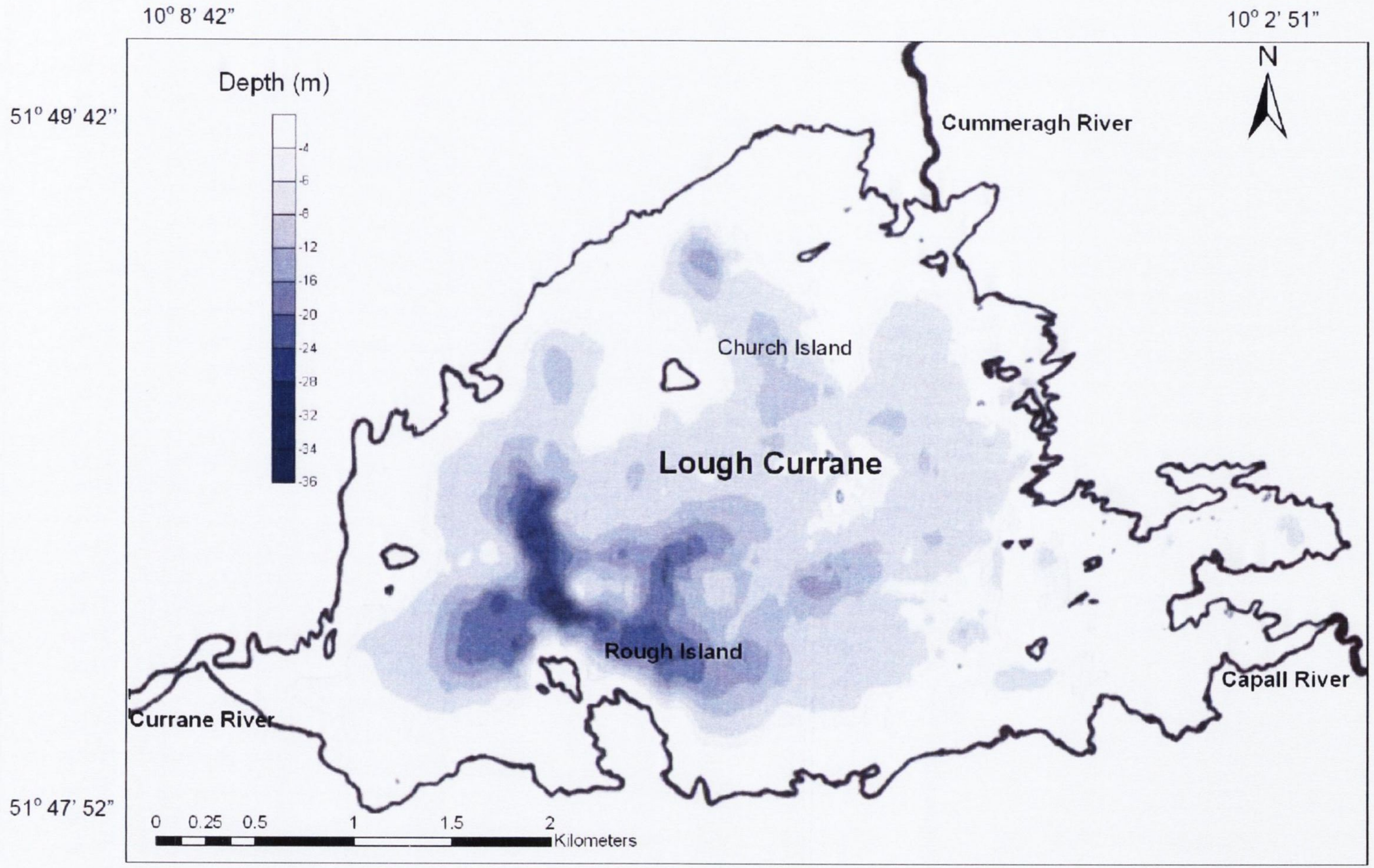


Figure 3.2: Bathymetric map of Lough Currane

The south and south-west of the catchment is underlain by Valentia slate of mid Devonian age, composed of purple and green siltstones with well developed cleavage (Pracht, 1996). Devonian sandstones are considered to be poor aquifers (Pracht, 1996), so the influence of groundwater is likely to be negligible in the catchment. The catchment of Lough Currane is mountainous and the soils in the catchment of Lough Currane are primarily peats and podzols as shown in Figure 3.4. The soils located close to the inlet from the Cummeragh River are characterised by Gleys, brown podzolics, brown earths and peats while the areas around the north-east and south-east shores of Lough Currane are characterised by well drained brown podzolics (Kerry County Committee of Agriculture, 1972).

Lake Name	Altitude (m.a.s.l)	Lake area (ha)	Maximum Lake Depth (m)	Catchment Area (km^2)
Lough Currane	6	1000	35	104
Lough Cloonaghlin	109	128	27	10

Table 3.1: Physical characteristics of both Lough Currane and Lough Cloonaghlin, obtained from Flanagan and Toner (1975) and Free et al. (2006).

3.2.2 Water quality at Lough Currane

Lough Currane has been classified as a CRL by the EPA in Ireland (Free et al 2006), however the lake has shown signs of eutrophication. According to historical records of water quality from Lough Currane, nutrient enrichment commenced between the mid 1950s and mid 1970s. Faran (1947), cited in Grainger (1952), noted the presence in Lough Currane of the copepod *Diaptomus wierzejskii,* a taxon usually associated with oligotrophic conditions (Grainger, 1952); while Went (1971) reported that Irish Char (*Salvelinus alpinus*), a fish species that requires clean, cold water (Igoe et al., 2003) were found in Lough Currane up to the early 1950s. The reported presence of taxa such as *Diaptomus wierzejskii* and *Salvelinus alpinus* attest oligotrophic, largely unpolluted, conditions in the lake prior to the mid 1950s. Several studies since the mid 1970s have, however, recorded evidence of nutrient enrichment. For example, the presence of the cyanobacteria *Oscillatoria* (Flanagan and Toner, 1975) and high TP (83 µg l^{-1}) and Chlorophyll (13.4 µg l^{-1}) readings at an outlet from a mink farm in the catchment (Central Fisheries Board, 1985).

Intensive water quality monitoring has been carried out at Lough Currane since May 2001 (Dixon Brosnan, 2005). Samples were collected, on a monthly basis, using autosamplers and grabsamplers from several locations within the lake as outlined in Figure 3.5 (Lenihan, 2005). Physiochemical parameters measured for each sample include TP, MRP, NO3, chlorophyll, transparency, silica, pH and conductivity as displayed in Table 3.2. The TP and chlorophyll measurements are primarily used in the current research.

Lough Currane has largely remained within the boundaries of the mesotrophic range throughout much of the period of intensive monitoring (Table 3.3). In 2005, according to the TP measurements, the lake was classified as eutrophic. The mean TP reading of 63 µg l^{-1} was due to two extremely high TP measurements. For example TP of 875 µg l^{-1} was measured at the Currane River on 19th October and while TP of 165 µg l^{-1} was measured at the lake station 1 km north-east of Church Island on November 17th 2005. The maximum and mean chlorophyll values indicate that the lake reached eutrophic status in 2003, 2004 and 2009. Chlorophyll is a direct indicator of primary productivity and reflects the increased growth of algae and cyanobacteria in Lough Currane.

For the locations that were frequently sampled, lowest TP levels were measured at Reenaskinna bay and at the deepest point of the lake, 100 m north of Rough Island (Figure 3.5 and Table 3.4). Highest TP values were found at the mouths of the Cummeragh and Capall Rivers, as well as at the outlet of the lake close to the village of Waterville. Lowest chlorophyll values were found at a mid-lake site and at the mouth of the Cummeragh River, while highest chlorophyll values were found in the Currane River, and in Reenaskinna bay.

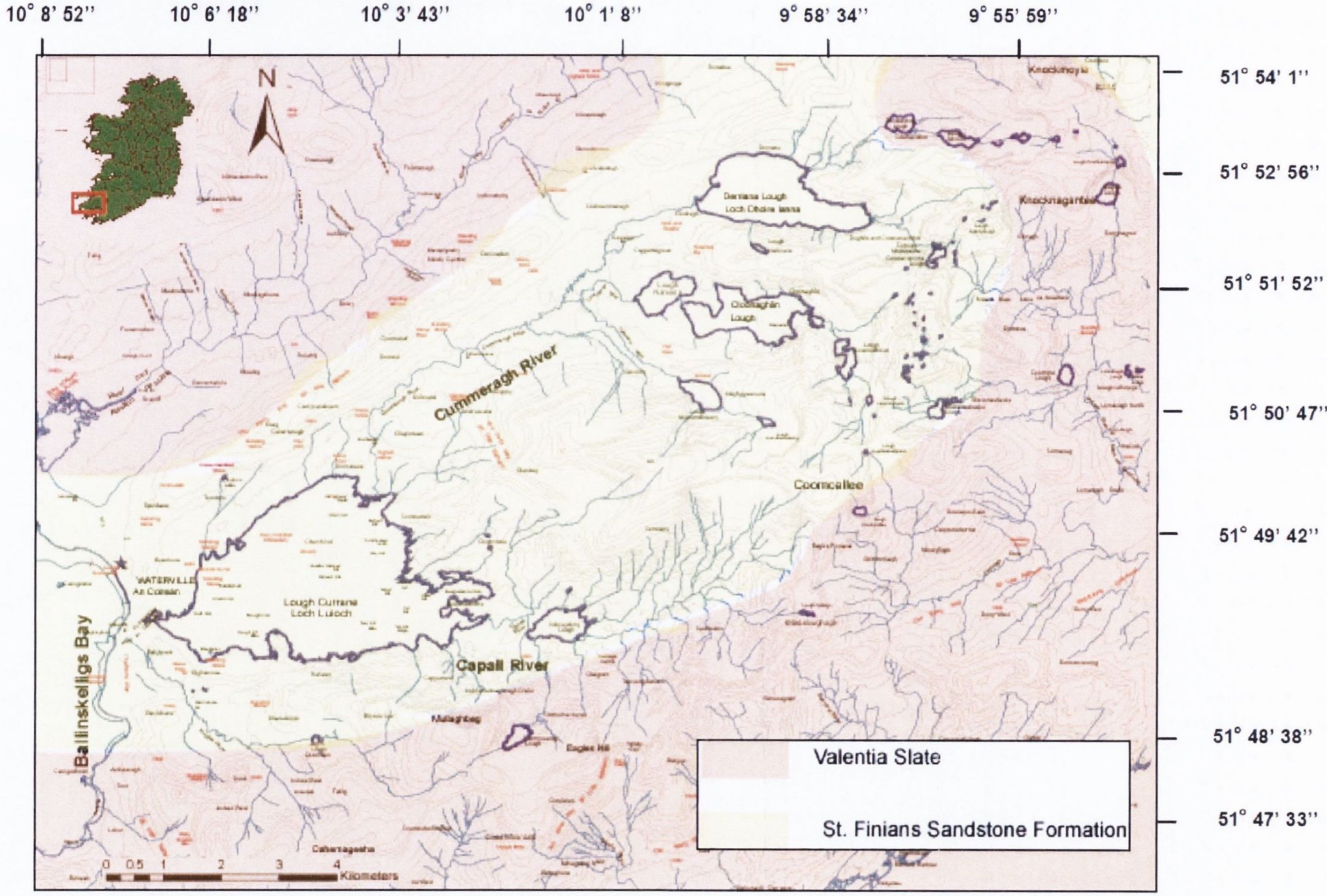


Figure 3.3: The geology of the Lough Currane catchment obtained from Pracht (1996)

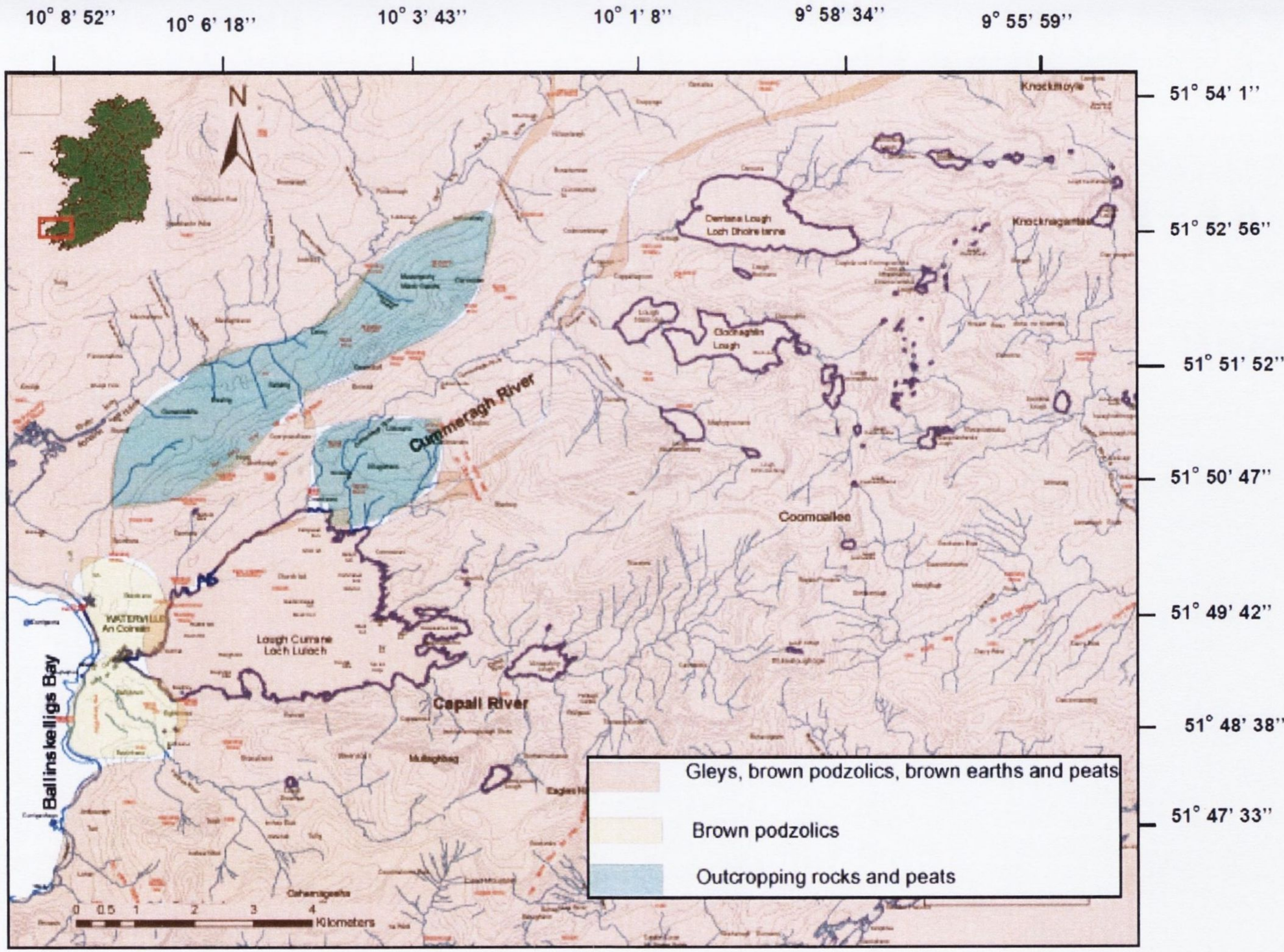


Figure 3.4: The soils of the Lough Currane catchment obtained from Kerry County Committee on Agriculture (1972).

Year	Alkalinity $CaCO_3$ mg l^{-1}	Ammonium NH_4 mg l^{-1}	Chlorphyll Mean µg l^{-1}	Conductivity @ 20 °C µS cm^{-1}	Dissolved Oxygen O_2 mg l^{-1}	pH pH units	Sechi Disk Depth m	Silica SiO_2 mg l^{-1}	TP µg l^{-1}	MRP µg l^{-1}	TON NO_3 mg l^{-1}
2001	5		5	75	10	7		1	13	10	0.16
2002	5		9	68	9	7	3	1	15	6	0.30
2003	6		10	69	10	7	3	1	24	9	0.52
2004	5	< 0.02	10	66	10	7	2	1	16	8	0.21
2005	7	< 0.02	8	68	10	7	3	1	63	27	0.80
2006	6	< 0.02	8	62	10	7	4	1	22	13	0.64
2007	6	< 0.02	8	74	11	7	4	1	13	10	0.62
2008	5	< 0.02	6	78	11	7	4	1	22		0.61
2009	5	<0.02	10	63	11	7	4	1	14		0.39

Table 3.2: Physiochemical parameters measured at Lough Currane for the years 2001 to 2009. The above parameters were measured by the water services division at Kerry County Council.

a. Trophic Status Lough Currane

Trophic Status	Year	TP (μgl^{-1}) Mean	Chlorophyll (ugl^{-1}) Mean	Chlorophyll (ugl^{-1}) Max
Mesotrophic	2001	13	5	9
Mesotrophic	2002	15	9	15
Mesotrophic	2003	24	10	25
Mesotrophic	2004	16	10	22
Eutrophic	2005	63	8	20
Mesotrophic	2006	22	8	16
Mesotrophic	2007	13	8	14
Mesotrophic	2008	22	6	22
Eutrophic	2009	14	10	44

b. Trophic Status Classification OECD (1982) and Toner et al (2005)

Trophic Status	TP (μgl^{-1}) Mean	Chlorophyll (ugl^{-1}) Mean	Chlorophyll (ugl^{-1}) Max
Oligotrophic	<10	<2.5	<8
Mesotrophic	10 – 35	2.5 - 8	8 - 25
Eutrophic	35 - 100	25 – 75	26 - 35

Table 3.3: a. Trophic status of Lough Currane and b. the trophic classification scheme outlined by the OECD. The modified chlorophyll values for the Irish version of the trophic classification are also included. The trophic status for Lough Currane was based on calculations from the data collected between 2001 and 2009 from the lake stations as part of the monitoring of the lake

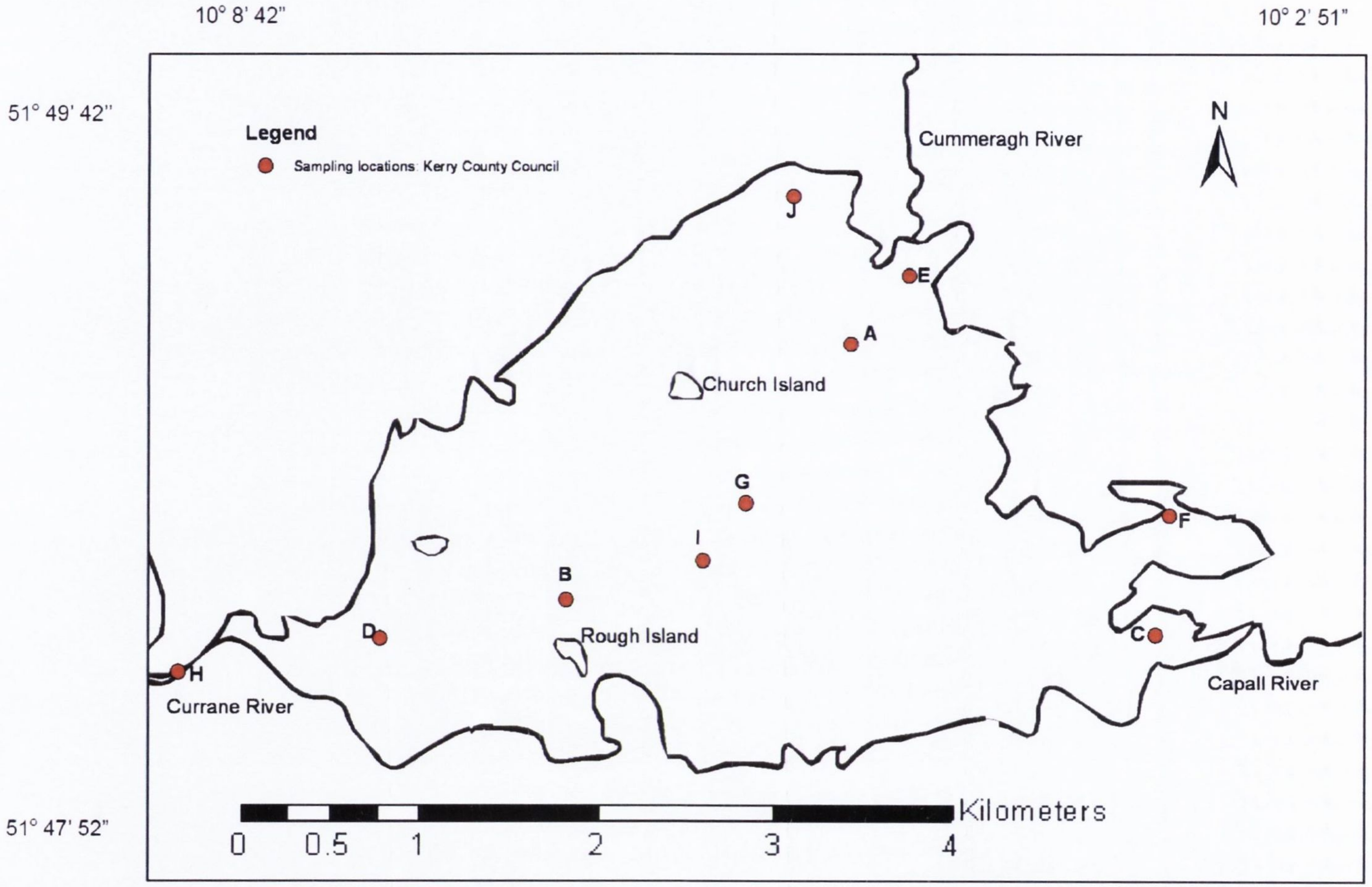


Figure 3.5: Sampling locations chosen by Kerry County Council for monitoring Lough Currane from 2001 to 2009.

a. TP

Map Reference	A	B	C	D	E	F	G	H	I	J	
Year	**1km NE of Church Island**	**100 m NE of Rough Island**	**Mouth Of Capall river**	**Currane River**	**Mouth Of Cumeragh**	**Reennaskinna Bay**	**Mid Lake**	**Outlet At Bridge**	**One km South of Church Island**	**Sandy Shore West Of Mink Farm**	**Annual Mean**
2001	17						13	10			**13**
2002	15	16	14	16					13		**15**
2003	28	18	30	25						17	**24**
2004	14	17	19	14							**16**
2005	45	32	64	104	69						**63**
2006	17	20	23	30	19						**22**
2007	12	14	13	13	13	10					**13**
2008	20	23	21	19	24	23					**22**
2009	13	12	11	18	18	13					**14**
Mean 2001 - 2009	**20**	**19**	**24**	**30**	**29**	**15**	**13**	**10**	**13**	**17**	

b. Chlorophyll

Map Reference	A	B	C	D	E	F	G	H	I	J	
Year	**1km NE of Church Island**	**100 m NE of Rough Island**	**Mouth Of Capall river**	**Currane River**	**Mouth Of Cumeragh**	**Reennaskinna Bay**	**Mid Lake**	**Outlet At Bridge**	**One km South of Church Island**	**Sandy Shore West Of Mink Farm**	**Annual Mean**
2001	9						4	3			**5**
2002	9	9	8	12							**9**
2003	10	11	7	12							**10**
2004	10	11	8	10							**10**
2005	9	10	8	10	6						**8**
2006	8	8	7	9	6						**8**
2007	7	8	6	9	5	12					**8**
2008	7	7	7	7	4	7					**6**
2009	11	12	7	12	7	12					**10**
Mean 2001 - 2009	**9**	**9**	**7**	**10**	**6**	**10**	**4**	**3**			

Table 3.4: Mean TP and chlorophyll values from each lake site (shown in Figure 3.5) sampled by Kerry County Council between 2001 and 2009.

Urban	Forestry	Pasture	Other Agriculture	Peat	Other
0	4	12	15	64	5

Table 3.5: The CORINE land cover data for Lough Currane, obtained from (Free et al., 2006). Data are expressed as a % of the catchment area.

3.2.3 Potential anthropogenic nutrient sources in the study catchment

The CORINE land cover data for the catchment of Lough Currane is shown in Table 3.5. According to this classification the catchment is composed primarily of peatlands (Free et al., 2006). The potential nutrient sources in the catchment of Lough Currane consist of housing, livestock farms, a mink fur farm and forestry plantations. In order to understand the contribution of all of these sources to the nutrient enrichment of Lough Currane, modern as well as historical documentary records have been utilised. The locations of the potential anthropogenic sources of nutrients to Lough Currane are shown in Figure 3.6.

3.2.3.1 Intermediate sources

- **Intensive Agricultural Production**

A mink farm, located close to the inlet from the Cummeragh River (51°50'47" north, 10°6'47" west), acts as an intermediate source of nutrients to Lough Currane as it displays characteristics of both point (via direct nutrient input from farmyard waste and slurry) and diffuse (via the spreading of manure on local land) sources of nutrients. Planning permission applications regarding the mink farm were obtained from Kerry County Council's planning department and from the Kerry County Council website (www.kerrycoco.ie). A FOI request was sent to the Department of Agriculture in order to determine any changes in the number of mink housed at the farm from its establishment to present. Details of planning applications and permissions associated with the mink farm at Dromkeare, Waterville are listed in Table 3.6. The first planning application with regard to the building of the mink farm was granted in 1966. There have been a number of extensions to the farm since this date namely, in 1981, 1987 and 1988. In a letter of objection to a planning application placed in 2006 there was a suggestion that there are 50,000 mink housed in the farm.

The FOI request was part-granted for files relating to mink licenses and inspector's reports for the mink farm from 1998 to present. Information on the name of the inspector of the mink farm, manager of the mink farm and number of breeding animals on the farm was not granted on the grounds of privacy issues (see Appendix A). However, the information granted through the FOI request showed that although the farm was extended a number of times since its establishment, this was to allow for improvements in cage size, with the total numbers of mink remaining the same. The information also stated that in 2006 the annual quantity of droppings from the mink was 250 tonnes, which was "*disposed per Nutrient Management Plan on local farm spreadlands in agreement with Kerry County Council*" (See Appendix A).

- **Housing and population**

Records on population and housing were obtained by plotting the locations of houses in the catchment (see Figure 3.6) and from census records acquired from the CSO for the period 1841 to 2006

Plotting locations of current houses in the catchment

The current locations of both houses and farms were plotted in order to visualise the most densely populated areas of the catchment and to locate farms in relation to the inflowing rivers and the shorelines of the lake. Mapping was carried out in March 2008 by visiting the catchment and recording the location (degrees longitude and latitude) of all houses and farms using a handheld Garmin etrex GPS. The locations of other potential nutrient sources were also recorded. On return to Dublin the locations recorded using the GPS were entered into a Microsoft Excel spreadsheet and were converted to the Irish National Grid using the transverse mercator calculator on www.dmap.co.uk (Dmap, 2008). The locations of houses and farms were then mapped using Arc G.I.S version 9 software.

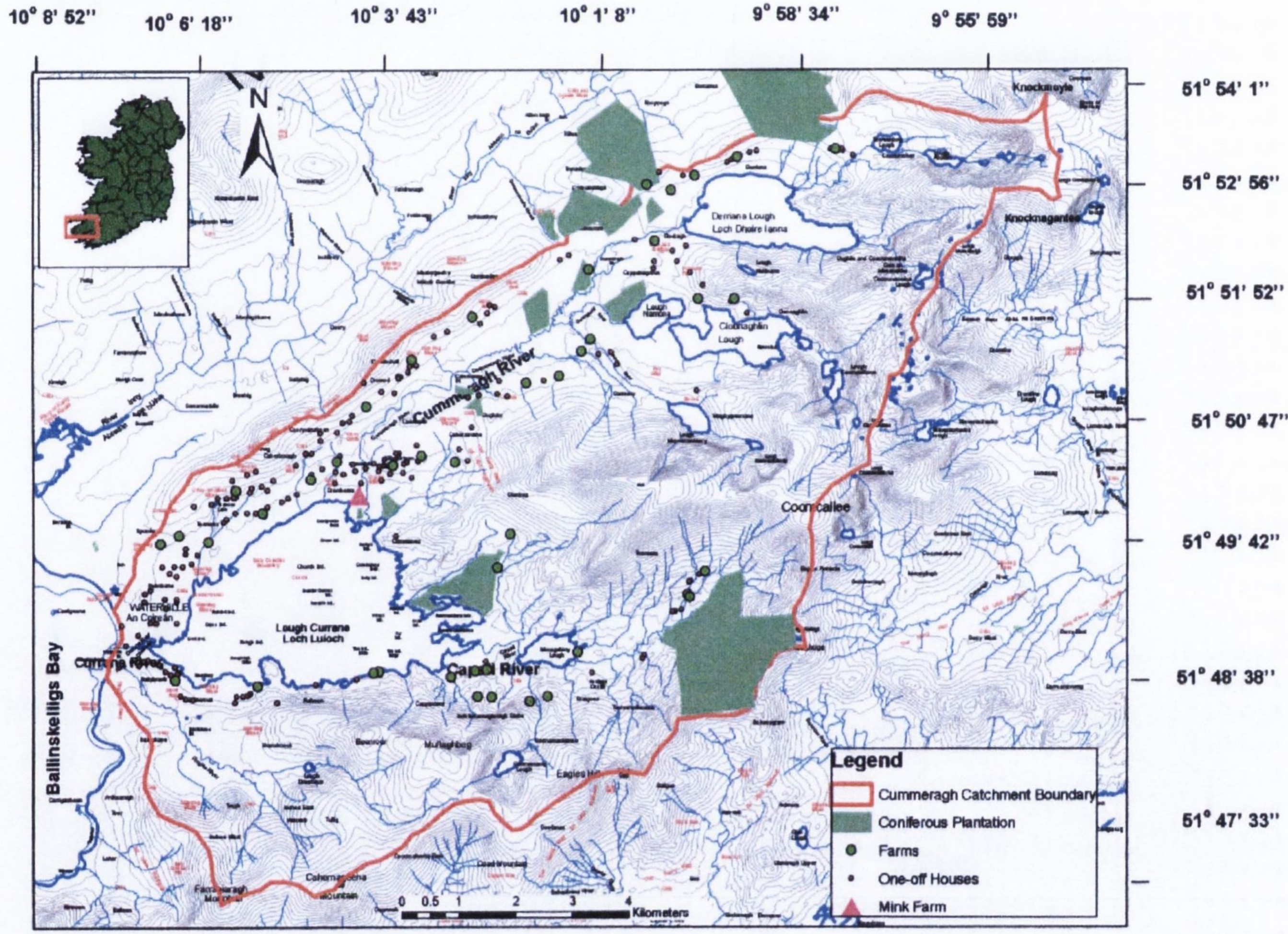


Figure 3.6: The potential anthropogenic nutrient sources in the catchment of Lough Currane

File No.	Date	Application details	Granted/Denied	Appeals
2477	19th September 1966	Constrcution of a Water Filter	Granted	
2770	28th November 1966	Construction of a split level flat roofed dwelling - Ardrow inch	Granted	
2388/80	12th January 1981	Erection of extension to mink farm bungalow - Dromkeare Waterville	Granted	
1339/86	2nd January 1987	Erection of 2 mink sheds	Granted	Appealed to an Bord Pleanala - granted 29th April 1987
653/88	30th August 1988	Extension to dwelling house car ports	Granted	
06/4304	15th November 2006	Construction of a slurry tower to disassemble and reconstruct one by one all animal housing and associated ancillaries and all site works		Objections: **Patricia O'Connor**. Senior Environmental Officer, Regional Fisheries Board. **John Murphy**. Manager Waterville Fisheries Development Group. There was a suggestion in his letter of objection that there were 50 thousand mink associated with the farm. **Catherine McMullan**. AnTaisce

Table 3.6: All planning applications by and permissions granted to Willow Herb Mink Farm, Dromkeare Waterville 1966 to 2006. Data were compiled from planning files held by Kerry County Council Planning Department.

The majority of houses and farms within the study catchment are situated to the north of the lake and in particular, close to the Cummeragh River. Although potential nutrient sources to the lake originating from the Capall River are apparent, there are fewer houses and farms compared to those bordering the Cummeragh River.

Census Records

In order to be able to access the correct census information for Lough Currane, the boundaries for the catchment had first to be determined. Catchment boundaries were determined from Ordnance Survey Ireland's Discovery Series 1:50,000 map number 83 of Kerry. The catchment boundaries were traced onto the map and the grid co-ordinates of the borders of the catchment were subsequently mapped using Arc G.I.S. version 9 software (Figure 3.6). Census records are recorded on the basis of DEDs or 'Electoral Divisions within Registrars' Districts' for the censuses from 1841 to 1911. Arc G.I.S DED shapefiles, obtained from Claire Downes (TCD) were overlain on the Lough Currane catchment map (Figure 3.7). This was done in order to identify the DEDs that comprise the Lough Currane catchment. Once the DEDs within the Lough Currane catchment were identified, census records of population and numbers of houses/households were obtained from the library at the CSO, Skehard Road, Cork.

The catchment of Lough Currane comprises 4 DEDs: Ballybrack, Derriana, Lough Currane and Mastergeehy (Figure 3.7). Information relating to the number of households by type of sewerage facility for each DED in the Lough Currane catchment was obtained for the censuses of 2002 and 2006 from the SAPS section of the CSO website (Central Statistics Office, 2009). No published records exist for type of sewerage facility for censuses pre-2002.

As displayed in Table 3.7., between 12% and 17% of houses, as well as the hotels, in the catchment are connected to a public sewerage scheme. Domestic sewage is treated and discharged to the sea (Smith et al., 2007). The majority of houses in the catchment, between 80% and 82%, are serviced by an individual septic tank.

The census of Ireland was undertaken every ten years from 1841 to 1911. Following the formation of the Irish state, the first census was undertaken in 1926 and was subsequently undertaken in 1936 and 1946. From 1951 the census was undertaken at 5 year intervals with the exception of 1976 when it was cancelled and postponed until 1979. From 1981 censuses continued to be undertaken at 5 year intervals. The last census was carried out in 2006 (Central Statistics Office, 2009). The format of the census has altered over time. Although data on population was always recorded in the same way, the recording of housing units and households has been inconsistent. From 1841 to1911 the number of houses (occupied, unoccupied and building) was recorded. From 1926 to 1979 no records of any type of housing unit or households were found in the census records after extensive searches by the author. From 1981 to 2006 occupied houses/households were enumerated (see definitions on Figure 3.9). For the purposes of this research only occupied houses/households were studied.

Variations in population from 1841 to 2006 in the catchment of Lough Currane (DEDs: Ballybrack, Derriana, Lough Currane and Mastergeehy) are shown in Figure 3.8. In 1841 the population of the catchment was 3361. Population levels declined thereafter, with 731 people recorded in 2006. Slight deviations from a trend of declining numbers are evident in 1881 (2852 people) and in 1946 (1607 people).

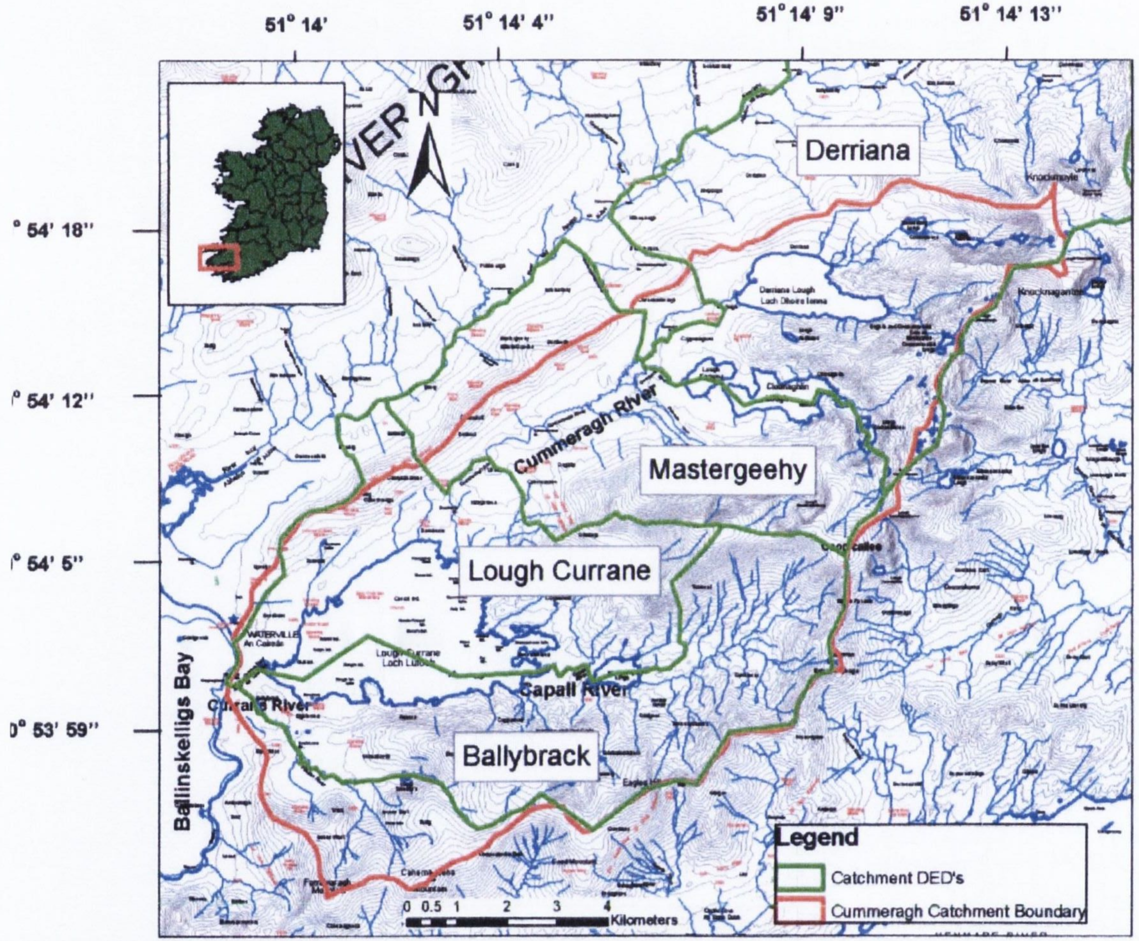


Figure 3.7: The DEDs of that comprise the catchment of Lough Currane. The contour intervals are shown at 25m intervals

a. 2002

Sewerage Facility	Ballybrack	Derriana	Lough Currane	Mastergeehy	Total	% Total
Public Scheme	1	0	41	0	**42**	**16.73**
Individual Septic Tank	37	69	62	32	**200**	**79.68**
Other Individual treatment	0	0	1	0	**1**	**0.40**
Other	0	2	3	0	**5**	**1.99**
No sewerage					**0**	**0.00**
Not stated	0	1	2	0	**3**	**1.20**
				Total Houses	251	

b. 2006

Sewerage Facility	Ballybrack	Derriana	Lough Currane	Mastergeehy	Total	% Total
Public Scheme	0	1	36	1	**38**	**11.62**
Individual Septic Tank	39	81	70	77	**267**	**81.65**
Other Individual treatment	1	8	4	5	**18**	**5.50**
Other	0	1	0	1	**2**	**0.61**
No sewerage	0	1	0	1	**2**	**0.61**
Not stated	1	2	3	1	**7**	**2.14**
				Total Houses	327	

Table 3.7: Number of houses by type of sewerage facility in the catchment of Lough Currane from the censuses of a. 2002 and b. 2006. The catchment is comprised of 4 DEDs: Ballybrack, Derriana, Lough Currane and Mastergeehy.

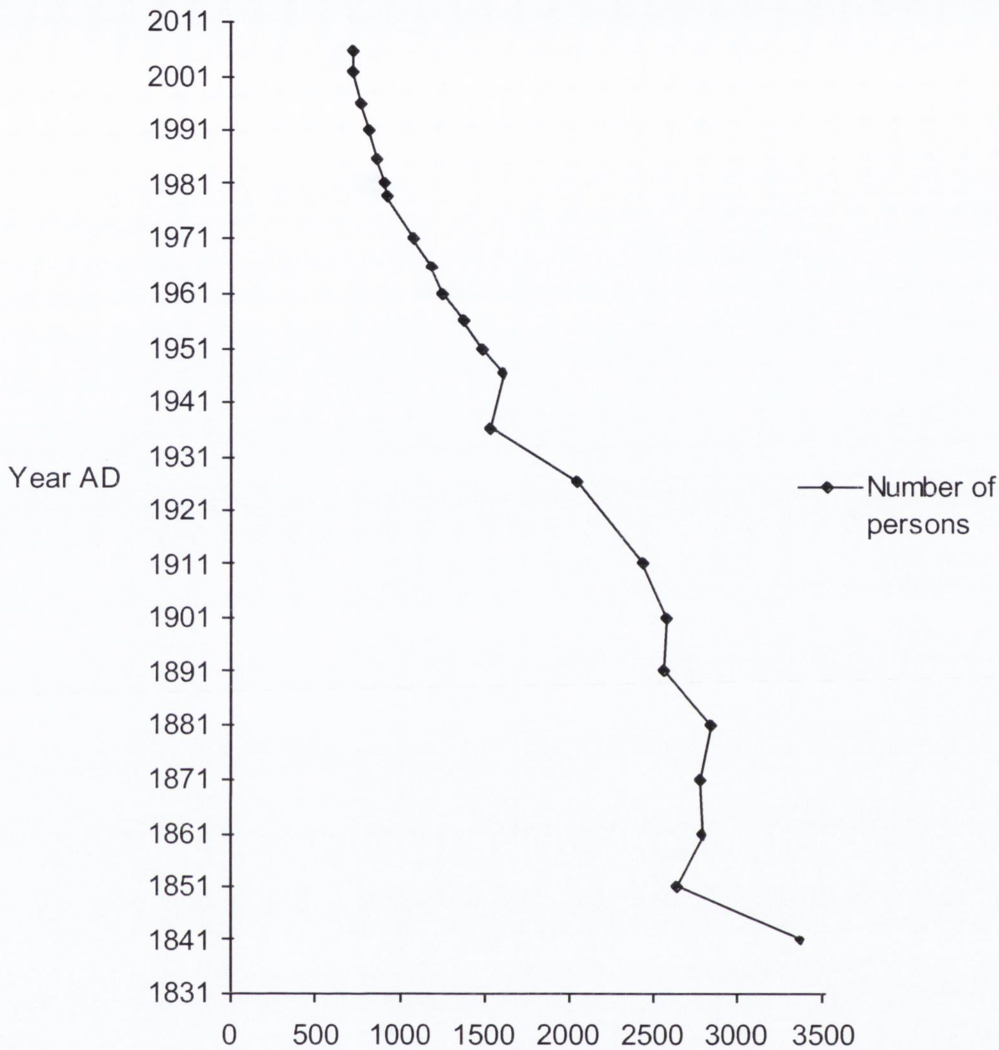
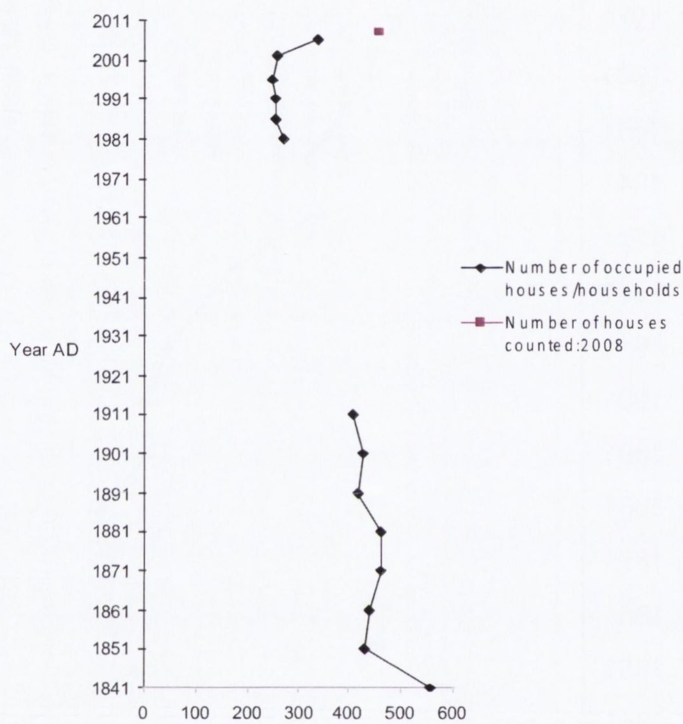


Figure 3.8: Lough Currane catchment population 1841-2006. The catchment is comprised of 4 DEDs: Ballybrack, Derriana, Lough Currane and Mastergeehy.

Figure 3.9 illustrates variations in the number of houses and households in the catchment of Lough Currane. In 1841 a total of 557 occupied houses were listed. This number had declined to 431 by 1851 and remained relatively constant until 1911. In 1980 the number of occupied houses (271) was substantially lower than the number of houses recorded in 1911. This is not unexpected given the decline in population. The number of occupied houses remained steady until 2006, when their number increased to 339. The number of houses recorded when mapping the catchment in 2008 was 458 and is close to the number of occupied houses recorded in the earlier censuses of 1841 to 1911. A relatively high proportion of holiday and seasonal houses (i.e. non-permanently occupied) best explains the large difference between the numbers of occupied houses recorded in the census of 2006 and the number of houses counted in 2008.



Censuses 1981 and 1986 - Permanent Household : Number of private households in permanent housing units (CSO 1981)

Censuses 1991 and 1996 - Permanent Private Household: A private household occupying a permanent dwelling such as a dwelling house, flat or bedsitter.(CSO, 2002)

Census 2002 and 2006 - Private Household: Comprises either one person living alone or a group of people (not necessarily related) living at the same address with common housekeeping arrangements - that is sharing at least one meal a day or sharing a living room

Figure 3.9: Lough Currane Catchment Houses/Households 1841 to 2006. Housing was recorded in different ways for the censuses of 1981 to 2006 so the definitions for the criteria used for the enumeration of houses are shown. No records of numbers or forms of housing were made in censuses from 1926 to 1979. The catchment is comprised of 4 DEDs: Ballybrack, Derriana, Lough Currane and Mastergeehy.

3.2.3.2 Diffuse Sources

- **Livestock grazing**

Records of animal numbers from 1881 to 2000 were obtained from the census of agriculture (1881 to 1911, 1991 and 2000) and from agricultural statistics published by the CSO (1926 to 1980). Both the census of agriculture and the agricultural statistics are recorded by rural district. The catchment of Lough Currane is in the Cahersiveen rural district. Records were obtained from the library at the CSO, Skehard Road, Cork with the assistance of Eileen Philpott (CSO). Total numbers of cattle and sheep were the only livestock variables used for the current research as they were the only two variables consistently recorded in every survey.

According to the census of agriculture for the year 2000, the area farmed in the Cahersiveen rural district is 34,130 ha. Variations in the numbers of cattle and sheep ha^{-1} in the Cahersiveen rural district from 1881 to 2000 are shown in Figure 3.10. Maximum and minimum densities of cattle in the district were respectively, 1.2 and 0.8 head ha^{-1}. The density of cattle increased steadily from 1881 reaching 1.2 head ha^{-1} by 1901. Cattle density subsequently declined reaching 1 head ha^{-1} by 1926. Cattle numbers then increased to 1.2 head ha^{-1} by 1933, and then declined to 1 head ha^{-1} by 2000.

Sheep are now farmed in much greater numbers than cattle in the Cahersiveen rural district. Moreover, stocking densities of sheep have varied markedly during the period for which data are available, from a minimum of 0.5 head ha^{-1} to a maximum of 3.9 head ha^{-1}. Densities of sheep increased steadily between 1881 and 1981, after which date there was a rapid increase, with densities peaking in 1991 probably as a result of financial incentives provided to farmers under the CAP. Numbers of farm animals recorded in the 2000 census of agriculture were published by DED. There are 22 DEDs in the Cahersiveen rural district. Highest sheep numbers for the year 2000 were found in Derriana, one of the constituent DEDs of the catchment of Lough Currane. In Derriana the number of sheep accounted for 13% of the total sheep farmed in the Cahersiveen rural district.

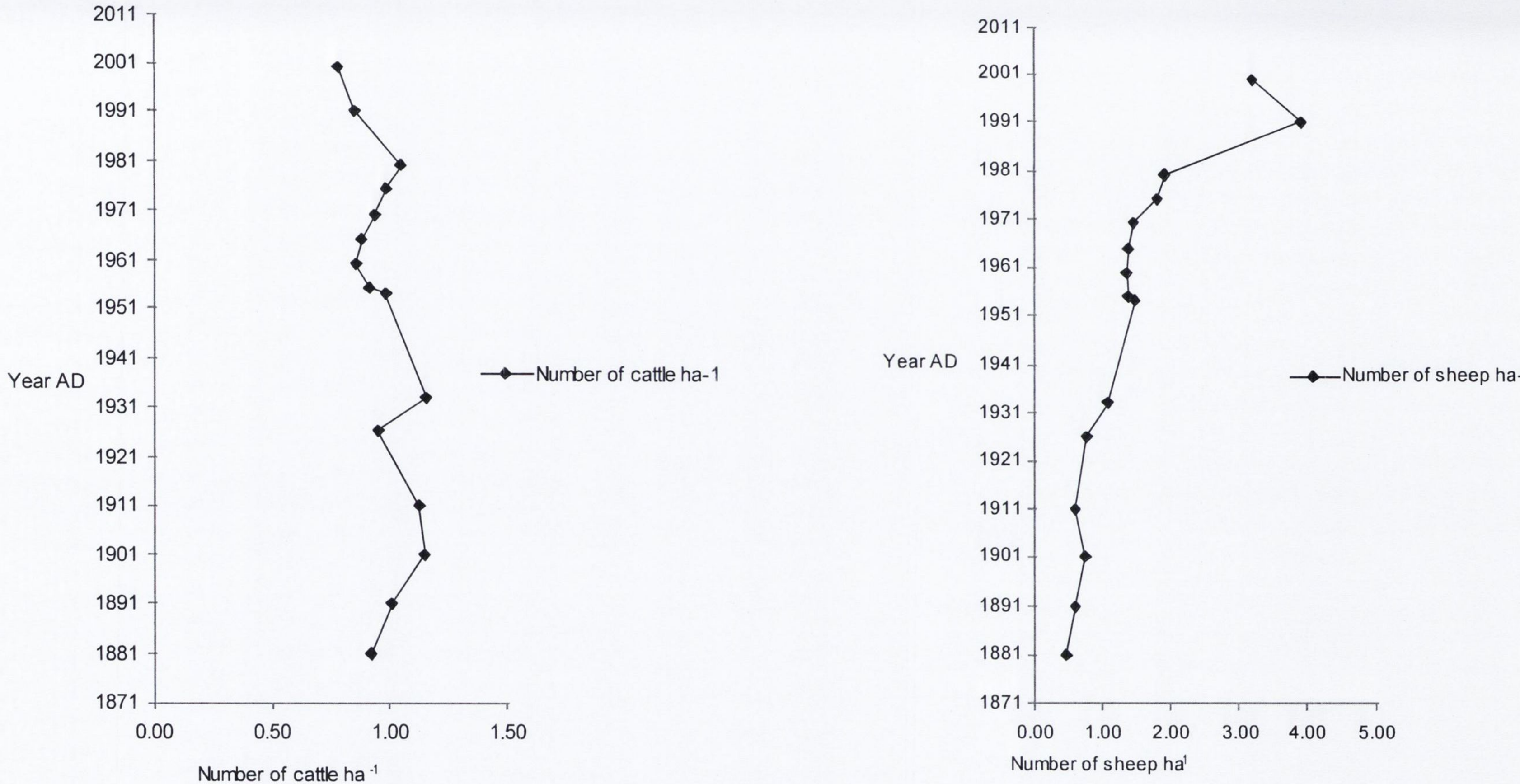


Figure 3.10: Density of cattle and sheep in the Cahersiveen rural district from 1881 to 2000

The livestock carrying capacity of the soils in the catchment of Lough Currane is shown in Figure 3.11. Most of the soils in the catchment have a carrying capacity of 0.2 to 0.6 LU ha^{-1}, while the areas to the north-west and south-west of the lake have a livestock carrying capacity of 1.7 to 2.2 LU ha^{-1}. The area to the north of the lake, around the outlet from the Cummeragh River has a livestock carrying capacity of 1.2 to 1.7 LU ha^{-1}.

Forestry

The five coniferous forestry plantations located in the catchment of Lough Currane are shown in Figure 3.6. These are Cappanagroun, Caunteens, Cloghvoola, Coshcummeragh and Derrinaden. Data on stems planted and on the establishment of the plantations and subsequent thinning and clearfelling were obtained from Denis O'Sullivan and Larry Kelly (forester) in Coillte Teoranta, the Irish forestry company. The data was presented as number of stems planted and thinning/clearfelling years at each of the plantations. Details on fertiliser application to the plantations were not available for the plantations in the study catchment; however Coilte Toeranta follows a policy of minimum fertiliser application. Application of fertilisers at planting time is dependent on site fertility. If necessary, the normal fertiliser application at the time of planting is 0.4 tonnes granulated rock PO_4^{3-} ha^{-1}. All initial fertilising is carried out manually (Coillte, 2006).

Details on the planting, thinning and clearfelling of the five coniferous forestry plantations in the catchment are listed in Table 3.8. Establishment of the plantations occurred between 1969 and 1987 and thinning/clearfelling took place between 1984 and 2004. The largest plantations, Cloghvoola and Caunteens are situated close to the shores of the lake and the Capall River. Planting in Cloghvoola and Caunteens occurred between 1969 and 1972 while thinning/clearfelling commenced in 1984 and ended in 2004.

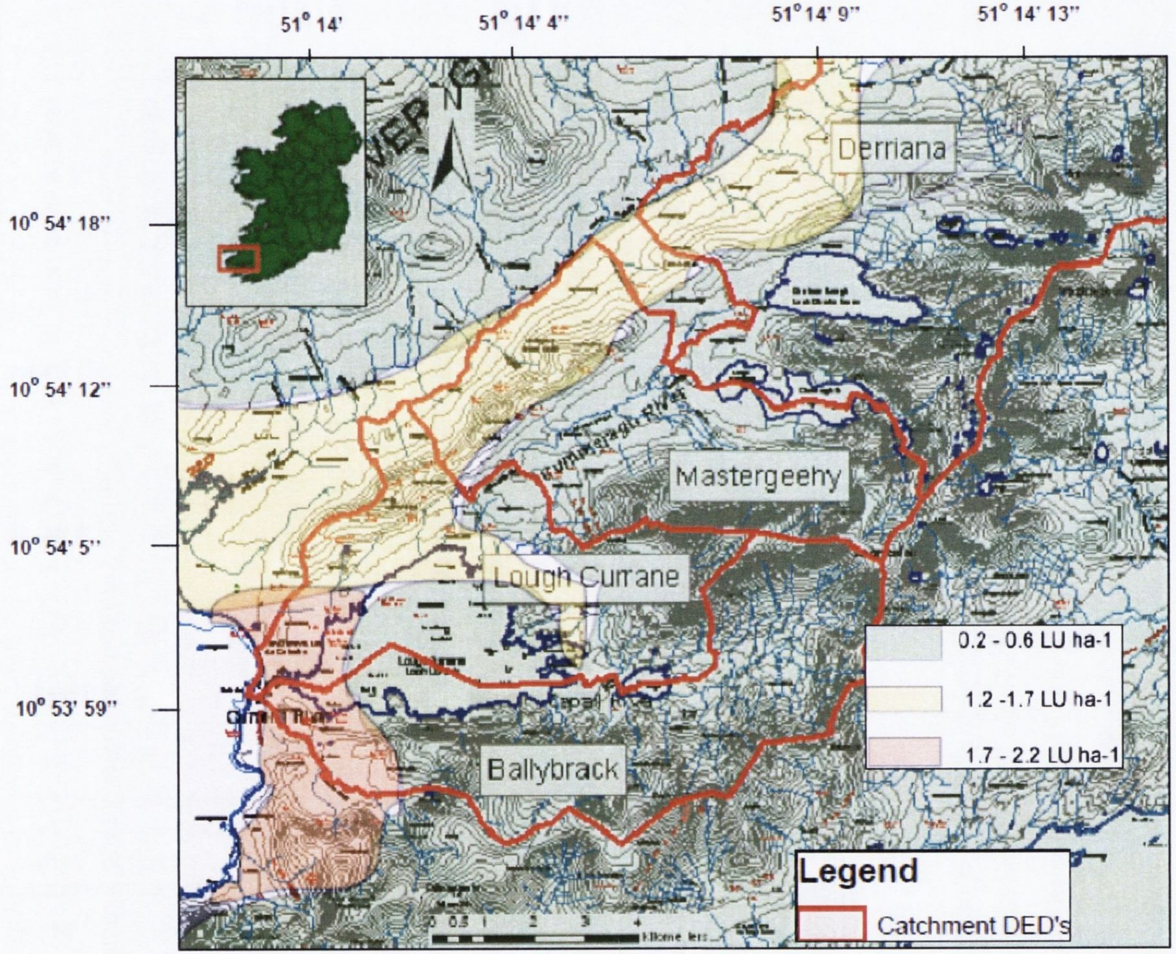


Figure 3.11: The livestock carrying capacity of the soils in the catchment of Lough Currane, obtained from Kerry County Committe on Agriculture (1972).

Plantation	Trees Planted (years)	Stems planted	Thinning/Clearfelling (years)
Caunteens	1969, 1970	54503	1984, 1987, 1990, 1991, 1992, 1994, 1995, 1997, 1998, 1999, 2000, 2004
Cloghvoola	1971, 1972	77183	1992, 1993, 1994, 1995, 1996, 1997, 1998
Coshcummeragh	1974, 1977, 1978	10513	1999, 2000
Derrineden	1980	4248	
Cappanagroun	1981	2050	
Derreen/Dromakilty/Gortlea	1987	2100	

Table 3.8: Records of planting, thinning and clearfelling of all the coniferous forestry plantations located in the Lough Currane catchment.

3.2.4 Climate records for the area

Lough Currane is located c.16 km from the Valentia Observatory, Ireland's oldest weather reporting station. The observatory has been in operation since 1868. Dr. Eleanor Jennings (DKIT) and Liz Moran (Met Eireann) obtained monthly mean data on precipitation and temperature, at the Valentia Observatory, for the period between April 1892 (January 1893 for precipitation) and December 2001.

The monthly reports from the weather observing station of Valentia were acquired from the library in Met Eireann Headquarters and daily data on precipitation and temperature from July 1873 (August 1873 for precipitation) to December 1892 were transcribed by the author. Once transcribing was completed, data recorded in imperial measurements (°F and inches) were converted to metric measurements (°C and mms). Annual totals, annual means and monthly means were calculated from the daily data on temperature and precipitation and were subsequently graphed using Microsoft Excel. Data on precipitation and temperature at Valentia from 2002 to 2009 were obtained from the European climate assessment and dataset website (http://eca.knmi.nl/). The frequency of storms between 1873 and 2009 was also calculated from the daily data for Valentia obtained from Eleanor Jennings (DKIT) (1873 to 1940) and the European climate assessment and dataset website (http://eca.knmi.nl/) (1941 to 2009). Storm conditions were defined following Heathwaite and Dils (2000) as greater than 10 mm of rain in a 24 hour period.

3.2.4.1 Temperature

Variations in annual mean temperature (°C) from 1873 to 2009 are shown in Figure 3.12. Maximum and minimum annual mean temperatures were 11.6°C (1949) and 9.5 °C (1879) respectively. The years 1945 (11.6 °C), 1921 (11.5 °C) and 1873 (11.5 °C) had relatively high annual mean temperatures and the years 1985 (9.7 °C), 1979 (9.8 °C), 1963 (9.8 °C), 1917 (9.7 °C) and 1874 (9.6 °C) had relatively low annual mean temperatures. Generally, temperature increased between 1923 and 1960 and between 1963 and 2009.

3.2.4.2 Precipitation and storm frequency

Variations in annual total precipitation (mm) from 1873 to 2009 are shown in Figure 3.13, while variations in the frequency of storms are shown in Figure 3.14. Maximum and minimum values for total annual precipitation were 1804mm (1994) and 990mm (1971), respectively. Total annual precipitation fluctuated frequently between 1874 and 2001. The years 1998 to 2000 (1775 to 1785mm), 1982 (1785mm), 1980 (1775mm), 1928 (1781mm), 1914 (1755mm) and 1903 (1713mm) had relatively high annual total precipitation while the years 1952 (1064mm), 1893 (1101mm) and 1887 (1091mm) had relatively low annual total precipitation. In general, Figure 3.13 shows an increasing trend in total annual precipitation between 1970 and 2009. Maximum and minimum numbers of storms year^{-1} were 23 (1971) and 73 (2002) respectively. Figure 3.14 shows an increasing trend in the annual frequency of storms from 1930 to 1960 and from 1973 to 2009.

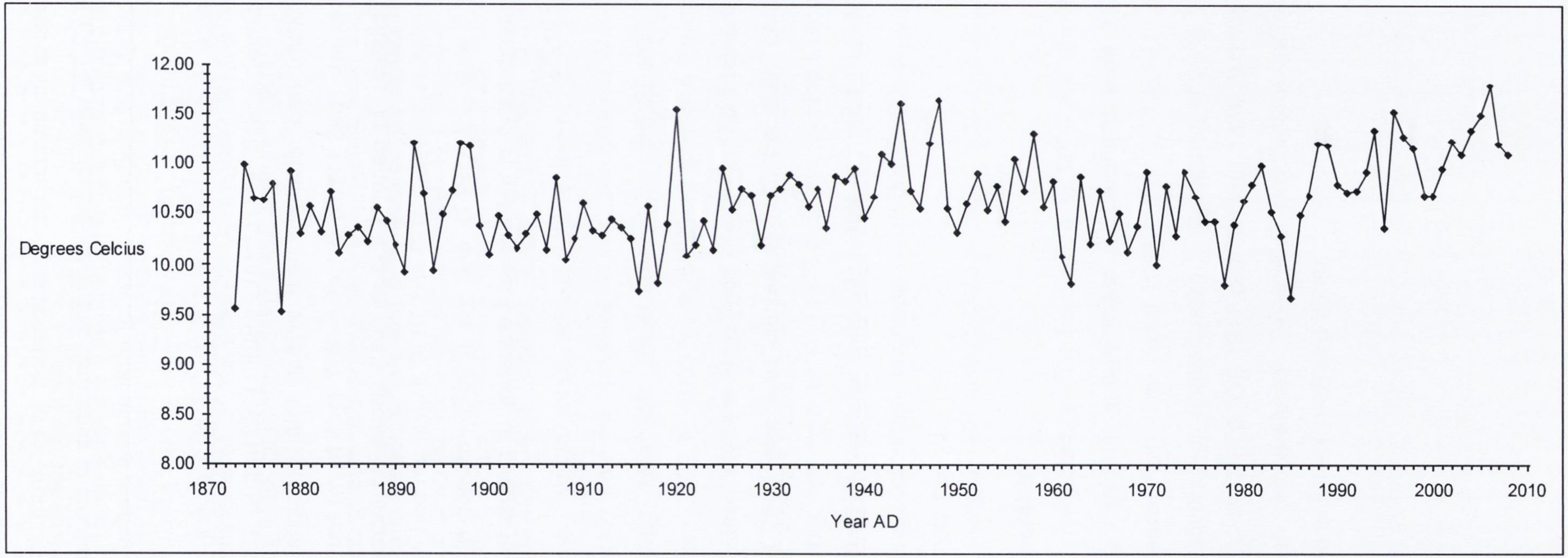


Figure 3.12: Annual mean temperature (°C) for the Valentia weather reporting station for the period 1873 to 2009

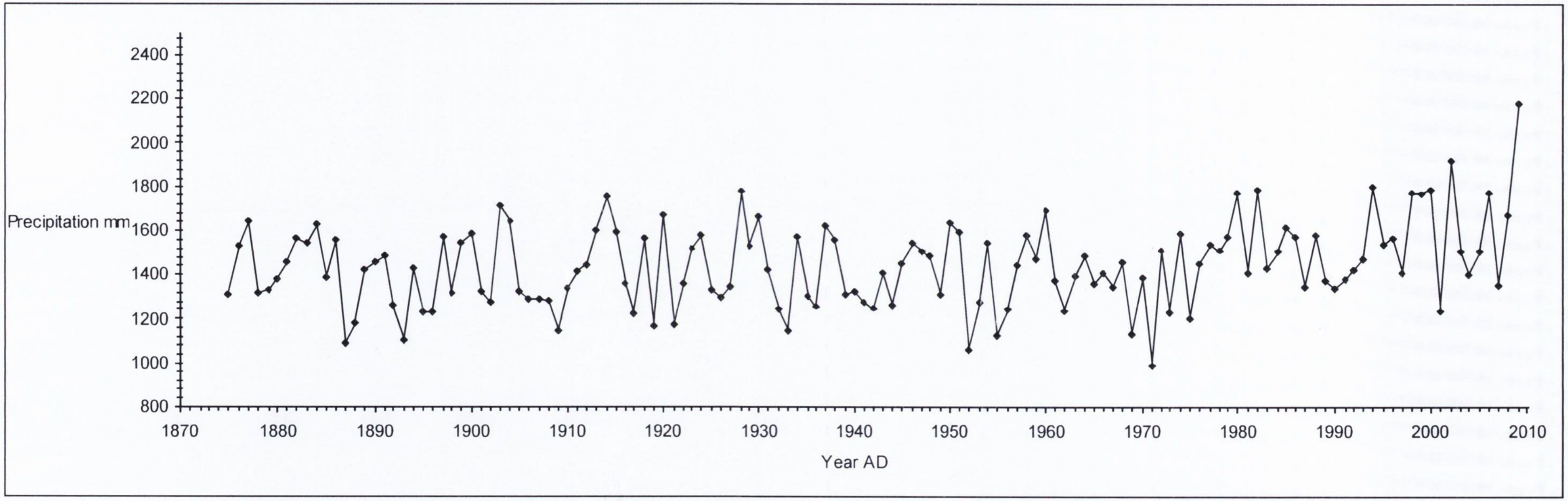


Figure 3.13: Annual total precipitation (mm) for the Valentia weather reporting station for the period 1873 to 2009

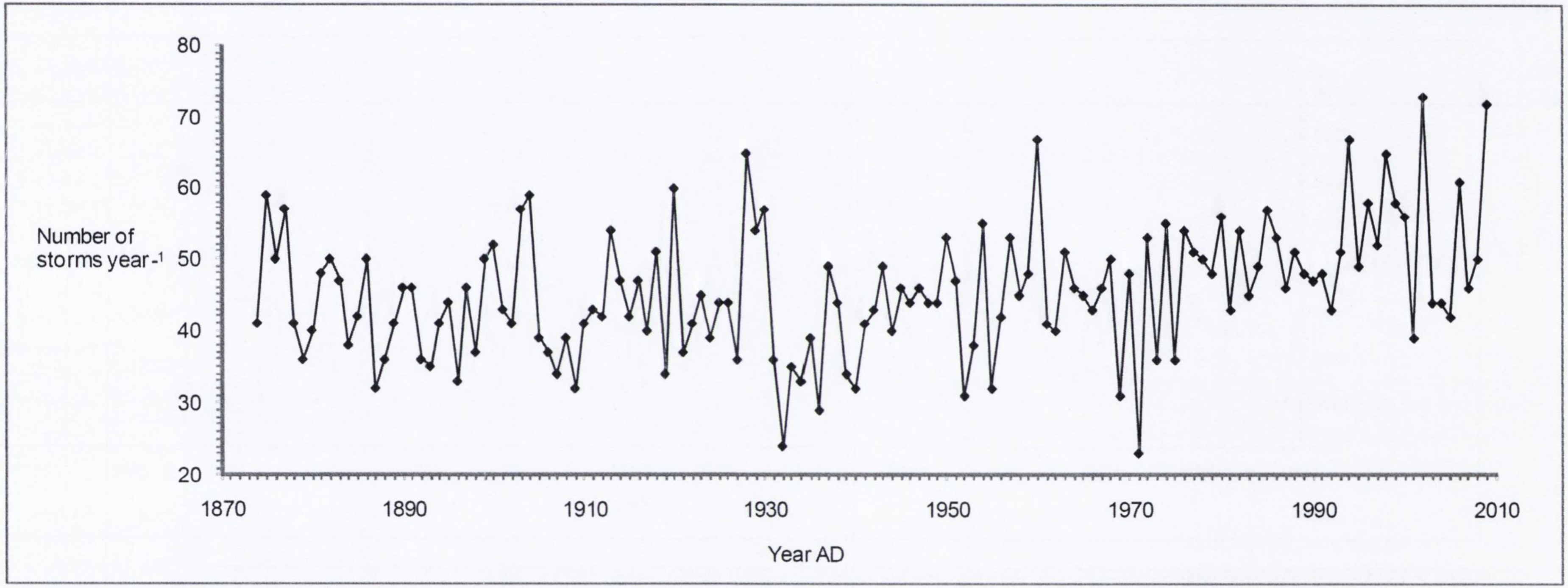


Figure 3.14: Number of storms year^{-1} at Valentia from 1873 to 2009. Data were obtained from the European climate assessment and dataset website (http://eca.knmi.nl/). Storm conditions were defined following Heathwaite and Dils' (2000) as greater than 10 mm of rain in a 24 hour period.

Chapter Four: Limnological and Palaeolimnological Methods & Techniques

This chapter outlines the methodological framework used in the current research. The field and laboratory techniques deployed range from initial selection of sites through to the analysis of primary and secondary data. A range of palaeolimnological methods were to address the first research question: "To what extent is recent eutrophication caused by anthropogenic factors?" These methods included the selection of coring sites and collection of sediment cores. Chronological control was provided by ^{210}Pb, ^{137}Cs, SCP and ^{14}C analyses while analyses of % organic content, grain size and pollen provided a record of land use change in the lake's catchment. Analysis of diatoms and reconstructions of DI-TP were used to assess temporal changes in water quality at each coring site. In order to assess the contribution of the potential drivers of ecological change at Lough Currane, outlined in chapter three, gradient analysis was used to assess the relationship between temporal variations in DI-TP and historical variations in population, housing, livestock density and climatic factors at all of the coring sites

Both limnological and palaeolimnological methods were used to address the second research question: "To what extent does the response to increased nutrient loads vary spatially within a lake basin?" Surface water and surface sediment samples were collected in order to assess spatial variability in TP, DI-TP and sedimentary components. This variability was assessed graphically using Arc G.I.S. Within-lake variability in the temporal changes in diatom assemblages was assessed for the three coring sites using gradient analysis. The organisation of limnological and palaeolimnological techniques used in the current research is shown in Figure 4.1. These techniques are described in full below. Field based techniques are outlined first, followed by the laboratory based techniques and the numerical methods used in this research.

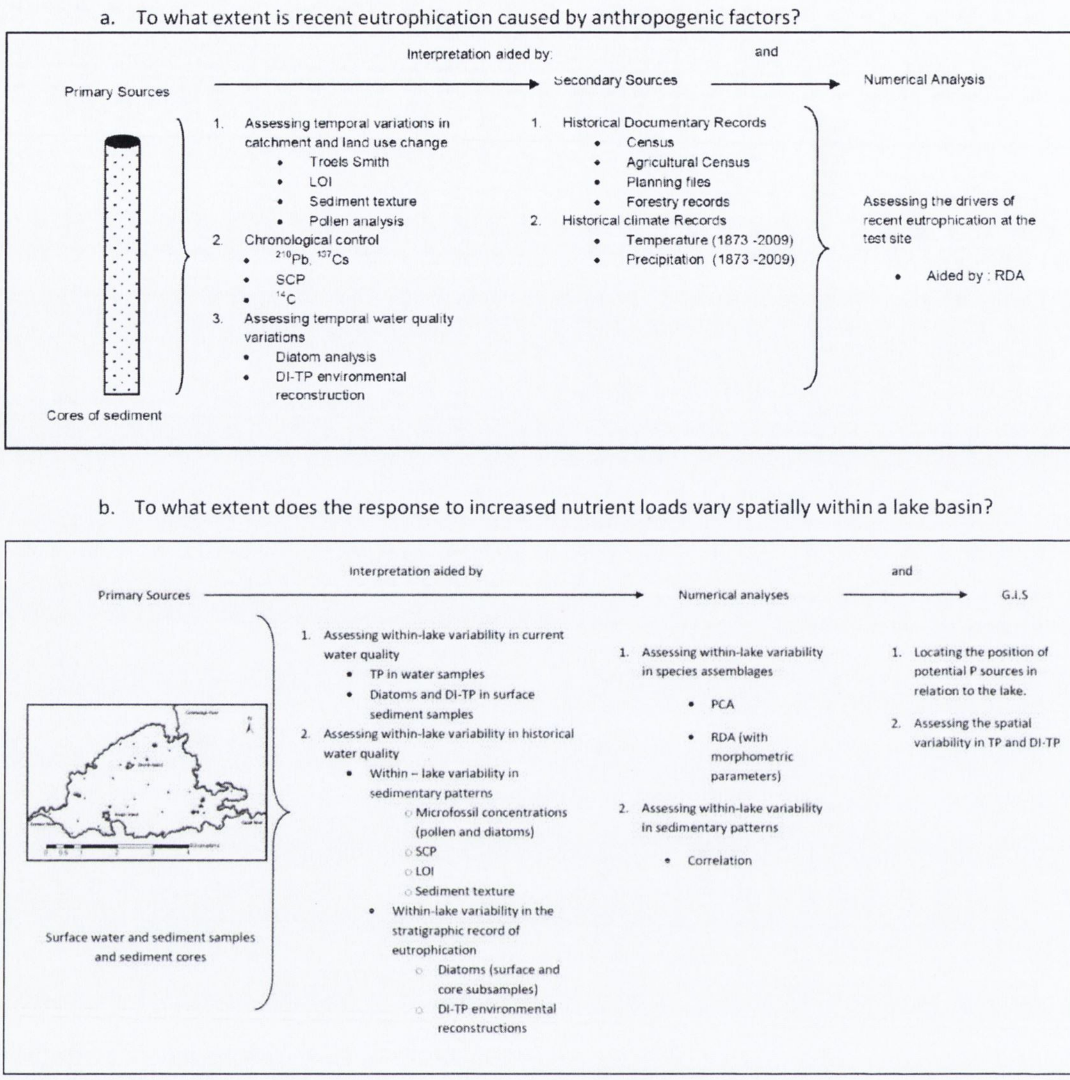


Figure 4.1: The methodological framework used in the current research to address: a. the first research question and b. the second research question

4.1 Field based techniques

4.1.1 Collection of limnological data

Water and surface sediment samples were collected from Lough Currane in order to study within-lake spatial variability in TP and sedimentary components.

4.1.1.1 Sampling strategy

Reliable sample collection is the first and most crucial step in a limnological investigation; an error encountered during sample collection can rarely be corrected by subsequent analyses (Glew et al., 2001). Several different sampling approaches can be used in the collection of environmental data. These approaches include non-statistical methods such as judgemental sampling where sampling locations are based on professional judgement; and probabilistic methods such as random sampling, stratified sampling and systematic sampling.

Random sampling involves the arbitrary selection of sampling points by a process that gives each sample unit in the population the same probability of being chosen (Zhang, 2007). However, a distribution of sampling points that is unrepresentative of the total, such as a concentration of sampling points in a particular area may result from random sampling (Townsend et al., 2008). Systematic and stratified random sampling can provide a solution to this problem and involve dividing a population into several strata and selecting points at random within each stratum. These strata could be defined, for example, according to substrate type or water depth. Systematic sampling involves selecting sampling points according to a specified pattern, such as along a line or according to a grid (Zhang, 2007). Transect sampling , a form of systematic sampling, has been used in the study of the spatial variability of phytoplankton populations in lakes (Moos et al., 2005; Adler and Hübener, 2007), and is suitable when there is a known or expected linear relationship between the variable that is being studied and the points along the transect. Systematic random sampling subdivides a study area into a grid and samples are randomly selected from within each grid cell. This approach provides a uniform distribution of sampling points over the study area and ensures that the entire sampling area is represented (Zhang, 2007).

Systematic random sampling was used in the current research, as an efficient means of ensuring the collection of a representative selection of surface water and surface sediment samples. The 1 km^2 grid on the OSI map number 83 of Kerry was used as the basis for the sampling grid. The squares that comprised Lough Currane were labelled A to T (Figure 4.2). Each 1 km^2 grid square was then divided into 25 numbered squares and two numbers were chosen from each 1 km^2 grid square using the random number generator on www.random.org. A total of 30 sampling sites were selected. The locations of the chosen sampling sites are shown in figures 4.2 and 4.3. The grid co-ordinates of the sampling sites were input into a Garmin etrex GPS so that they could be located in the field.

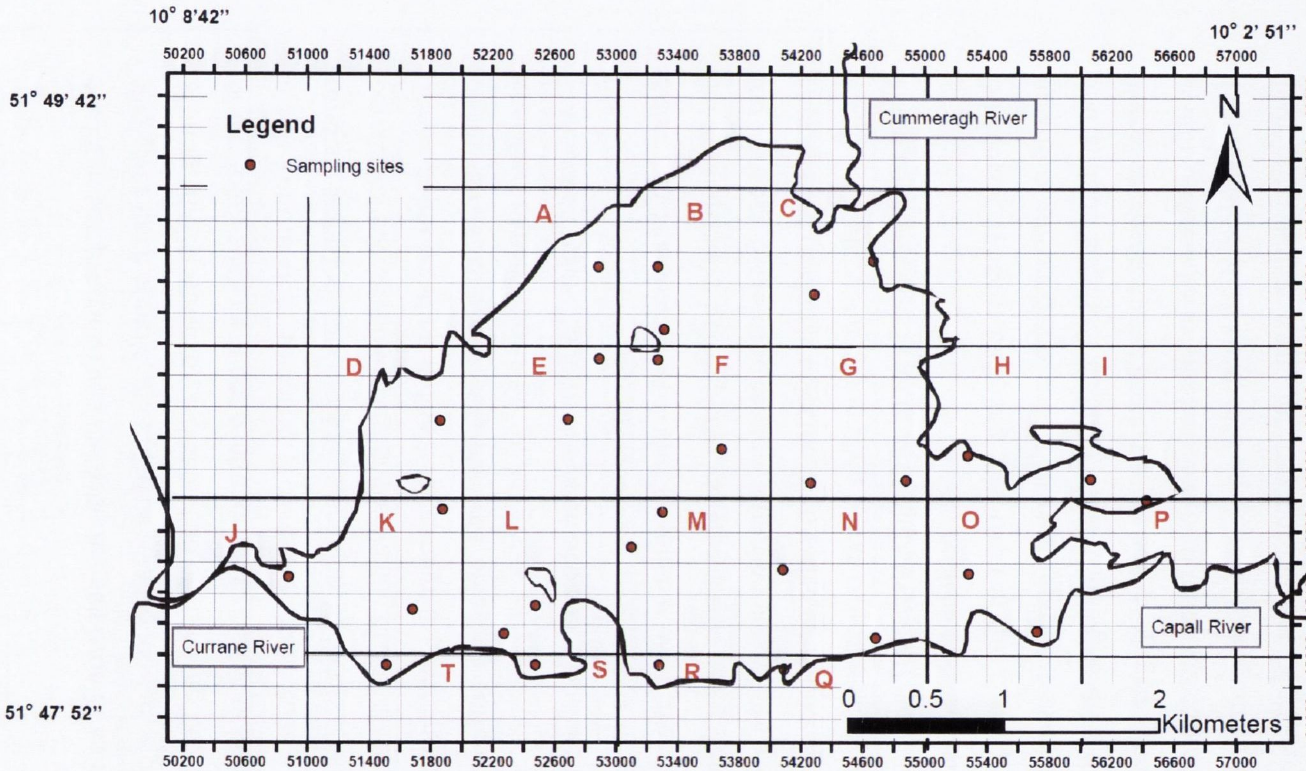


Figure 4.2: The sampling grid used for stratified random sampling in the current research and the chosen surface sampling sites at Lough Currane

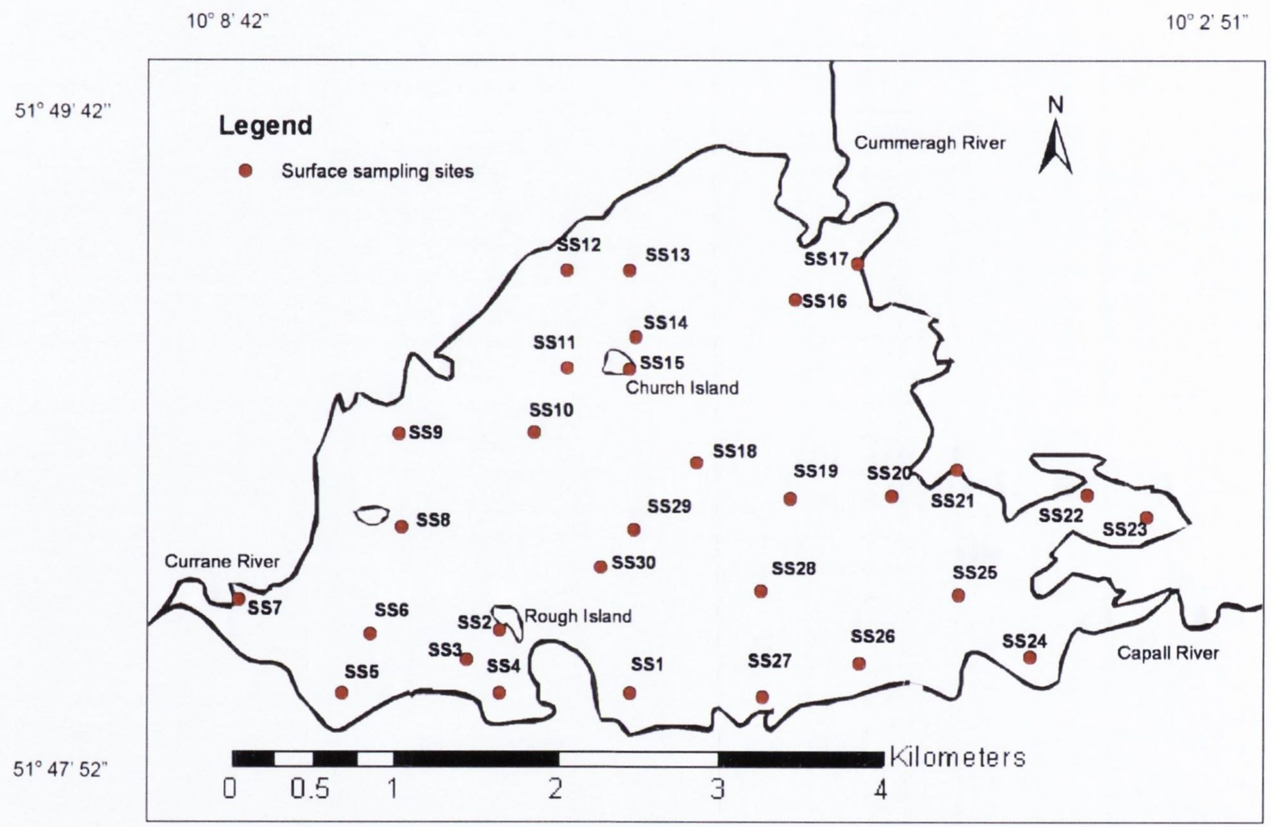


Figure 4.3: The chosen surface sampling sites at Lough Currane

4.1.1.2 Collection of water and surface sediment samples

Water and sediment samples were collected at Lough Currane of the 29th April 2010 in order to sample the spring overturn of P. Water depth was measured at each of the 30 pre-selected sampling sites using a handheld echo-sounder, the location of each site having first been verified using a Garmin etrex GPS. Water samples, for the determination of TP, were collected from c.50 cm below the water surface at each of the 30 sampling sites shown in Figure 4.3. Samples for the analysis of TP were measured in triplicate. For this reason, three samples were collected from each surface sampling site using 250 ml polyethylene bottles. As soon as possible after collection, 25 ml subsamples were taken from each bottle and were transferred to 50 ml glass bottles to prevent the degradation of TP. Sediment samples were collected from 16 of the 30 sampling sites using an Eckman grab sampler (Figure 4.4). The collection of sediment samples from 14 of the 30 sampling sites was not possible because of the presence of rocks on the lake bed. The entire grab sample obtained from each surface sediment sampling site was stored in a pre-labelled (name/number of sampling site) ziploc bag, which was placed in a cool box. Sediment samples were subsequently transported to TCD where they were stored at 2°C to 4°C until needed for further analysis.

4.1.2 Sediment coring

Sediment coring is the most common method of obtaining materials used in the study of lake histories (Cohen, 2003). The aim of sediment coring is to recover an undisturbed sample, usually including the sediment-water interface. There should be no disturbance in structure in the core, no change in water content and no change in constituent composition (Hvorslev, 1949; Glew et al., 2001). Sediments accumulating in the deepest point of a lake are often targeted for coring, owing to preferential deposition of microfossils (Davis et al., 1971) or sediment focussing (Davis and Ford, 1982).

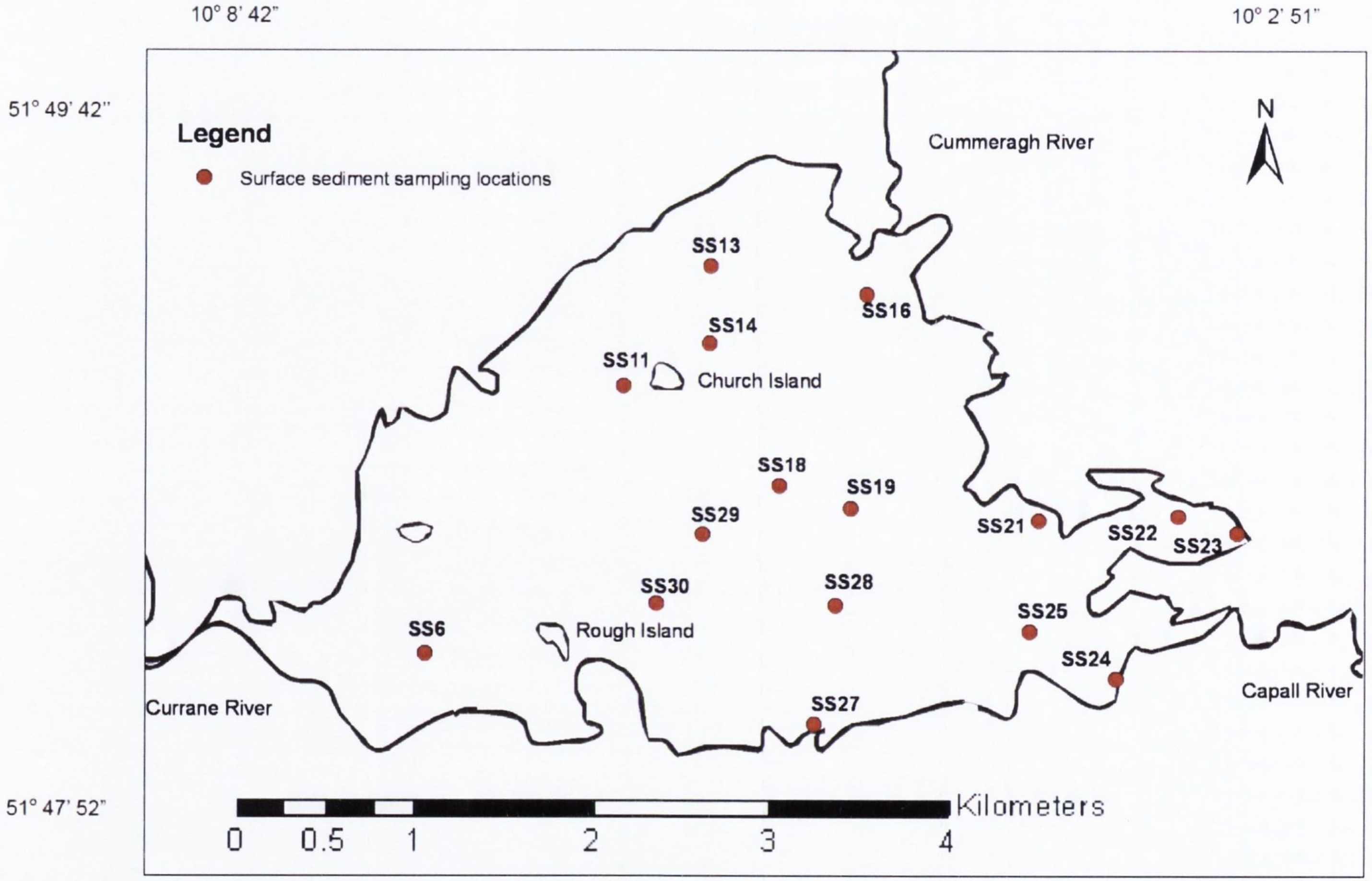


Figure 4.4: Locations of the 16 sampling sites at Lough Currane from which surface sediment samples were obtained.

Several types of sediment corers are available including gravity corers, piston corers, freeze samplers and percussion corers (Glew et al., 2001). However, for short cores of sediment covering relatively recent timescales, the most commonly used samplers are open barrel and gravity corers (Glew et al., 2001). Gravity corers such as the Hon-Kajak type (Glew, 1991; Renberg and Hansson, 2008) consist of an open tube suspended from a wire or rope that is driven vertically into the sediment and is sealed by a closing mechanism before the corer is removed. Sediment is generally extruded on site using vertical push rod-type extruder. Gravity coring is a simple and quick method for recovering relatively short cores (30 to 70cm long) and if employed correctly can provide largely undisturbed sequences of recently deposited lake sediments (Glew et al., 2001).

4.1.2.1 Coring site selection

Optimal coring locations within Lough Currane were chosen using the bathymetric map produced by Dixon-Brosnan Environmental Consultants (Figure 3.2) and the TP results from the monitoring of Lough Currane. Three coring sites were chosen for the current research, one of which was at the deepest point of the lake (51° 49' 27.2" north, 9° 35' 41.3" west) located 2.7 km from the Cummeragh River, 2.7 km from the Capall River and 0.7 km from the shore and at 35 m water depth. In palaeolimnology, the deepest point of a lake is assumed to be representative of limnological conditions (Anderson, 1998). Since water depth (Anderson, 1998; Punning et al., 2004; Punning et al., 2005; Adler and Hübener, 2007; Selby and Brown, 2007), proximity to shoreline (Anderson, 1998; Havens and Walker, 2002; Moos et al., 2005) and proximity to inflowing rivers (Pla et al., 2005) were found to be important in explaining spatial variability in water quality and sediment components in lakes, these factors were considered in the selection of the other two coring sites. Coring Site 2 (51° 50' 12.1" north, 10° 7' 24.4" west) is located at 14.5 m depth, 1.1 km from the mouth of the Cummeragh River and 1.1 km from the shore. Site 3 (51° 49' 24.5" north, 10° 6' 6.7" west) is located at 4.5 m depth, 1.4 km from the Capall River and 0.4 km from the shore. High TP readings, measured by Kerry County Council, have also been found at the mouth of the Cummeragh and Capall Rivers (Figure 3.5, Table 3.3). The locations of the three selected coring sites are shown in Figure 4.5.

4.1.2.2 Sediment coring

Water depth at each coring sites was measured using a handheld echo-sounder. Three cores of sediment were then extracted from each coring site using a gravity corer (Renberg corer, HTH Teknik Varvagan 37, SE951 49 Lulea) (Renberg and Hansson, 2008). Cores were collected from Coring Site 1 in May 2006 and from Coring Sites 2 and 3 in May 2007. Cores were visually inspected in the field to detect any changes in sediment composition and to ensure the sediment-water interface was relatively intact and undisturbed. Details of the sediment cores are shown in Table 4.1.

4.1.2.3 Subsampling

Subsampling of the sediment cores was carried out in the field using a vertical push rod-type extruder. The upper 10 cm of each core was subsampled at 0.5cm intervals; subsampling was carried out at 1 cm intervals below 10 cm. This subsampling strategy was used in order to ensure the highest resolution for the most recent period recorded by the sediment core. Two cores from Coring Site 1 (cores 1 and 2) were subjected to laboratory analyses. Subsamples from core 1 were used to determine the rate of sediment accumulation, microfossil (diatom) content and organic content. Subsamples from core 2 were used to determine organic and microfossil (pollen) content and particle size. For Coring Sites 2 and 3 all analyses were carried out on one core. Sediment core subsamples obtained from all cores were stored in pre-labelled (name of coring site, core number and depth) ziploc bags which were placed in a cool box. Samples were subsequently transported to Trinity College Dublin. Subsamples from Coring Site 1 were initially frozen as no other storage facilities were available at the time of sampling. Once storage facilities became available, core subsamples were subsequently stored at 2°C to 4°C. Subsamples from Coring Sites 2 and 3 were stored at 2°C to 4°C until needed for further analysis

Coring Site	Location	Number of cores used for analysis	Length of core (cm)	
			Core 1	Core 2
1	51° 49' 27.2" north, 9° 35' 41.3" west	2	40	35
2	51° 50' 12.1" north, 10° 7' 24.4" west	1	37	
3	51° 49' 24.5" north, 10° 6' 6.7" west	1	22	

Table 4.1: Details of the sediment cores collected from Lough Currane

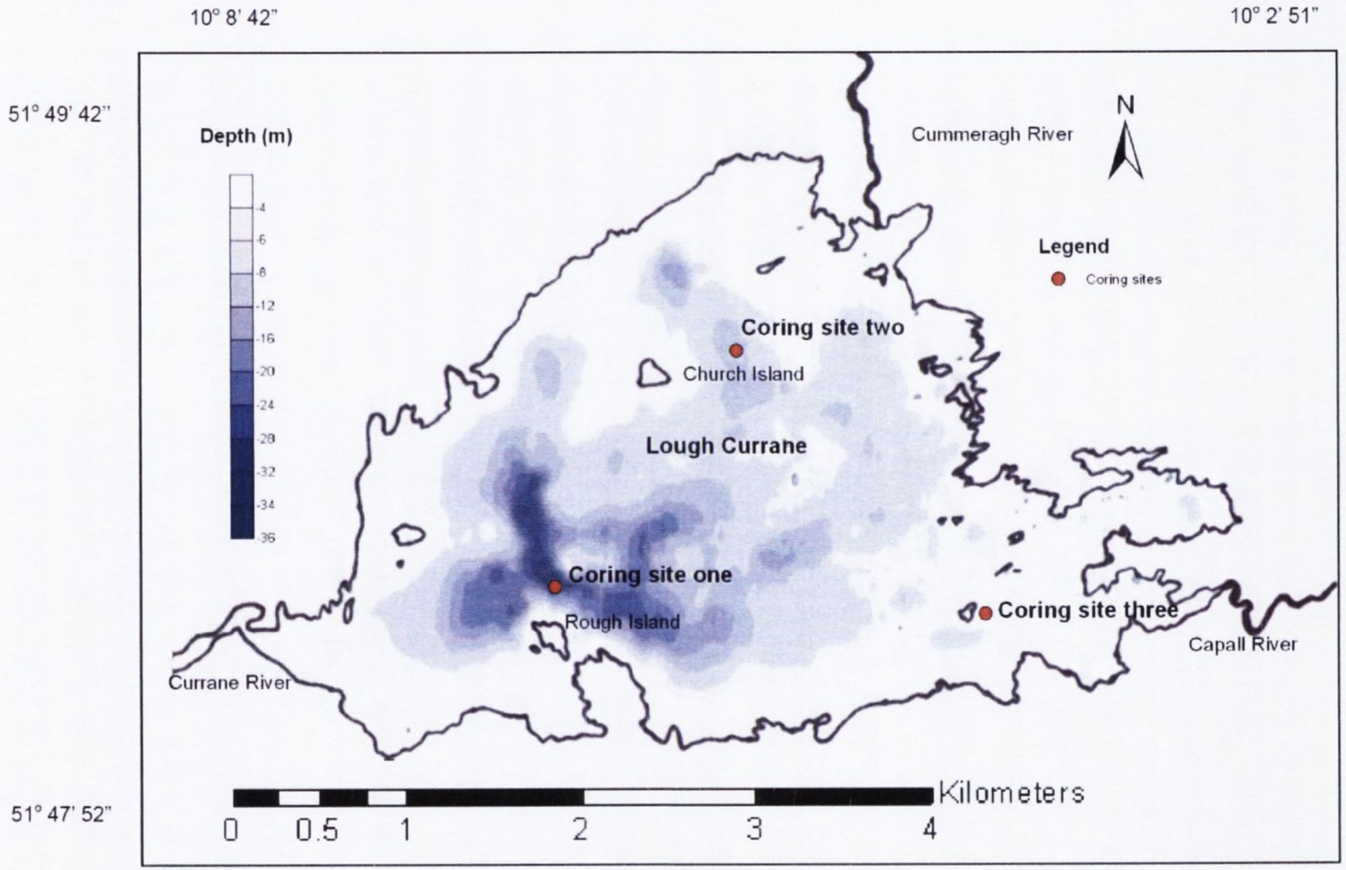


Figure 4.5: The Coring Sites chosen at the test site, Lough Currane. The bathymetry of the lake is also shown.

4.2 Laboratory based techniques

4.2.1 Proxies assessing variations in sedimentary components and land use change

4.2.1.1 Troels-smith

The analysis of the physical properties of the sediment can yield clues as to the source and mechanisms of transport of the sediment; past physical, chemical, environmental and limnological conditions at the depositional sites; and palaeoclimatic and palaeohydrological conditions within the surrounding catchment (Last, 2001). The Troels-Smith (1955) system is based around the principle that the physical properties of a deposit reflect sedimentary conditions at the time of deposition. The system is widely used in sediment based studies of environmental change, and was deployed in the current research.

The Troels-Smith system of classification was carried out on each core with particular attention paid to any apparent changes in sediment composition. Sediments were analysed according to degrees of darkness, stratification, dryness and elasticity. The sharpness of boundaries between adjacent sediment horizons was recorded and the degree of humification and the components of the deposit (e.g. clay, sand, organics etc) were also described (Long et al., 1999).

4.2.1.2 Determination of organic content

Determination of the organic content can provide a rough indication of the amount of sedimentary components as well as variations in productivity and inorganic inputs (Shuman, 2003). The determination of organic content in multiple sediment cores from the same site can also provide a basis for inter-core correlation of sediment-based evidence (Battarbee, 2000). The organic content of lake sediments largely comprises the remains of plants that were growing in and around the lake (Meyers and Teranes, 2001). The LOI method is used to determine the relative proportions of organic and inorganic material in a sediment sample. Dried sediment is placed in a muffle furnace at 500°C to 550°C in order to oxidise organic matter to CO_2 and ash. The weight lost during the reaction is measured by weighing samples before and after heating.

The LOI technique used in the current research followed methods outlined in Bengtsson and Enell (1986) and Heiri et al. (2001). One cm^3 sediment subsamples were placed in pre-weighed nickel crucibles and were weighed and dried at 50°C for 36 to 48 hours. The subsamples were then re-weighed to determine % dry weight. The dried subsamples were placed in a Nabertherm L9/11/B170 muffle furnace set to 550°C for 4 hours. After ignition subsamples were transferred to a dessicator to cool fully before re-weighing to establish % LOI.

Three replicate subsamples were analysed for % LOI in each of the surface sediment samples. A subsampling interval of 1 cm and 2 cm was used for each core in order to determine up-core variations in sediment composition. The third replicate analysis for each core was carried out at a subsampling interval of 2 cm to ensure there was sufficient sediment available in the cores for the analysis of sediment texture and biological proxies. The final LOI results from the surface sediment and core subsamples were thus expressed as the mean of two or three measurements.

4.2.1.3 Sediment texture

Analysis of sediment texture or the relative abundances of sediment particles of different sizes can be useful in palaeolimnology and has been used to study anthropogenically induced change in lakes associated with land clearance and urbanisation (van Hengstum et al., 2007) and to track past climate change and water level fluctuations (Campbell, 1998; Last, 2001; Dieffenbacher-Krall and Nurse, 2005; Bird and Kirby, 2006). PSA has also been used as a basis for examining variability in sedimentation and sedimentary components in lakes (Last, 2001; Kumke et al., 2005). The Wentworth-Udden particle size classification is widely used in sedimentology. The system has a logarithimic scale with one limit set at 1 mm and others successively halved or doubled (Chesworth, 2008). Krumbein (1936) devised the ø scale which represented the geometric intervals of the Wentworth scale on an arithmetic scale by means of the relationship:

$$Ø = -\log_2 (\text{particle diameter in mm})$$

The ø scale is shown in Table 4.2. Coarser sediments have negative ø values while finer sediments have positive ø values (Last, 2001). The ø scale was used in the PSA of sediments from Lough Currane.

Size mm	Size ø	
32	-5	Pebble
16	-4	
8	-3	
4	-2	
2	-1	
1	0	Sand
0.5	1	
0.25	2	
0.13	3	
0.063	4	
0.031	5	Silt
0.016	6	
0.008	7	
0.004	8	
0.002	9	Clay
0.001	10	

Table 4.2: The ø scale, adapted from Last, (2001)

PSA measures the proportions of different size fractions within a sediment matrix and can be used to characterise lake sediments (Murray, 2002). Laser diffraction using LLAS assumes that particles passing through a laser beam of known wavelength will scatter light at an angle that is directly related to their size. LLAS using a particle size analyser is the most common method of determining sediment particle size. A particle size analyser measures the angular distribution and intensity of the diffracted light by particles in suspension. Large particles scatter light at narrow angles with high intensity whereas small particles scatter light at wider angles with low intensity (Sperazza et al., 2004; Malvern Instruments Ltd, 2008).

PSA was carried out on surface sediment subsamples and sediment core subsamples using a Malvern Mastersizer 2000 particle size analyser with the Hydro2000G dispersion unit and Autosampler 2000. The Mastersizer 2000 utilises the Mie theory of diffraction in the prediction of laser particle size results. The Mie theory assumes that: particles are spherical; the suspension is dilute; the optical properties (RI and absorption) are known and that the particles are homogenous (Eshel et al., 2004; Sperazza et al., 2004; Malvern Instruments Ltd, 2008). PSA deployed in the current research followed procedures outlined in Sperazza et al. (2004). Before subsamples were analysed, they were sieved to 1 mm diameter. Subsequently, 20 ml 50 g l^{-1} $(NaPO_3)_6$ solution was added to each subsample and left overnight. This was done in order to de-flocculate the clay content of the sediment. Before inputting subsamples to the Autosampler 2000, subsamples were agitated for c.2 hours to prevent clumping of clays. The PSA process is fully automated once subsamples are added to the Autosampler 2000. Choice of pump speed (2000RPM), stirrer speed (850RPM), measurement time (12 seconds), measurement cycles (3 cycles), mixing time (30 seconds), RI (1.52) and absorption (1) all followed procedures outlined in Sperazza et al. (2004). Output from the Mastersizer 2000 is usually expressed as a series of graphs. However, in order to display temporal changes in grain size more clearly, % of total sand (0 to 4 ø), total silt (5 to 8 ø) and total clay (> 9 ø) were calculated from the output and plotted using the C2 programme (Juggins, 2003). C2 is software designed for ecological and palaeoecological data analysis.

The mean grain size of a sample was calculated as the IGM, which is the standard in particle size analysis (Wang et al., 2009). Sorting, which refers to the degree of uniformity of the particle size distribution, is usually expressed as the IGSD. Material that is well sorted and contains a small range of particle sizes has a low IGSD, while high IGSD values indicate that the distribution is poorly sorted (Last, 2001). For the surface sediment subsamples the IGM and IGSD values were plotted on the map of the test site, Lough Currane.

4.2.1.4 Pollen analysis

Palynology refers to the study of fossil pollen and spores that may be preserved under anaerobic conditions that prevail in water-logged sediments, such as those accumulating in lakes and peat bogs (Bennett and Willis, 2001). Most pollen released by flowers and plants is not used in the process of plant reproduction, and some of this excess pollen is eventually transported to sedimentary basins where it is incorporated in deposits as they accumulate. The abundance of pollen accumulating at a site is a function of the abundance of plants in the living assemblage; the amount of pollen produced by different plants; the transportation mechanisms of particular taxa as well as the preservation of the pollen grains once they are deposited (Davis et al., 1971). Pollen grains vary in diameter from about 10 µm to about 100 µm, depending on species. The outer walls of pollen grains are made of a mixture of cellulose and sporopollenin which is a polymer with saturated and unsaturated hydrocarbons and phenolics. It is this sporopollenin in the exine or outer wall of a pollen grain that leads to the preservation of pollen under anaerobic conditions in sediments. Sporopollenin is resistant to most forms of chemical and physical degradation; during extraction, strong chemicals can be used to remove extraneous material thus concentrating pollen for subsequent analysis (Moore et al., 1991; Bennett and Willis, 2001).

Analysis of pollen can be very useful in palaeolimnological studies. Sedimentary remains of aquatic plants, including pollen, provide a record of temporal changes in the submerged vegetation of lakes (Davidson et al., 2005). In palaeolimnological studies pollen analysis can give an indication of historical land use changes and can aid in the interpretation of changes in trophic status. Lakes sediments are excellent preservers of air-borne and stream-borne materials. Pollen transported and subsequently preserved in lake sediments enables land use change to be assessed over both long (millennia) and short (decadal) time scales and records the landscape impacts of woodland clearance, grazing and crop cultivation (Huang and O'Connell, 2000; Edwards and Whittington, 2001). Pollen can also highlight the processes involved in lake catchment change, for example, from clearfelling of forests to introduction of new crops. The use of pollen analysis in a eutrophication study supports other proxy results and can be used to interpret changes in trophic status in a lake catchment.

- **Sample preparation**

Subsamples for pollen analysis were taken every 2 or 3 cm down core at Coring Site 1 as it was the main core used for assessing variations in land use change. At Coring Sites 2 and 3, subsamples for pollen analysis were taken every 4 cm down core. Subsamples were also taken according to variations in sediment composition found from the LOI analysis. Seventeen subsamples were analysed from Coring Site 1, 14 subsamples from Coring Site 2 and ten subsamples from Coring Site 3. Subsamples were processed following standard procedures (Faegri and Iversen, 1989; Moore et al., 1991). One *Lycopodium clavatum* tablet (c.12542 spores tablet^{-1}) was added to each subsample prior to chemical digestion in order to determine pollen concentration. Pollen concentrations were determined following methods described in Bonny (1972) (Figure 4.6). Subsample treatment included sediment digestion in HCl_{aq}, $NaOH_{aq}$, HF_{aq} and acetolysis. Subsamples were stained with safranine and mounted using silicon oil.

$$\text{Fossil pollen concentration} = \frac{\text{exotic pollen added x fossil pollen counted}}{\text{Exotic pollen counted}}$$

Figure 4.6: The equation used to determine fossil pollen concentrations. Obtained from Bonny (1972) and Bennett and Willis (2001).

- **Enumeration and identification**

Pollen enumeration and identification was carried out using a Leica DMLS research quality microscope at x 400 magnification on horizontal transects offset by 2 mm to ensure no pollen grain was encountered more than once. At least 300 pollen grains were counted per subsample (Bennett and Willis, 2001). The key and illustrations of Moore et al. (1991) as well as reference material held in the School of Natural Sciences TCD, were used to aid the identification of pollen grains. The pollen sum included all identifiable pollen grains and spores, excluding those from aquatic plants. Abundances of pollen grains from aquatic plants were calculated based on the total number of pollen and spores encountered, including those from aquatic plants (Bennett and Willis, 2001). Concentrations and % abundances of pollen were stratigraphically plotted using the C2 programme (Juggins, 2003).

4.2.2 Chronological control

Establishing a reliable chronology, or good chronological control, is one of the most important stages in a palaeolimnological investigation. Without a depth-age profile, the timing and rate of trends and events recorded in lake sediments cannot be established (Smol, 2008). Radiometric dating methods are now frequently used in palaeolimnological investigations to establish chronological control (Cohen, 2003). These methods are based on the fact that certain naturally occurring elements are unstable and undergo spontaneous changes in their atomic structure and organisation in order to achieve more stable atomic forms. This process of decay is time dependent; if the rate of decay of the isotopes is known, the age of the host material can then be determined (Lowe and Walker, 1997). An atom that undergoes radioactive decay is termed a parent nuclide while the decay products are often referred to as daughter nuclides. The decay of the radionuclides occurs exponentially and is considered in terms of the half life or the length of time that is required to reduce a given quantity of the parent nuclide to 1 half. The concept of the half life of the parent nuclide underpins all forms of radiometric dating (Walker, 2005)

4.2.2.1 ^{210}Pb dating

Due to its short half life of 22 years, ^{210}Pb dating is one of the most widely used dating methods for recently deposited sediments (150 to 200 years) (Cohen, 2003). ^{210}Pb occurs naturally in lake sediments as one of the radioisotopes in the ^{238}U decay series (Figure 4.7) (Battarbee, 1991). A portion of the ^{222}Rn atoms formed by ^{226}Ra diffuse through the soil into the atmosphere where they eventually decay to ^{210}Pb.

^{238}U (4.5 x 10^9y) → ^{230}Th (8.3 x 10^4y) → ^{226}Ra (1622y) → ^{222}Rn (3.8d) →

^{218}Po (3.05m) → ^{214}Pb (26.8m) → ^{214}Bi (19.7m) → ^{214}Po (150μs) →

^{210}Pb (22.3y) → ^{210}Bi (5d) → ^{210}Po (140d) → ^{206}Pb (stable)

Figure 4.7: ^{238}U decay series

^{210}Pb is removed from the atmosphere by rain, snow, or dry fallout, falling either onto the land surface, where it is trapped in surface soils, or into lakes or oceans (Appleby and Oldfield, 1983). ^{210}Pb falling into lakes is scavenged from the lake waters 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 ^{210}Pb fallout, ^{210}Pb and ^{226}Ra would be in radioactive equilibrium. The unsupported ^{210}Pb concentration in each sediment layer declines exponentially with time in accordance with the radioactive decay law. This law can be used to calculate the age of the sediment provided that the initial unsupported ^{210}Pb concentration when laid down was estimated in the same way (Appleby and Oldfield, 1983, 1992; Appleby, 2001). Two of the models used in ^{210}Pb dating are the CIC model and the CRS model. The CIC model assumes that the dilution of ^{210}Pb throughout the period of deposition is constant. Thus, initial activity of unsupported ^{210}Pb g^{-1} dry weight is assumed to have remained unchanged throughout the deposition of the core. The CRS model requires that an excess reservoir of ^{210}Pb is available in the water column at all times for scavenging by settling particles and is useful in lakes where sedimentation rates have remained relatively constant throughout the study period (Appleby, 2001). The model assumes that the absolute flux rate of ^{210}Pb to the sediment-water interface remains constant, regardless of background sedimentation, such that a higher rate of background sedimentation will lead to a lower ^{210}Pb concentration (Cohen, 2003).

Due to financial constraints, resources were only sufficient for the radiometric dating of sediment samples from two of the three coring sites. Up-core variations in organic content and diatom assemblages were very similar at Coring Sites 1 and 2 while the core from Coring Site 3 showed marked differences in these sedimentary components when compared with the other two coring sites. For this reason, cores from Coring Sites 1 and 3 were chosen for radiometric dating (^{210}Pb analyses). Eighteen samples were analysed from Coring Site 1, while 13 samples were analysed from Coring Site 3. Analyses were carried out at Flett Research Laboratories, Winnipeg, Canada by Misuk Yun. The choice of laboratories for ^{210}Pb analysis was informed by costs and by the time constraints on the current research.

Determination of ^{210}Pb activity was made indirectly through ^{210}Po, a grand-daughter isotope of ^{210}Pb. ^{210}Po was distilled out of the sediment at a high temperature, acid digested and plated onto silver discs for analysis by alpha spectrometry using an Ortec 'Octet' alpha spectrometer (Eakins and Morrison, 1978). Measurements of ^{226}Ra can be used as a proxy of supported ^{210}Pb within the sediment (Appleby, 2008). Determinations of ^{226}Ra were made for two samples from site 1 (20 to 23cm, 38 to 40cm), using a bare photomultiplier tube and multi-channel analyser following the method of Mathieu et al. (1988), in order to estimate supported ^{210}Pb activity.

Up-core irregularities in excess ^{210}Pb and dry bulk density were apparent upon initial examination of the core from Coring Site 1. As a result the CRS model (Appleby and Oldfield, 1978) was applied. The core from Coring Site 3 displayed a relatively constant decline in excess ^{210}Pb activity as a function of depth in the uppermost 4 cm of the core. For this reason the CIC model (Robbins, 1978) was applied. The ^{137}Cs activity profile was examined for both Coring Site 1 and Coring Site 3 to validate the ^{210}Pb profile (see the following subsection). The CRS model was not applied at Coring Site 3 as it failed to predict the position of the 1963 ^{137}Cs peak.

4.2.2.2 Validating the ^{210}Pb profile

- **^{137}Cs**

Material associated with the widespread global dispersal of artificial radionuclides from atmospheric testing of nuclear weapons from about the mid 1940s until c.1980 can be used to validate the results of analysis of ^{210}Pb activity (Leslie and Hancock, 2008). Atmospheric fallout of radionuclide debris is transported by surface or groundwater to lakes, and is ultimately incorporated in sediments (Cohen, 2003). The principal radionuclides in the fallout are ^{137}Cs, ^{90}Sr and $^{239,240,241}Pu$ (Appleby, 2001). ^{137}Cs is the most widely used of these radionuclides for the validation of radiometric age estimates (Cohen, 2003). Up-core variations in ^{137}Cs activity should reflect the historical records of ^{137}Cs fallout. ^{137}Cs fallout begins in 1954, attains an initial peak in 1958/1859, reaches a maximum in 1963, and declines rapidly to background values by 1968 (Battarbee, 1991). The accident at the Chernobyl nuclear power plant in the Ukraine in 1986 released large quantities of radionuclides into the atmosphere. These radionuclides included ^{131}I, ^{137}Cs and ^{134}Cs. In parts of Scandinavia, central Europe and Britain, deposition of ^{137}Cs associated with Chernobyl was far greater than total deposition from weapons fallout (Appleby, 2001). This release of radionuclides resulted in a second peak in ^{137}Cs activity in sediment stratigraphies (Appleby, 2008). Departures from the traditional ^{137}Cs pattern can be explained by erosion or sediment mixing, for example, by bioturbation and resuspension, as ^{137}Cs can be mobile after deposition (Battarbee, 1991)

Analysis of ^{137}Cs activity was carried out at Flett Research Laboratories, Winnipeg, Canada by Misuk Yun. Subsamples from Coring Sites 1 and 3 were measured by gamma ray spectrometry using an HPGe coaxial detector (R. Flett personal communication). Only one peak in ^{137}Cs activity was evident at each of the cores analysed at Lough Currane. For this reason further validation of the ^{210}Pb chronologies was provided by SCP dating.

- **SCPs**

SCPs are the products of the incomplete combustion of fossil fuels. There are no natural sources of SCPs and so they can provide a clear record of industrially derived atmospheric deposition. The SCP record is seen as being 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). In the UK the beginning of the SCP record coincides with the development of coal and oil burning around the mid-nineteenth century. Following this, there was a steady increase in SCP concentrations with a sharp increase occurring after World War Two due to increased consumption of fossil fuels. In the UK, the peak in SCP concentration occurs around 1970. Due to particle removal efficiency and implementation of pollution control legislation, SCP concentrations generally decrease in the mid 1970s (Rose, 2001).

In Ireland, there are variations in the deposition of SCPs between the east and west coasts owing to the relative influences of air masses from Britain and continental Europe on different parts of the country. Local sources of atmospheric pollutants may also be important in Ireland (O' Dwyer and Taylor, 2010). However, throughout Ireland the SCP record generally begins between 1880 and 1890 and the peak in SCP concentration occurs between 1970 and 1980 (Rose et al., 1995). Declines in the concentration of SCPs from the 1970s are in agreement with trends in the levels of atmospheric deposition throughout Europe, due to the introduction of particle arrestor technology and changes in fuel type (Rose et al., 1995; O' Dwyer and Taylor, 2010). Upper Killarney Lough was included in O'Dwyer and Taylor's (2010) research on variations in the levels of atmosphere-borne pollutants in Ireland and is located c.40 km from the test site, Lough Currane. The SCP record from Upper Killarney Lough was used for comparison with the SCP records from Lough Currane. The SCP record at Upper Killarney Lough begins in 1900, the increase in SCP concentration was apparent in the mid 1950s and SCP concentration reaches a peak in 1980.

Sediment core material from the three coring sites were analysed for SCPs. SCPs were enumerated in ten subsamples from Coring Sites 1 and 2 and nine subsamples from Coring Site 3. Preparation of samples for SCP analysis followed the procedure outlined in Rose (1994). Between 1 and 2 grams of dried sediment were subjected to chemical digestion in nitric acid to remove organics, HF_{aq} to remove siliceous materials and $HCl_{aq,}$ to remove carbonates; leaving carbonaceous material and a few persistent minerals. A known fraction of the final suspension was 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).

4.2.2.3 Radiocarbon dating

Radiocarbon, or ^{14}C, dating was one of the first radiometric dating techniques to be developed and remains the most widely used of all radiometric techniques for Quaternary sediments (Lowe and Walker, 1997). The limit of measurement of ^{14}C is generally eight half lives or c.45, 000 years. ^{14}C is one of the three isotopes of C, the others being ^{12}C and ^{13}C. ^{14}C atoms are formed in the upper atmosphere where cosmic ray flux leads to collision of free neutrons with other atoms and molecules. This leads to the loss of a proton from nitrogen atoms (^{14}N) to produce ^{14}C. This process produces ^{14}C atoms that combine with O to create a particular form of CO_2, $^{14}CO_2$, which in turn mixes with the non-radiocarbon containing molecules of CO_2. $^{14}CO_2$ then becomes part of the global C cycle, is mixed throughout the atmosphere and is absorbed by oceans and by living organisms during tissue building (Bjorck and Wohlfarth, 2001; Walker, 2005). During an organism's lifetime, the level of C used for tissue building is in isotopic equilibrium or is equal to the level of C in the atmosphere. When the organism dies the uptake of CO_2 stops and since ^{14}C is an unstable isotope, radioactive decay of ^{14}C can begin. Radiocarbon dating is based upon this process of decay. The internationally agreed half life of ^{14}C is 5570 +/- 30 years (Mook, 1986; Walker, 2005).

There are two approaches for radiocarbon dating of organic material. These are beta counting and AMS. Beta counting involves the detection and counting of β emissions (decay products) from ^{14}C atoms for a period of time and is based on the principle that the rate of emissions reflects the residual level of ^{14}C within a sample (Bjorck and Wohlfarth, 2001). AMS uses particle accelerators as mass spectrometers to count the relative number of ^{14}C atoms in a sample, as opposed to β emissions (Walker, 2005). The AMS approach is now more widely used as material with c. 200 µg of final C can be analysed (Walker, 2005). The method can be used to date different sedimentary components, for example, macrofossils, and has reduced many of the errors and uncertainties associated with the β counting method (Bjorck and Wohlfarth, 2001). Due to measuring uncertainties, varying atmospheric ^{14}C content, combustion of fossil fuels and nuclear weapons tests, ^{14}C dating is not usually used to date organic material dating to the last 300 years (Walker, 2005) and all calendar and radiocarbon ages are related to the year 1950 (Bjorck and Wohlfarth, 2001). For sediments deposited over more recent timescales, other radiometric dating methods can be used, such as ^{210}Pb dating.

Due to a discontinuity in the dry bulk density at Coring Site 1 and due to the fact that background ^{210}Pb levels were reached at 26 cm, samples from above and below 26 cm were chosen for ^{14}C dating. Since a sediment accumulation rate was not provided for Coring Site 2, samples were chosen from the coring site for ^{14}C dating. In order to compare the sediment age at Coring Site 2 with Coring Site 1, samples for ^{14}C dating were chosen from the same depths in the cores from both sites. The samples were taken at 22 cm and 32 cm depth in each core. The core from Coring Site 1 was initially frozen and this freezing process destroyed the macrofossils preserved in the sediment. Obtaining macrofossils from Coring Site 2 also proved difficult, so bulk sediment subsamples were analysed for ^{14}C from both coring sites.

Subsamples for ^{14}C dating were analysed by Beta Analytic Inc, Miami Florida. Samples were pre-treated by acid washing in HCl_{aq}. AMS results were derived from reduction of the sample C to graphite (100% C), along with standards and backgrounds. The graphite was then detected for ^{14}C content in an AMS. Results were expressed as 'measured radiocarbon age' and 'conventional radiocarbon age'. The conventional radiocarbon age is the result after applying $^{13}C/^{12}C$ corrections to the measured age and is the standard result used for most chronologies (Stuiver and Polach, 1977). The conventional radiocarbon age was used in the current research.

4.2.3 Inter-core correlation

In order to compare the fossil records provided by different sediment cores collected in the same lake basin, including at the same coring site, and to compare the timing of ecological events recorded by those cores, a reliable means of correlating between cores is needed (Birks and Birks, 2006). Core correlation can often be based on simple sedimentary characters such as dry weight, organic content and magnetic susceptibility (Battarbee, 2000). Up-core variations in % organic content, obtained from LOI analysis and SCP concentrations were used to cross-correlate the cores from Lough Currane. SCP concentrations were used to cross-correlate the uppermost sections of the cores, while % organic content was used to for cross-correlation on the lower portions of the cores. Inter-core correlation was carried out using plots of up-core variations in organic content and SCP concentration. The depths at which peaks in % organic content and SCP concentration occurred were matched between core 1 from Coring Site 1 (dated using ^{210}Pb and ^{14}C) and the remaining cores used for analyses within the lake. Linear interpolation was used to provide matched dates between the peaks in order to assign an interpolated chronology to 1 cm sediment subsections in each core.

4.2.4 Assessing temporal and spatial water quality variation

4.2.4.1 Analysis of TP

Three samples from each of the 30 surface sampling sites were analysed for TP following methods outlined in Murphy and Riley (1962). Analysis of the TP content of water samples requires that all condensed and organic P compounds first be converted to PO_4^{3-}, so that they can be determined colorimetrically. This was accomplished by digesting each sample in acid persulphate at 120°C to oxidise the organic matter and release P as PO_4^{3-}. The absorbance of the PO_4^{3-} which was formed was measured using a Hach DR5000 spectrophotometer. The final TP results for each sampling site were the mean of three measurements.

4.2.4.2 Diatom analysis

Diatoms are classified as algae, division Bacillariophyceae. They are ecologically diverse and occur throughout the world in almost all aquatic environments (Battarbee et al., 2001). These environments include lakes and ponds, reservoirs, free flowing streams, rivers and estuaries (Patrick, 1978). Diatoms are unicellular organisms that colonise virtually every microhabitat in lakes (Dixit et al., 1992). Distinct diatom communities are found in the open waters of lakes (plankton) and in association with plants (epiphyton), rocks (epilithon), sand (episammon) and mud (epipelon) in littoral and benthic lacustrine habitats (Patrick, 1978; Hall and Leavitt, 1999; Battarbee et al., 2001). Composition of the communities of diatoms found in lakes depend on the range and extent of suitable habitats, as well as on the combination of physical, chemical, and biological conditions that prevail in the water column and in these habitats specifically (Battarbee et al., 2001).

Diatoms are characterised by their highly resistant siliceous cell walls known as frustules or valves. The uniqueness of diatoms is primarily related to silica as it leads to the rigidity of the valves, constrains aspects of reproduction, and leads to the preservation of diatom valves as fossils. Diatom valves are essentially systems of silica ribs, which grow out from a circular or elongate pattern centre during formation. It is this difference in the organisation of the primary rib system that underlies diatom identification and the distinction between centric (circular) and pennate (elongate) forms (Round et al., 1990). Each diatom cell consists of two more or less identical valves, one slightly larger than the other. The valves fit neatly together like the two halves of a Petri dish and are held together with girdle bands or copulae. Each valve face is intricately patterned allowing even most fossil taxa to be identified at the specific level (Battarbee et al., 2001).

Diatoms have been used successfully in limnological and palaeolimnological studies as indicators of past and present water chemistry and changes in diatom assemblages have been used to reconstruct long term trends in pH, nutrients (trophic history), hydrology, climate and water level fluctuations (Guilizzoni et al., 2006). The remains of diatoms have been used extensively in eutrophication research as they are directly affected by changes in nutrient and light availability in the water. They also respond rapidly to eutrophication and oligotrophication since they replicate and immigrate quickly (Dixit et al., 1992; Hall and Smol, 1999). Individual species have narrow optima and tolerances for many environmental variables, including nutrient levels, and so species abundances will alter as environmental determining factors vary (Dixit et al., 1992; Bennion et al., 2004). Oligotrophic lakes usually display large abundances of *Cyclotella* and *Tabellaria*, while *Asterionella formosa*, *Fragilaria crotoensis* and *Melosira granulata* may characterise eutrophic conditions (Mason, 2002; Saros et al., 2005).

- **Sample preparation**

A modification of the procedure set out by Battarbee et al. (2001) was used in the preparation of diatom subsamples for analysis. Diatom subsamples were prepared for each of the 16 surface sediment samples collected in the lake. For each coring site the top 5 cm of the core was subsampled for diatom analysis at 0.5 cm intervals in order to obtain high resolution records from the most recent sediments. Further subsamples were extracted at 2 cm intervals throughout the core. Twenty-eight subsamples in total were analysed for Coring Site 1, 26 for Coring Site 2 and 19 for Coring Site 3. Preparation of the subsamples involved digestion in H_2O_{2aq} to digest organic material. Subsamples were washed with deionised water a number of times and 0.5 ml of poly (styrene-co-divinylbenzene) microsphere solution (6.35×10^6 microspheres ml^{-1}) was added to each subsample in order to provide a basis for determining diatom concentrations. Subsamples were mounted onto glass slides using Naphrax mounting medium. Diatom concentrations were calculated using procedures outlined in Battarbee and Kneen (1982) (Figure 4.8). At Coring Site 1, the 0.5 cm core subsections were amalgamated for the first 5 cm of the core after diatom relative abundances were calculated. Samples for the calculation of diatom concentrations were prepared and enumerated after the 0.5 cm subsections were amalgamated and for this reason, at Coring Site 1, diatom concentrations were provided at 1 cm intervals for the top 5 cm of the core. At Coring Sites 2 and 3, diatom relative abundances and concentrations were calculated simultaneously and were provided at 0.5 cm intervals for the top 5 cm of the cores.

$$\text{Diatom concentration} = \frac{\text{microspheres introduced x diatoms counted}}{\text{Microspheres counted}}$$

Figure 4.8: The equation used to calculate diatom concentrations, obtained from (Battarbee and Kneen, 1982) and (Battarbee et al., 2001)

- **Enumeration and identification**

Diatom enumeration and identification was carried out using a Meiji Techno ML5000 research quality microscope at x 1000 magnification provided with x 100 oil immersion objective and a phase contrast condenser. Diatom valves were enumerated on transects running horizontally along the microscope slide beneath the coverslip. Each transect was offset by 2 mm to ensure no diatom valve was encountered more than once. Due to the high abundance of *Cyclotella comensis* and *Cyclotella krammeri* in all sites, at least 600 diatom valves were counted sample^{-1} in order to obtain a good representation of the overall floristic composition of the sample. Reference collections of drawings and photographs by Krammer and Lange Bertalot (Krammer & Lange-Bertalot 1986-1991) were primarily used in the identification to species level. Supplementary references (Belcher et al., 1966; Prygiel and Coste, 2000; Hausmann and Lotter, 2001; Knie and Hübener, 2007; Potapova and Hamilton, 2007) as well as the EDDI (European Diatom Database, 2009) aided in the identification of problematic taxa. Photographs of the diatom taxa enumerated in the sediment subsamples from Lough Currane were taken using a Leica DM1000 microscope with a Leica DFC camera attachment, and Leica Application Suite software. Proportional abundances of diatom taxa were stratigraphically plotted using the C2 programme (Juggins, 2003).

- **Taxonomy**

Diatom taxonomy followed standard flora (Krammer & Lange-Bertalot 1986-1991). Three training sets were used for the purpose of producing reconstructions of DI-TP from the surface and core subsamples at Lough Currane. A training set is a dataset of modern samples with associated indicator species and environmental variables for a range of lakes. The present ecology of these species is used to infer past environmental conditions (Smol, 2008). The training sets that were used were the Irish Ecoregion training set (Chen et al., 2008), the north-west European training set (Bennion et al., 1996) and the combined TP training set (European Diatom Database, 2009). Details of the training sets are outlined in Table 4.3. MAT was used to evaluate the suitability of the training sets used for analysis and will be outlined in more detail in section 4.3.2.1. Before MAT was performed, the taxonomy of the diatom assemblages in Lough Currane had to be synchronised with the diatom assemblages in each of the training sets. This involved matching the taxon codes for the taxa in each training set, with the taxa enumerated at Lough Currane. For the purposes of gradient analyses, an unpublished French diatom list (M. Coste pers. Comm) was used for coding the diatom taxa in this study (see Appendix C).

4.3 Numerical methods

4.3.1 Correlation

Correlation is a statistical technique that describes how strongly pairs of variables are related. The correlation coefficient is used to determine the strength of these relationships. The most commonly used correlation coefficient is the Pearson's product moment correlation coefficient, usually referred to as Pearson's R (Jackson, 2006). The R (linear correlation coefficient), R^2 (coefficient of determination) and p-values are used to determine statistically significant relationships between variables.

Pearson's product moment correlation was carried out, using the PAST programme (Hammer et al., 2001), to determine the relationship between mean grain size as well as the degree of sorting and site depth, distance to shore and distance to inlet in the surface sediment samples. These relationships will aid in the analysis of sedimentation in the lake

4.3.2 Multivariate analyses

Most numerical methods used in palaeolimnology are carried out using multivariate data where the purpose of the analysis is to simplify the data so that major trends are emphasised and minor variation ignored (Kovach, 1995). These methods include numerical zonation and ordination methods such as CA and RDA. Some multivariate numerical methods such as MAT, transfer functions (Birks, 1995) and ordination methods, such as CCA and RDA, attempt to relate changes in biological assemblages to defined environmental variables and co-variables (Kovach, 1995).

Training set	Types of lakes included in the training set	Number of lakes	Number of diatom taxa	Maximum depth range of lakes (m)	TP range of lakes ($\mu g l^{-1}$)	Mean TP of the training set ($\mu g l^{-1}$)
Irish Ecoregion	Small lakes <200ha, <2000ha catchment area.	70	233	1.1 - 45.7	4 - 142.3	25.9
North-west European	Lowland, small, shallow, slightly acid to alkaline waters with agricultural activity in their catchments	152	298	0.7 - 37.7	5 - 1189	172
Combined-TP		347	719	0.7 - 410	2 - 1189	98.6

*** The North-west European training sets consists of a number of regional training sets. These ate: the Welsh, Danish, Northern Irish, UK meres, Southern England and SWAP datasets**

*** The Combined-TP training set consists of a number of regional training sets. These are : the Welsh, Central European, Danish, French Massif Central, Northern Irish, UK meres, Southern England and Swiss datasets**

Table 4.3: Details of the training sets used for MAT and environmental reconstructions in the current research.

Environmental variables are the variables that are of prime interest to a researcher in explaining variability in the primary dataset. Co-variables are also explanatory variables with an acknowledged influence on variability in the primary dataset. The influence of these variables needs to be quantified before focussing on the variables of prime interest in the dataset (Lepš and Šmilauer, 2003).

Two models of species response to environmental gradients are generally used in the multivariate analysis of environmental data; these are linear and unimodal response models (Birks, 1995). Linear response models assume that species and environmental variables are related in a deterministic way and are appropriate for analysing data spanning a narrow range of environmental variation. Unimodal models assume that a species abundance increases to a maximum before declining. Maximum species abundances are assumed to equate to optimum environmental conditions for that taxon. Unimodal response models are more suitable for analysing data spanning a wide range of environmental variation (ter Braak and Prentice, 1988).

One of the underlying assumptions of most multivariate methods is that the data are normally distributed. This is not always the case, especially when variables are measured on different scales. For this reason data often need to be transformed to fit the normal distribution. The most common transformations used in the environmental sciences are square root and logarithm transformations. These transformations are particularly useful for count data and continuous measurements which are often used in the environmental sciences (Kovach, 1995; Lepš and Šmilauer, 2003). MAT and the transfer functions carried out on the diatom assemblages from surface and core subsamples from Lough Currane are first outlined below, followed by the numerical zonation of pollen and diatom data. Finally, the ordination methods used in this research are described.

4.3.2.1 MAT

MAT is a palaeoecological method that employs a similarity or dissimilarity measure (chord distance, squared chord distance) to compare, numerically, biological assemblages in fossil samples with biological assemblages in a training set of modern samples with associated environmental data (Birks, 1995). MAT is mainly used for palaeoenvironmental reconstructions. The technique attempts to find matches for fossil sediment samples in a modern training set (Simpson et al., 2005). The environmental variables associated with the most similar modern samples in the training set are used to infer the environmental conditions that existed when the fossil samples were deposited (Birks, 1995; Simpson et al., 2005). The technique can also be a useful tool in identifying the most similar modern analogues for fossil samples in a number of modern training sets (Juggins, 2001) and in evaluating the suitability of different training sets for the production of environmental reconstructions based on methods such as WA (Birks, 1995; Jones and Juggins, 1995). Environmental reconstructions are likely to be most accurate when they are based on a training set which includes samples that are good modern analogues for the fossil assemblages (Bennion et al., 1996).

MAT was performed on diatom assemblages identified for each surface sediment subsample and each coring site within Lough Currane. The technique was used to assess the applicability of a number of diatom training sets that would potentially be used for environmental reconstructions of TP in the lake. In order to assess the applicability of each training set, the minDC between a core sample and the training set samples was used (Simpson, 2007). A general rule of thumb is that any fossil sample with a minDC value of 100 to 150 has no close analogs in the training set (Juggins, 2001). Therefore, the training set that yielded the lowest minDC values was considered for the final reconstruction of DI-TP.

MAT was performed for the north-west European and combined TP training sets using Ernie Version 1 software (Juggins, 2001).The software performs environmental reconstructions using the training sets included in EDDI. MAT was performed for the Irish Ecoregion training set using the C2 programme (Juggins, 2003) as this training set is not included in the Ernie Version 1 software. The C2 programme can be used to create environmental reconstructions utilising the same methods used in the Ernie version 1 software.

4.3.2.2 Environmental reconstruction

Environmental reconstructions using DI-TP have been used extensively in eutrophication research. The most commonly used environmental reconstruction methods used in palaeolimnology are transfer functions, using

WA and WAPLS. These models assume a unimodal relationship between species and environmental variables (Racca et al., 2001). The underlying principle behind WA regression is that the optimum for each taxon is estimated from the training set, based upon the abundances of diatoms in the surface sediment and the measured environmental variables where the taxon is present (Racca et al., 2001). Thus, diatoms with their TP optima close to ambient TP will be the most abundant taxa present. The estimate of a taxon's TP optimum is the average of all TP values for the lakes in which the taxon occurs, weighted by the taxon's relative abundance (WA regression). Equally, an estimate of a lake's TP is the weighted average of the TP optima of all the taxa present in the lake (WA calibration) (Birks et al., 1990). WAPLS is an extension of simple WA in which successive components are extracted from the calibration data set (Racca et al., 2001). Once calibrated against present day TP concentrations, the WA models are applied to fossil diatom assemblages to provide inferences about past TP concentrations (Bennion et al., 2005).

Transfer function performance is estimated mainly by the RMSEP value. A number of transfer functions are usually applied to the same fossil data using various cross validation techniques (leave one out, bootstrapping, jack-knifing) and the model that is most accurate will have the lowest RMSEP value. The inferred TP values should also correlate well with known surface environmental variables, such as TP and pH, for the lake being researched (Birks, 1995).

Transfer functions were performed for each coring site in Lough Currane using the Irish Ecoregion training set (Chen et al., 2008), the north-west European training set (Bennion et al., 1996) and the combined TP training set (European Diatom Database, 2009). Reconstructions were performed on north-west European and combined TP training sets using Ernie Version 1 software (Juggins, 2001). WAPLS was used for the north-west European training set and WA was used for the combined TP training set. A reconstruction was performed on the Irish Ecoregion training set using the C2 programme (Juggins, 2003) and following procedures outlined in Chen et al. (2008). WA was used with leave-one-out cross validation. The training set with lowest minDC from MAT, lowest RMSEP values and with reconstructed DI-TP values closest to measured TP at each sampling site was used for the final environmental reconstruction. The final reconstructed DI-TP values were then added to stratigraphic diagrams using the C2 programme (Juggins, 2003).

4.3.2.3 Numerical zonation

Numerical methods are often used in palaeolimnology to divide data into assemblage zones, in order to aid in the interpretation of up-core variations in species abundances (Birks and Gordon, 1985). Two methods are commonly used in numerical zonation of stratigraphic sequences. These are agglomerative techniques and divisive techniques. With agglomeration (e.g. CONISS), all objects begin by being alone in groups of one. Close or stratigraphically adjacent groups are then gradually merged until all the data are in a single group. A dendrogram is produced in order to consider the distinction between zones and subzones (Gordon and Birks, 1972; Manly, 2005). With divisive procedures all data are placed into one group initially. The procedure then determines the best location for a marker to divide the dataset in two. The division of the zone is based on placing a zone marker at a location that results in the greatest reduction in the variance of the dataset as a whole. After the initial division, the data are then successively spit into smaller and smaller groups until there is little further reduction in the variance of the entire dataset (Gordon and Birks, 1972; Bennet, 1996; Manly, 2005).

Bennett (1996) formulated the broken stick model in order to determine the optimum number of zones in a stratigraphic sequence. Prior to its formulation judgements relating to the optimum number of zones rested entirely with the analyst. The broken stick model is based on greatest reduction in the variance of a dataset. If the reduction in variance due to the creation of a particular zone exceeds the proportion expected from a model of the same data arranged at random, the zone is considered significant. The technique is repeated until any further creation of zones does not produce a significant reduction in variance (Bennet, 1996). The broken stick model works well with binary divisive techniques and can also be used for agglomerative techniques (Bennet, 1996; Birks, 1998).

Diatom and pollen assemblage zones were produced via numerical zonation. For each coring site, taxa comprising at least 5 % abundance at any one level were included in the dataset. Taxa at lower proportions have little numerical importance for zonation, however they can be of considerable value in interpretation (Gordon and Birks, 1972; Bennet, 1996). The agglomerative technique of CONISS was used in the determination of assemblage zones and broken stick model was used to determine the number of statistically significant zones. Numerical zonation was carried out using the psimpoll programme (Bennet, 2002), with zone boundaries subsequently plotted using the C2 programme (Juggins, 2003).

4.3.2.4 Gradient analysis

Gradient analysis, or ordination, when applied to biological data, refers to the examination of the relationships between species composition and environmental gradients. Gradient analysis includes indirect gradient analysis (ordination) and direct gradient analysis (constrained ordination) (ter Braak and Prentice, 1988). When dealing with biological data, ordination can be described as the process of finding the axes of greatest variability in the community composition of a dataset and visualising the similarity structure of the samples and species in the dataset. Community composition can then be interpreted in terms of latent, not measured, environmental gradients. Constrained ordination aims to find the variability in species composition that can be explained by measured environmental variables (Lepš and Šmilauer, 2003).

Ordination methods are based on eigenanalysis where each axis produced through ordination is described by an eigenvalue and an eigenvector. Eigenvalues indicate the relative amount of total variation in the data that is summarised on one axis and eigenvectors are a set of scores for each object in the original data matrix (Kovach, 1995; Manly, 2005). Ordination is useful in palaeolimnology as it can be used to reduce complexity so that patterns in a dataset become more obvious (Birks and Birks, 2006).

- **Datasets**

Gradient analysis was used in the current research to address both of the research questions.

1. To what extent is recent eutrophication caused by anthropogenic factors?

Ordination was used to aid in the identification of the most significant drivers of a change in trophic status at each of the three coring sites. Three primary datasets were produced, consisting of DI-TP as well as diatom taxa comprising > 5 % max relative abundance for the depths and corresponding dates (provided by ^{210}Pb dating) shown in Appendix D. Linear interpolation was used to provide DI-TP values and diatom relative abundance values for the years between those provided by ^{210}Pb dating. Population density, housing density, sheep density, cattle density, annual total precipitation, storm frequency and annual mean temperature were used as environmental or explanatory variables. These data were used in order to explain variation in the primary datasets. Linear interpolation was used to provide yearly data on population, housing and livestock density for the between census years shown in Appendix E. Climate data were recorded on a yearly basis.

Data corresponding to the mink farm and the forestry plantations were not used for ordination. The data that were available relating to the mink farm were based on the year of its establishment and a suggestion that there were 50,000 animals associated with the farm. The forestry data that were obtained were in a similar format and related to establishment, thinning and harvesting years. These types of data could only be used as binary (presence/absence) data and would not correspond with the other types of data that were available (e.g. census and climate data). While data relating to the mink farm and the forestry plantations were not used for ordination, they were considered when making an overall assessment of the drivers of a change in trophic status at the lake. The ordination method used assumes a homogenous distribution of people and livestock within the catchment of the test site, Lough Currane.

2. To what extent does the response to increased nutrient loads vary spatially within a lake basin?

Gradient analysis was also used in the current research to assess the spatial variability in the response to increased nutrient input at Lough Currane. Datasets consisting of relative abundances of diatoms from the surface sediment subsamples in Lough Currane and from the three coring sites in the lake were the primary datasets used for analysis. Taxa with > 50% missing or zero values in the datasets were deleted (Lepš and Šmilauer, 2003). Data were log-transformed (x+1) before input to CANOCO for Windows version 4.5 software so that they would fit the normal distribution. The environmental variables used to assess dissimilarity between sites were i) Site Depth, ii) Distance to nearest shoreline (Shore), iii) Distance to nearest inlet/river (Inlet) and iv) Distance to nutrient source (P-Source) as these variables were most important in explaining within-lake variability in other lakes. Up-core change in biological assemblages is expected to have an influence on variability in the primary dataset. For this reason sample depth was treated as a co-variable in the coring sites dataset, as it was not of prime interest in explaining variability in the dataset.

- **Choice of response model**

DCA is usually used to determine if the species data are more suited to a linear or unimodal model. The results of the DCA provide an estimate of gradient length in relation to the underlying environmental gradients. The length of gradients is expressed in SD units of species turnover. If the longest gradient length is < 3 SD units, the species data are generally homogenous and linear methods are appropriate. If the longest gradient length is > 4 SD units there are species in the dataset that show a clear unimodal response along the gradient and so unimodal methods are appropriate (Lepš and Šmilauer, 2003). The most widely used linear models used for analysing palaeoecological data are PCA (ordination/indirect gradient analysis) and RDA (constrained ordination/direct gradient analysis). CA and its related techniques of DCA (ordination/indirect gradient analysis) and CCA (constrained ordination/direct gradient analysis) are commonly used unimodal models in palaeoecology.

DCA was carried out on the datasets used for ordination using CANOCO for Windows version 4.5 software. The lengths of gradients in all analyses were < 3. For this reason linear methods were deployed for all analyses. The methods used were PCA and RDA.

- **Linear methods**

PCA

PCA is a form of eigenanalysis and is a multi-species extension of multiple (least squares) regression (ter Braak and Prentice, 1988). The objective of PCA is to perform linear transformations on multidimensional data to extract a smaller set of new axes that account for most of the variance in the original dataset (ter Braak, 1995). The explanatory variables or axes are estimated from the species data alone. 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. The second PCA axis will account for the second largest amount of variance and will have the second largest eigenvalue and so on (Kovach, 1995).

In the standard form of PCA, or species centred PCA, each species is implicitly weighted by the variance of its abundance values. Species with high variance dominate the PCA solution; species with low variance have minor influence on the solution (Lepš and Šmilauer, 2003). In standardised PCA, where the abundance of each species is also divided by its standard deviation, all species receive equal weight. However, this may cause rare species to unduly influence the analysis. Standardisation is necessary when analysing variables that are measured in different units. For this reason, quantitative environmental variables are often standardised (ter Braak, 1995). The CANOCO for Windows version 4.5 programme centres and standardises all environmental variables and co-variables to bring their means to zero and their variances to one (Lepš and Šmilauer, 2003).

The results of a PCA analysis are often commonly displayed as a bi-plot where sites are marked by points and species by arrows. Sites or samples that plot close together are similar in species composition and the environments they exist in are assumed to be similar; sites that plot far apart are dissimilar in species composition. The species arrows point in the direction of maximum variation in species abundance and the length of the arrow is proportional to its maximum rate of change. Therefore species that plot far from the origin, at the edge of the diagram, are the most important for indicating site differences, and conversely species that plot near the origin are of minor importance (ter Braak and Prentice, 1988). Points that plot close to the origin have low magnitude of change from the average (Chen, 2006).

RDA

RDA, a constrained form of PCA produces an ordination of the species data in which the axes are constrained to be linear combinations of the environmental variables. The results of RDA can be displayed as a tri-plot, simultaneously displaying samples as points and species and environmental variables as arrows. The interpretation of the tri-plot is similar to that of the bi-plot in PCA. Through using RDA, it is also possible to estimate the correlations between species abundances and environmental variables. Arrows pointing in the same direction have high positive correlation, arrows pointing at right angles have near zero correlation and arrows pointing in opposite directions have high negative correlation. Environmental variables with the longest arrows can be interpreted as the most significant in the analysis (ter Braak and Prentice, 1988).

- **Gradient analysis on data from the test site**

PCA and RDA were carried out on the datasets described above using CANOCO for Windows version 4.5 software. Scaling of ordination scores was based on inter-sample distances. No transformation of species data was performed. The default option of centering by species was chosen, i.e. species means were subtracted from the values in the species data. This is appropriate for almost any linear analysis (Lepš and Šmilauer, 2003). Samples were not standardized or centred. For RDA, Monte-Carlo permutation tests were carried out for each analysis to test the significance of each environmental variable and were combined with automatic forward selection of environmental variables. Only those variables with $p \leq 0.05$ under 499 permutations were deemed significant. The PCA results were plotted using CanoDraw as bi-plots and in the core sample dataset samples from each coring site were colour coded for ease of interpretation. Samples from Coring Site 1 were represented by a blue circle (O), samples from Coring Site 2 by a red cross (+) and samples from Coring Site 3 by a green 'X' (X).

Chapter Five: Results and Analysis

This chapter details the results obtained from the palaeolimnological and limnological analyses carried out on both core and surface samples within the test site. The preliminary analyses of the proxies used for assessing variations in sedimentary components and catchment change are first outlined, followed by the chronological control for the current study. The results of the pollen analysis carried out on subsamples from the sediment cores, in order to determine variations in land use change are then described .The results of the analysis of the spatial variability of TP in the lake are outlined, followed by the analysis of the diatom assemblages identified for the current study. The numerical methods used to address the two research questions are then outlined. The results of the gradient analysis used to assess the spatial variability of the diatom assemblages identified for the surface and core subsamples are first described, followed by the statistical analysis of the drivers of ecological change at the lake. Finally, a summary of the results relating to the eutrophication of the lake is provided.

5.1 Assessing variations in sedimentary components and historical catchment change

Graphs of sediment lithology, variations in % organic content and variations in sediment texture for each coring site are shown in Figure 5.1.

5.1.1 Troels-Smith

Coring Sites 1 and 2 show very little change in sediment composition as shown in Figure 5.1. Both of these cores appeared to consist of fine sand (Grana arenosa), fine detritus mud (Limus humosus) and course and fine detritus (respectively Detritus herbosus and Detritus granosus). The core from site 3 displayed changes in sediment composition at 5 cm, 10 cm and 13 cm. The core changed from a composition of fine detritus mud (Limus humosus) and fine sand (Grana arenosa) to primarily consisting of fine sand (Grana arenosa) at these depths.

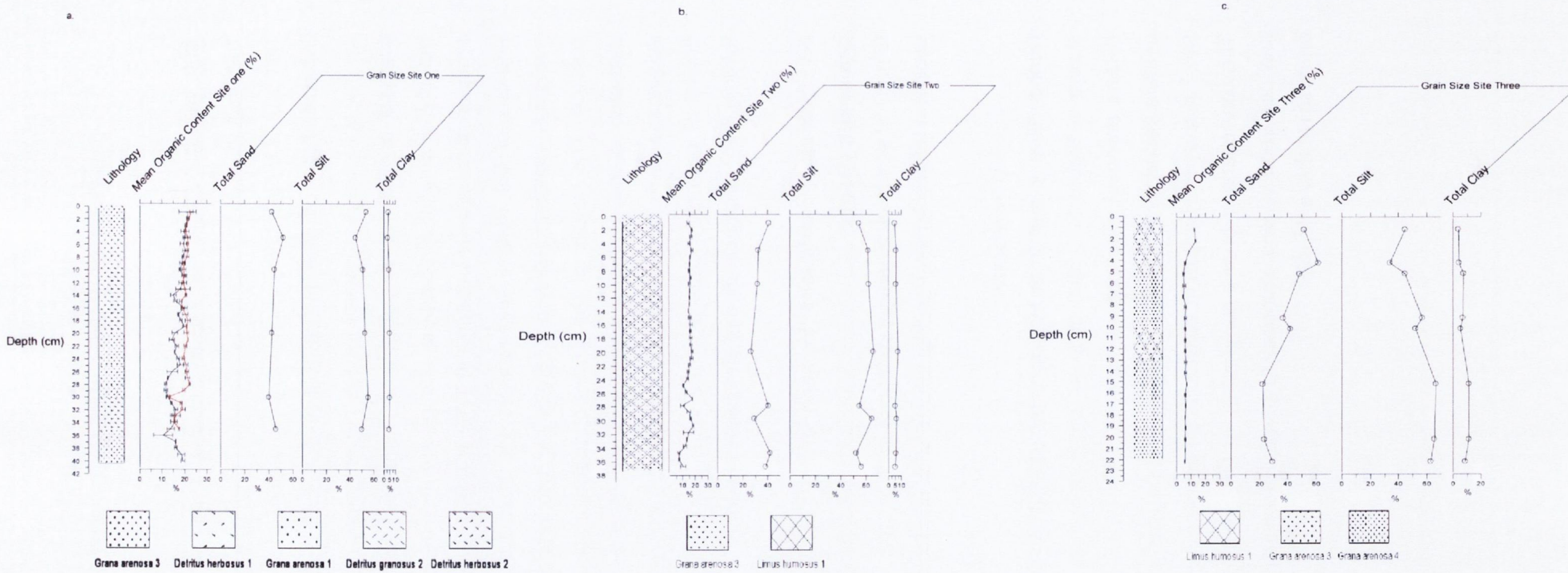


Figure 5.1: Graphs of sediment lithologies, variations in % organic content and variations in sediment texture at: a. Coring Site 1, b. Coring Site 2 and c. Coring Site 3 at Lough Currane

5.1.2 Determination of organic content

The % organic content of surface sediment subsamples, including those from the sediment cores, is shown in Figure 5.2. The organic content of the subsamples was spatially variable within the lake. Organic content ranged from 1 % close to the inlet from the Cummeragh River to 39% close to the inlet from the Capall River. In general, mid-lake sites and sites within the deeper zones of the lake displayed overall higher % organic content than peripheral sites.

In the sediment cores, overall % organic content was highest at Coring Site 1 ranging from 11% to 23%, while the % organic content at Coring Site 2 ranged from 7% to 18% (Figure 5.1). The % organic content at Coring Site 3 was very low, ranging from 5% to 13%. Each core displayed few up-core variations in % organic content. Decreases in % organic content were apparent at 36 cm, 30 cm and 14 cm at Coring Site 1 and at 35 cm, 28 cm and 25 cm at Coring Site 2. At Coring Site 3, % organic content increased steadily from 4 cm to the top of the core (Figure 5.1).

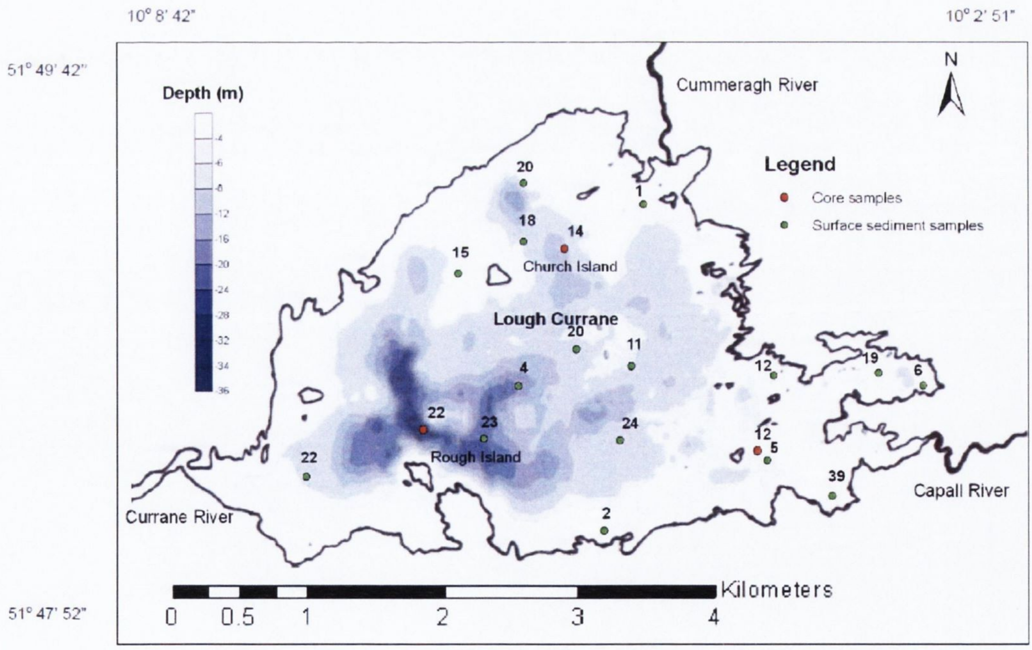


Figure 5.2: The % organic content of surface sediment subsamples at Lough Currane. The bathymetry of the lake is also shown

5.1.3 Sediment texture

Mean grain size (IGM) and the degree of sorting in the sediment (IGSD) for each surface sediment sample including those from the sediment cores are shown in figures 5.3 and 5.4. Highest mean grain size and the most poorly sorted sediment (characterised by lower ø sizes) were found in the shallow sites located closest to the shore while lowest mean grain size and the most well sorted sediment (characterised by higher ø sizes) were found at mid-lake sites. As shown in Table 5.1, a statistically significant relationship was established between distance to the shore and mean grain size ($p = 0.01$) and between distance to shore and SD or the degree of sorting ($p = 0.05$).

All of the sediment cores consisted primarily of sand and silt with relatively small quantities of clay and each coring site displayed generally the same variations in sediment texture as shown in Figure 5.1. Coring Site 1 had the highest mean grain size and the most poorly sorted sediment, while Coring Site 3 had the lowest mean grain size (Figure 5.5). Each core is characterised by an up-core increase in mean grain size, but this trend is more exaggerated at Coring Site 3. The % of total sand also increased steadily toward the top of each core, while the % of total silt decreased (Figure 5.1). Coring Site 2 displayed a peak in total sand and a decrease in total silt at 28 cm, but apart from this displayed a similar trend to the other two coring sites. At Coring Site 3, total sand increased by c.40% between 20 cm and 4 cm while total silt decreased by c.30% between the same depths. The % of total clay remained constant throughout each core at Coring Sites 1 and 2 and at Coring Site 3 decreased steadily toward the top of the core. At Coring Sites 1 and 3 a similar trend was apparent from 5 cm to the top of the cores; there was a decrease in the % of total sand with an increase in the % of total silt (Figure 5.1). At Coring Site 2 there was a slight increase in the % of total sand and a slight decrease in the % of total silt from 5 cm to the top of the core.

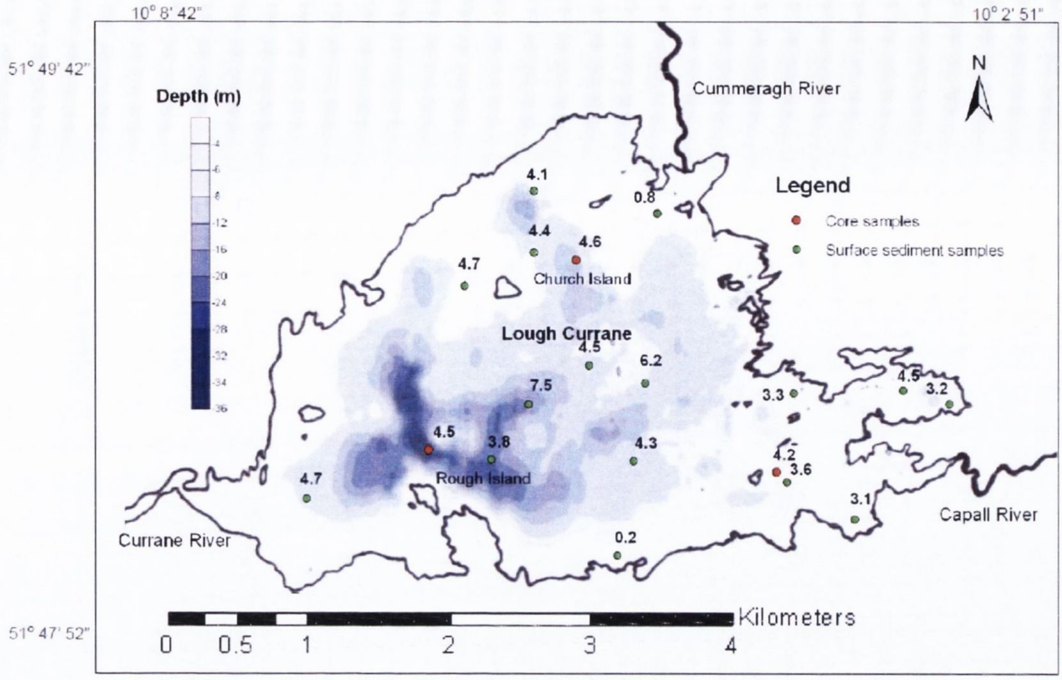


Figure 5.3: Mean grain size (IGM) (ø) of the surface sediment subsamples, including those from sediment cores, at Lough Currane. The bathymetry of the lake is also shown.

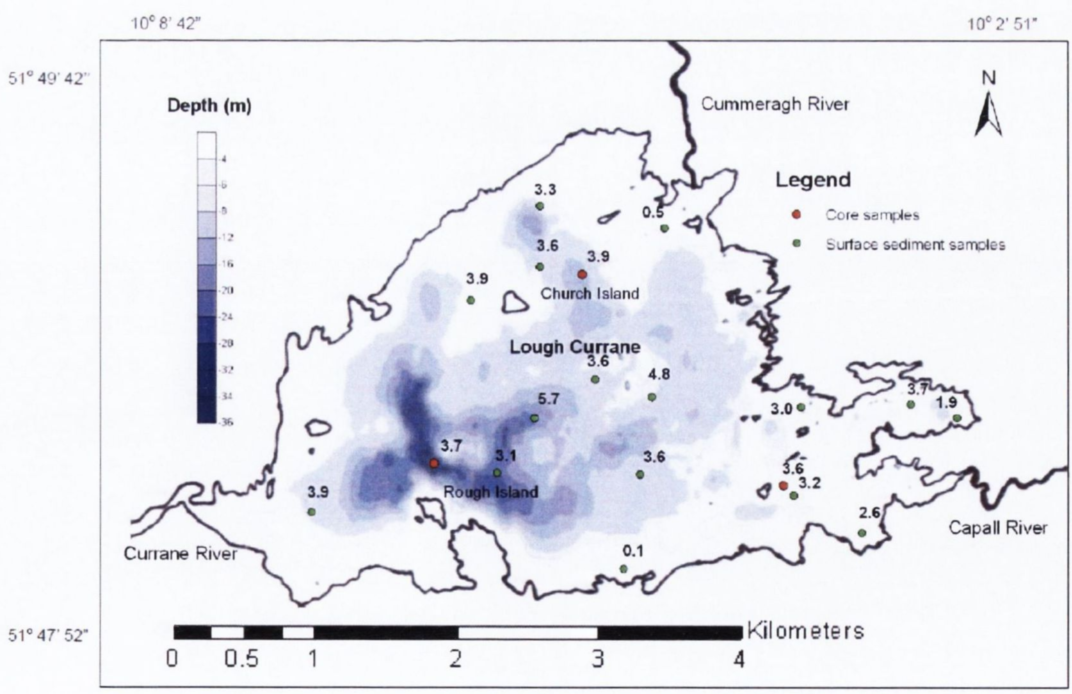


Figure 5.4: Standard deviation (IGSD) (ø) of the surface sediment samples, including those from sediment cores, at Lough Currane. The bathymetry of the lake is also shown.

a. Mean Grain Size

	P	R	R^2
Site depth	0.06	-0.49	0.24
Shore	0.01	-0.62	0.39
Inlet	0.33	-0.26	0.07

b. Sorting

	P	R	R^2
Site depth	0.18	-0.36	0.13
Shore	0.05	-0.49	0.24
Inlet	0.39	-0.23	0.05

Table 5.1: Results of the correlation carried out between a. mean grain size and b. the degree of sorting of the sediment and morphometric parameters at Lough Currane

5.2 Chronological control

5.2.1 ^{210}Pb dating

5.2.1.1 Coring Site 1

As illustrated in Figure 5.6, excess ^{210}Pb in Coring Site 1 displays an exponential decline with depth, with levels of activity decreasing from 60.9 DPM g^{-1} in the surface sample to 1.8 DPM g^{-1} in the basal core sample. Background levels of ^{210}Pb activity were reached at 26 cm. Due to irregularities in the dry bulk density profile from 28 cm to 40 cm and substantially lower ^{210}Pb activity in the basal sample, there was concern that this portion of the core was from a different sediment source or had been subject to reworking. With background levels at 26 cm the age of the 1963 ^{137}Cs peak was correctly predicted. Given that there were irregularities in the excess ^{210}Pb and dry bulk density profiles as a function of depth, the CRS model was applied to seven samples from Coring Site 1. According to the CRS model results, the average sediment accumulation rate for the uppermost 9 cm of the core was 0.025 g cm^{-2} $year^{-1}$. There were no substantial up-core variations in dry bulk density from 9 cm to 26 cm at Coring Site 1, so with knowledge that inaccuracies in ^{210}Pb dates can occur at older ages, the CRS model was extended to include samples from 1 cm to 19 cm (^{14}C dates were provided for subsamples positioned deeper in the core).

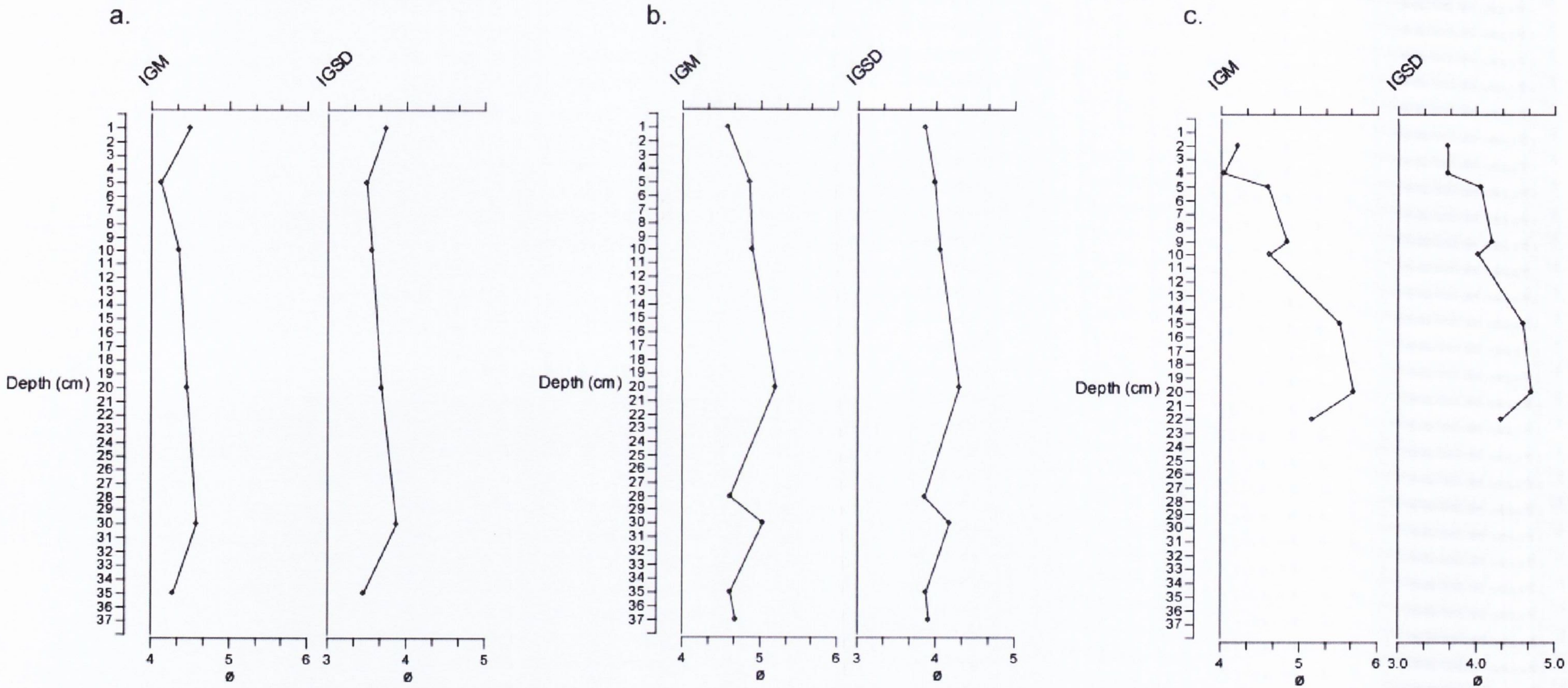


Figure 5.5: Up-core variations in IGM and IGSD at Lough Currane a: Coring Site 1, b: Coring Site 2 and c: Coring Site 3

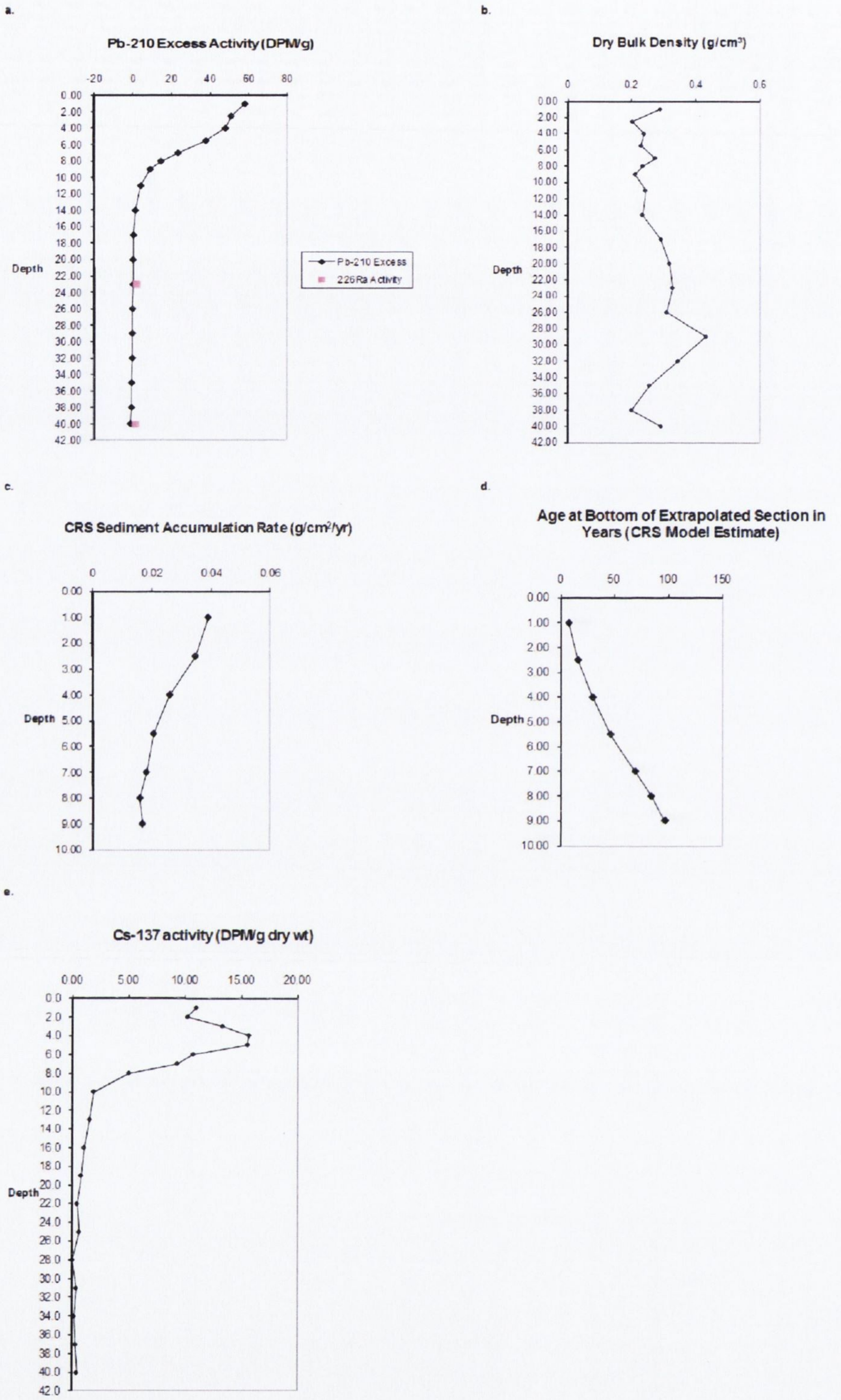


Figure 5.6: Lough Currane Coring Site 1 ^{210}Pb and ^{137}Cs results: a. Excess ^{210}Pb activity (DPM g^{-1}), b. Dry bulk density (g cm$^{3-1}$), c. CRS accumulation rate (g cm^{2} yr-^{1}), d. Age at bottom of extrapolated section in years (CRS Model Estimate) and e. ^{137}Cs Activity (DPM g^{-1} dry weight)

5.2.1.2 Coring Site 3

As illustrated in Figure 5.7 the core from site 3 displays an exponential decline in excess ^{210}Pb from the surface sample to 4 cm with levels of activity decreasing from 27.3 DPM g^{-1} in the surface sample to 2.4 DPM g^{-1} at 4 cm. Excess ^{210}Pb activity remains very low from 5 cm to 22 cm apart from a slight increase in activity at 10 cm. The average of excess ^{210}Pb activity from 5 cm to 22 cm was 0.47 DPM g^{-1}. Due to an exponential decline in ^{210}Pb activity from the surface sample to 4 cm the CIC model was applied to this section only. The CIC model predicts an average sediment accumulation rate of 0.011 g cm^{-2} yr^{-1} over the modelled range.

5.2.2 Validating the ^{210}Pb profile

Figure 5.8 shows the SCP records at Lough Currane and at Upper Killarney Lough. The SCP record at Upper Killarney Lough is described in O'Dwyer and Taylor (2010). Given the proximity of the two sites (c.40 km apart) and the absence of major local point sources of SCPs, Lough Currane and Upper Killarney Lough are expected to share similar SCP deposition profiles. Thus the radiometrically dated, relatively high resolution SCP record from Upper Killarney Lough is used here as the basis for verifying chronological control for Lough Currane.

At Lough Currane, SCP concentration was highest at Coring Site 1, the deepest site and was lowest at Coring Site 3, the shallowest site. The SCP records display the characteristic features seen in lake sediment cores throughout Europe including the rapid increase in SCP concentration and the SCP concentration peak (Rose, 2001). The beginning of the SCP record (c.1900 AD) occurs at 10 cm at Coring Site 1 and 16 cm at Coring Site 2. SCP concentration was very low at Coring Site 3 and the beginning of the record was not displayed. However, the peak and subsequent decline in SCP concentration occurs at the same depth at each site, at respectively 4 cm (c.1980 AD) and 2 cm. A second peak in SCP concentration occurs at 1 cm, corresponding to the mid 1990s in the Upper Killarney record.

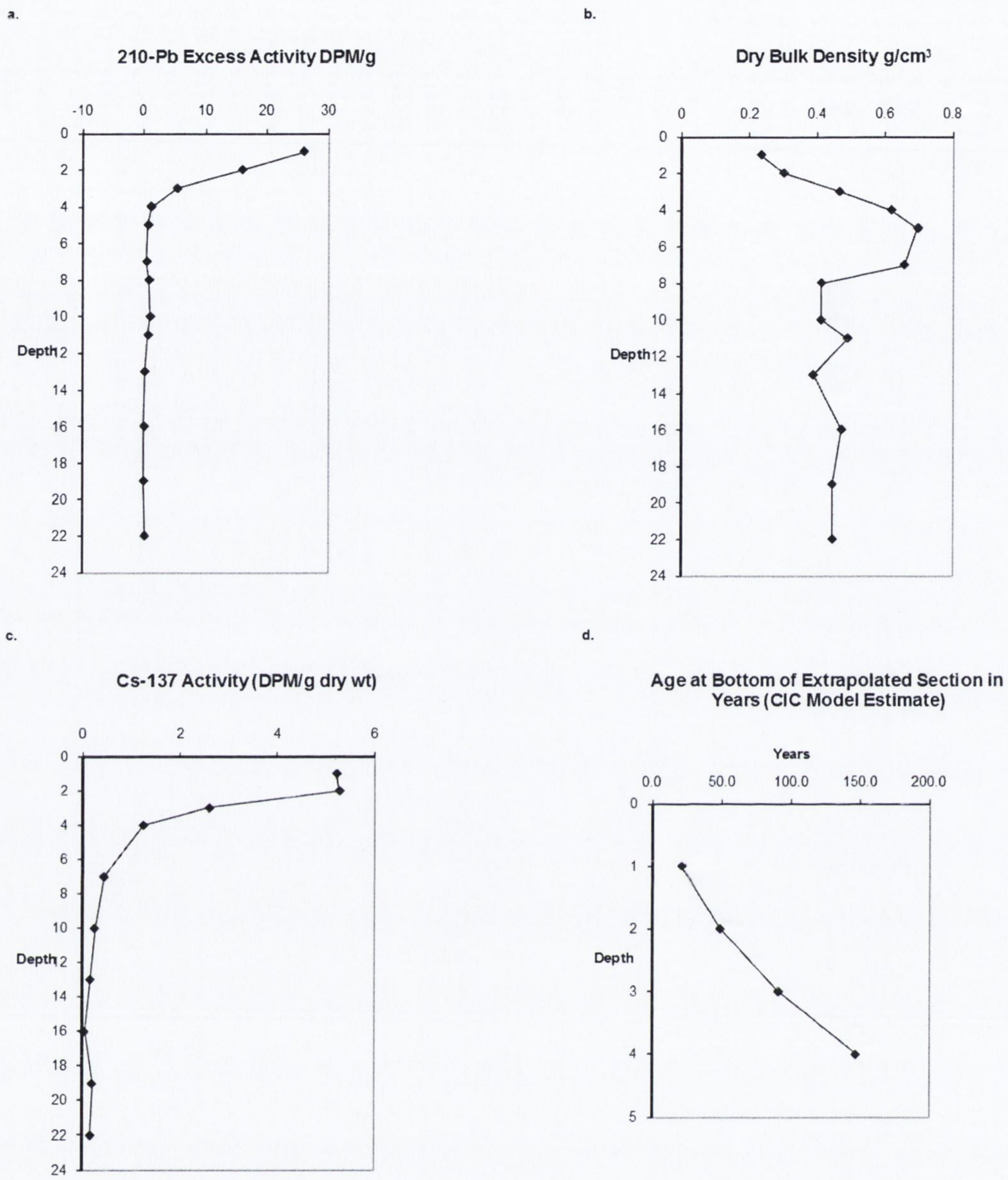


Figure 5.7: Lough Currane Coring Site 3 ^{210}Pb and ^{137}Cs results: a. Excess ^{210}Pb activity (DPM g^{-1}), b. Dry bulk density (g cm^{3-1}), c. ^{137}Cs Activity (DPM g^{-1} dry weight) and d. Age at bottom of extrapolated section in years (CIC Model Estimate).

^{137}Cs activity at Coring Site 1 displays a sharp increase at 10 cm and peaks at 5 cm (Figure 5.6). On initial inspection, the ^{137}Cs profile at Coring Site 1 displays only one peak. Typical ^{137}Cs profiles in the northern hemisphere display two peaks in ^{137}Cs activity, a 1963 peak associated with weapons testing and a 1986 peak associated with the Chernobyll reactor fire (Bjorck and Wohlfarth, 2001). The interpretation of the ^{137}Cs record can be difficult in water bodies with sediment accumulation rates of < 1 cm^{-2} yr^{-1} due to sampling problems. If sediment accumulation is low, sampling of horizons in the detail necessary to determine up-core variations in ^{137}Cs activity is difficult (Ritchie and McHenry, 1990). Both 5 cm and 4 cm displayed high levels of ^{137}Cs activity. Due to the relatively low sediment accumulation rate determined via the CRS model, the high levels of ^{137}Cs activity at 5 cm and 4 cm may represent both the 1963 and 1986 peaks in ^{137}Cs activity. According to the CRS model, 5 cm corresponds to c.1959 AD, while 4 cm corresponds to c.1976 AD.

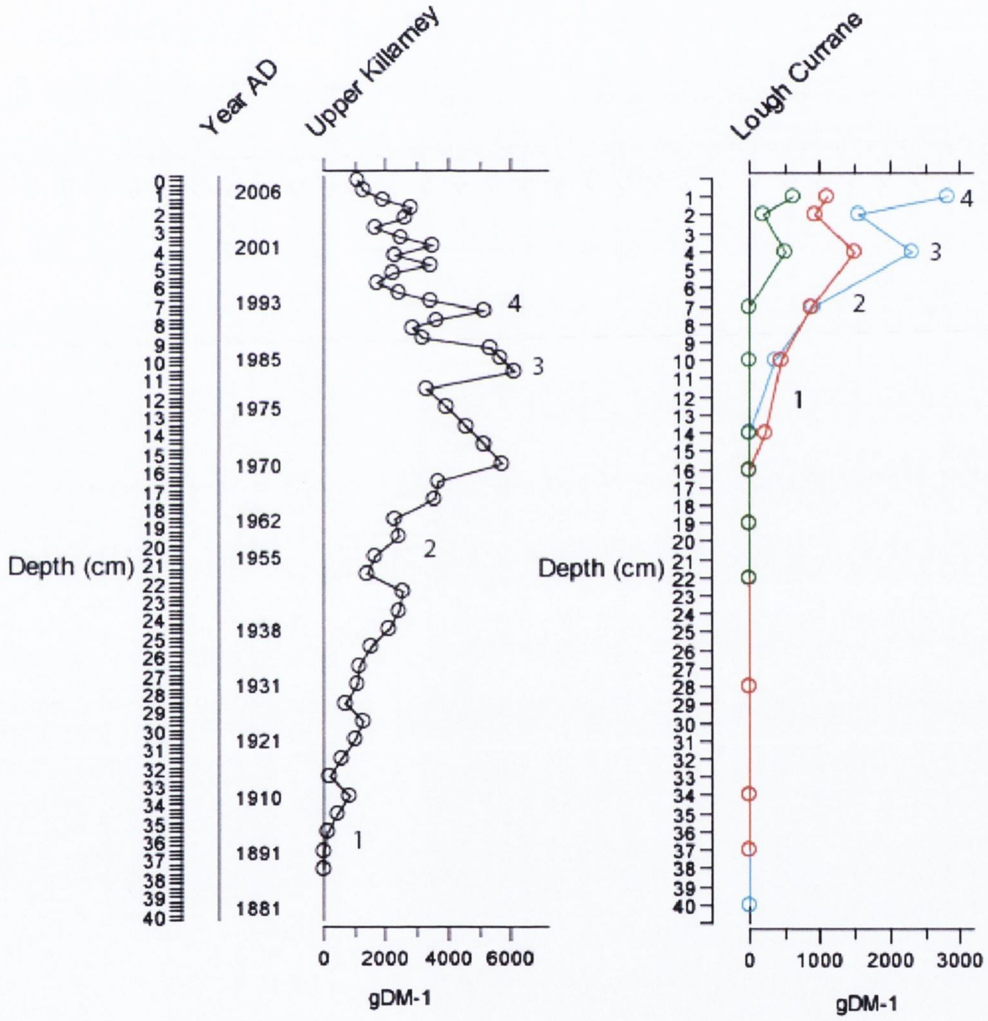


Figure 5.8: Up-core variations in SCP concentrations at Upper Killarney Lough (from O'Dwyer and Taylor 2010) and Lough Currane, Coring Site 1 (blue), Coring Site 2 (red) and Coring Site 3 (green). 1: the start of the SCP record, 2: the rapid increase in SCP concentration, 3: the peak in SCP concentration and 4: the second peak in SCP concentration.

Figure 5.9 shows that the ^{210}Pb record from Coring Site 1 was successfully validated using SCP and ^{137}Cs analyses. The peak in SCP concentration at Coring Site 1 at 4 cm (c.1980 AD) corresponds to a CRS date of c.1976 AD and the second peak in ^{137}Cs activity (1986) as shown in Figure 5.9. In addition, the beginning of the SCP record at Lough Currane at 10 cm (c.1900 AD) corresponds to a CRS date of 1886 AD ± 11 years.

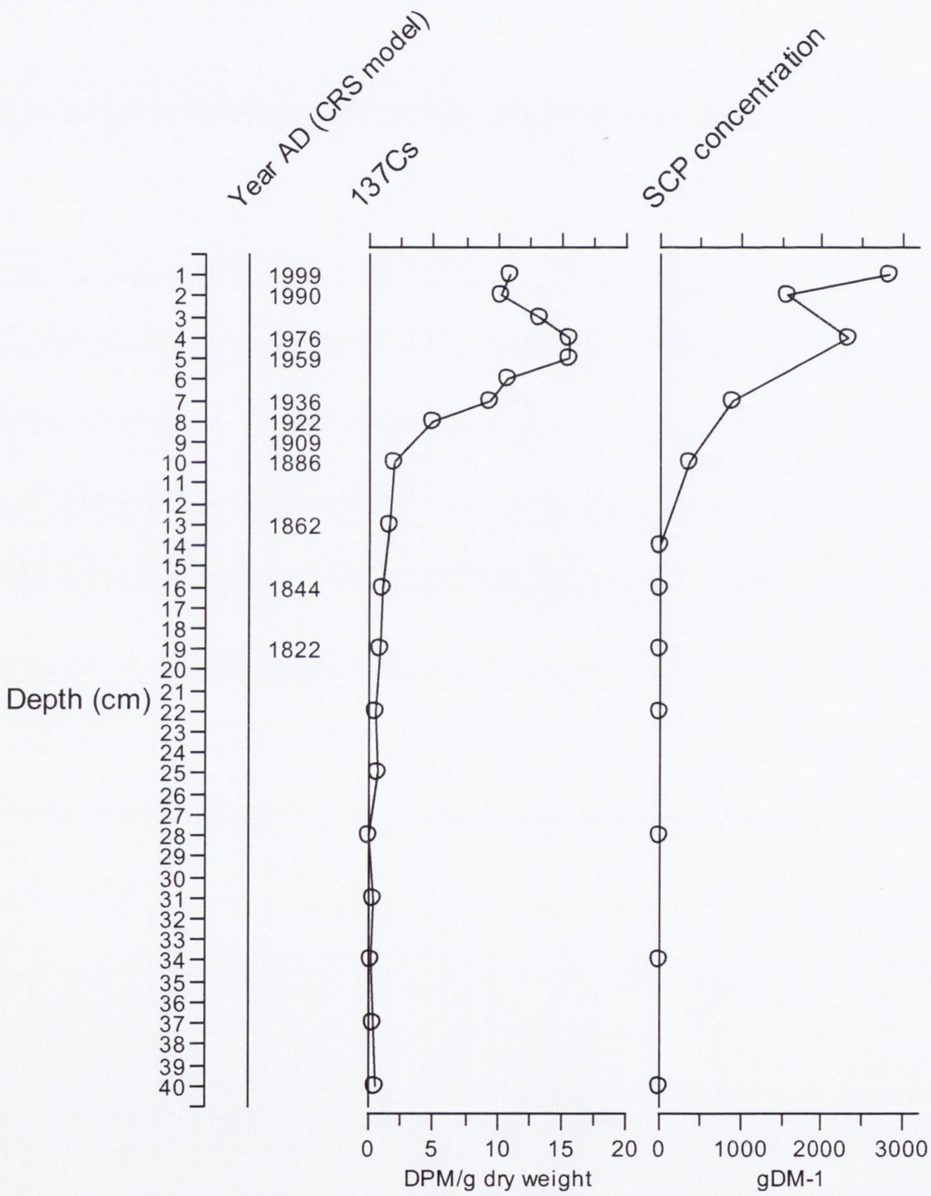


Figure 5.9: ^{210}Pb dates and up-core variations in ^{137}Cs activity and SCP concentration at Lough Currane Coring Site 1

The validity of the ^{210}Pb profile at Coring Site 3 was questioned. The peak in SCP concentration at 4 cm (c.1980) (Figure 5.10) corresponds to a ^{210}Pb date of c.1859 according to the CIC model as shown in Figure 5.10. The ^{137}Cs activity profile at Coring Site 3 indicates that the 1963 ^{137}Cs peak occurs at 2 cm (Figure 5.7) and the CIC model estimates an age of 49 years at 2 cm. ^{137}Cs activity is very low between 9 cm and 22 cm depth (Figure 5.7). However, the SCP data from Coring Site 3 suggests that the peak in ^{137}Cs activity at Coring Site 3 (2 cm) represents the 1986 Chernobyl peak in ^{137}Cs activity. The peak in SCP concentration occurs at 4 cm, corresponding to c.1980 AD while the second peak in SCP concentration occurs at 1 cm, corresponding to the mid 1990s. The peak in ^{137}Cs activity occurs between these two peaks in SCP concentrations, placing its date between c.1980 AD and the mid 1990s. Similar to Coring Site 1, the ^{137}Cs activity profile at Coring Site 3 displays only one peak in ^{137}Cs activity, but this may also be due to sampling problems, owing to the low sediment accumulation rate at the coring site. In the core from site 3, samples for the analysis of ^{137}Cs activity were taken at 7 cm and 4 cm. Based on the SCP chronology, it is likely that the 1963 ^{137}Cs peak would occur between these depths.

5.2.3 ^{14}C dating

The results of the ^{14}C dating of bulk sediment from Coring Sites 1 and 2 are illustrated in Table 5.2. The conventional radiocarbon age was used for interpretation. At site 1, the results indicate that 22 cm corresponds to c. 640 AD (1370 ± 40 BP) while 32 cm corresponds to c.240 AD (1760 ± 40 BP). At Coring Site 2 the results indicate that 22 cm corresponds to c.470 AD (1530 ± 40 BP) and 32 cm corresponds to c.640 AD (1370 ± 40 BP). Bulk sediment samples can yield ^{14}C dates that are erroneously old due to the presence of older C in the sediment matrix that has been reworked (Björck et al., 1998). For example, Bjorck et al. (1998) reported a mean difference of c.300 years between ^{14}C dates obtained from bulk sediment samples and ^{14}C dates obtained from terrestrial macrofossils in Sweden, while Grimm et al. (2009) reported errors of 500 to 2000 years in the ^{14}C dates obtained from bulk sediment samples in lakes in central North America. The radiocarbon dates provided for Lough Currane are probably subject to larger errors than stated due to the fact that bulk sediment samples were used for dating.

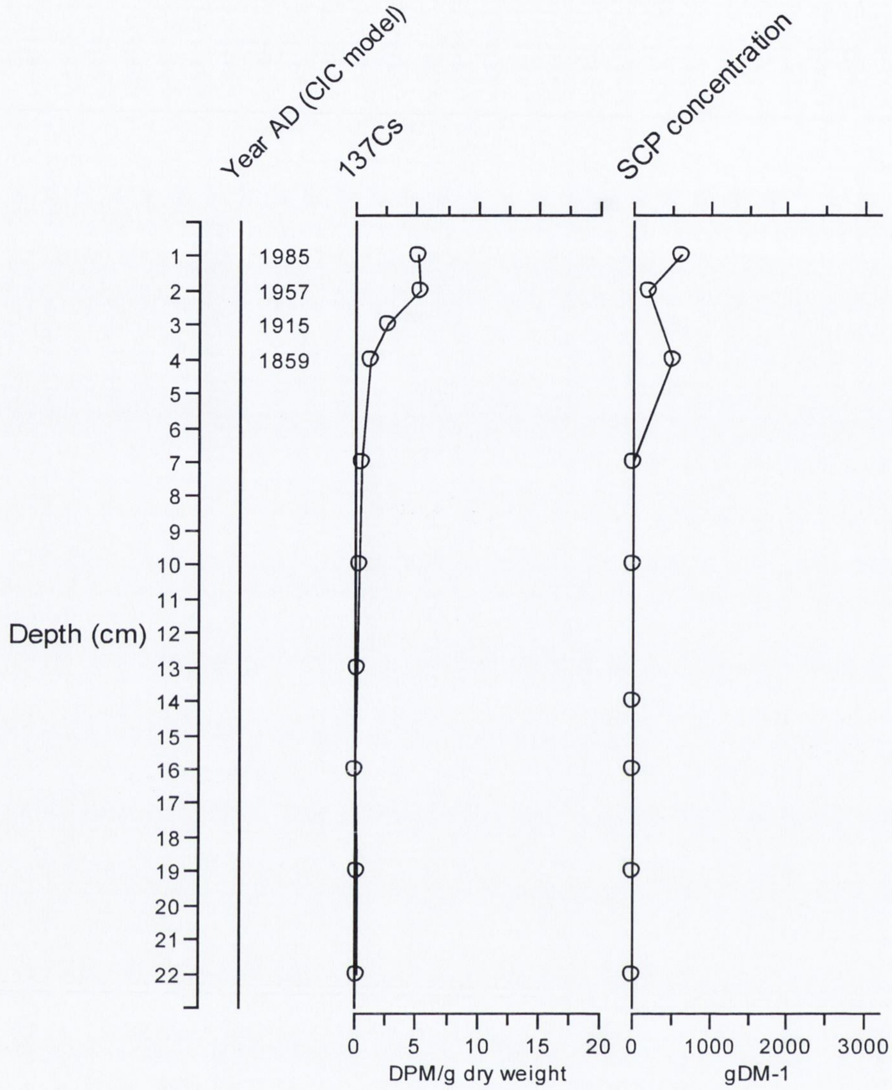


Figure 5.10: ^{210}Pb dates and up-core variations in ^{137}Cs activity and SCP concentration at Lough Currane Coring Site 3

5.2.4 Final chronologies used for the current research

5.2.4.1 Inter-core correlation

Up-core variations in SCP concentrations and % organic content were used in order to correlate between cores. Figures 5.11 and 5.12 show respectively, the SCP and % organic content profiles for each coring site in Lough Currane. The start of the SCP record and the peak and subsequent decline in SCP concentration (numbered 1 to 3 in Figure 5.11) were used as markers for cross-correlating the upper portions of the cores while the variations in % organic content (numbered 1 to 10 in Figure 5.12), were used for cross-correlating the lower portions of the cores.

Coring site one

Sample ID	Lab Reference Number	Type of Material	$^{13}C/^{12}C$ Ratio	Measured Radiocarbon Age	Conventional Radiocarbon Age	Two Sigma Calibrated Result: Calender Year AD
22cm	Beta 251497	Organic sediment	-26.5 o/oo	1390 ± 40 B P	1370 ± 40 B P	610 to 690
32cm	Beta 245604	Organic sediment	-26.7 o/oo	1790 ± 40 B P	1760 ± 40 B P	140 to 390

Coring site two

Sample ID	Lab Reference Number	Type of Material	$^{13}C/^{12}C$ Ratio	Measured Radiocarbon Age	Conventional Radiocarbon Age	Two Sigma Calibrated Result: Calender Year AD
22cm	Beta 248402	Organic sediment	-26.3 o/oo	1550 ± 40 B P	1530 ± 40 B P	420 to 610
32cm	Beta 248403	Organic sediment	-26.0 o/oo	1390 ± 40 B P	1370 ± 40 B P	610 to 690

Table 5.2: Results from the ^{14}C dating of samples from Lough Currane Coring Site 1 and Coring Site 2

These variations in SCP concentration and % organic content were matched between core 1 from Coring Site 1 and the other cores in the lake. For example, a marked decline in % organic content (marker 2 in Figure 5.12) at 36cm in core 1 from Coring Site 1 corresponds to a decline in % organic content at 30 cm in core 2 from Coring Site 1 and at 28 cm in the core from Coring Site 2. The plots used for inter-core correlation are shown in Appendix F and display the matched depths at which there were variations in SCP and % organic content and the linearly interpolated trend lines between these depths.

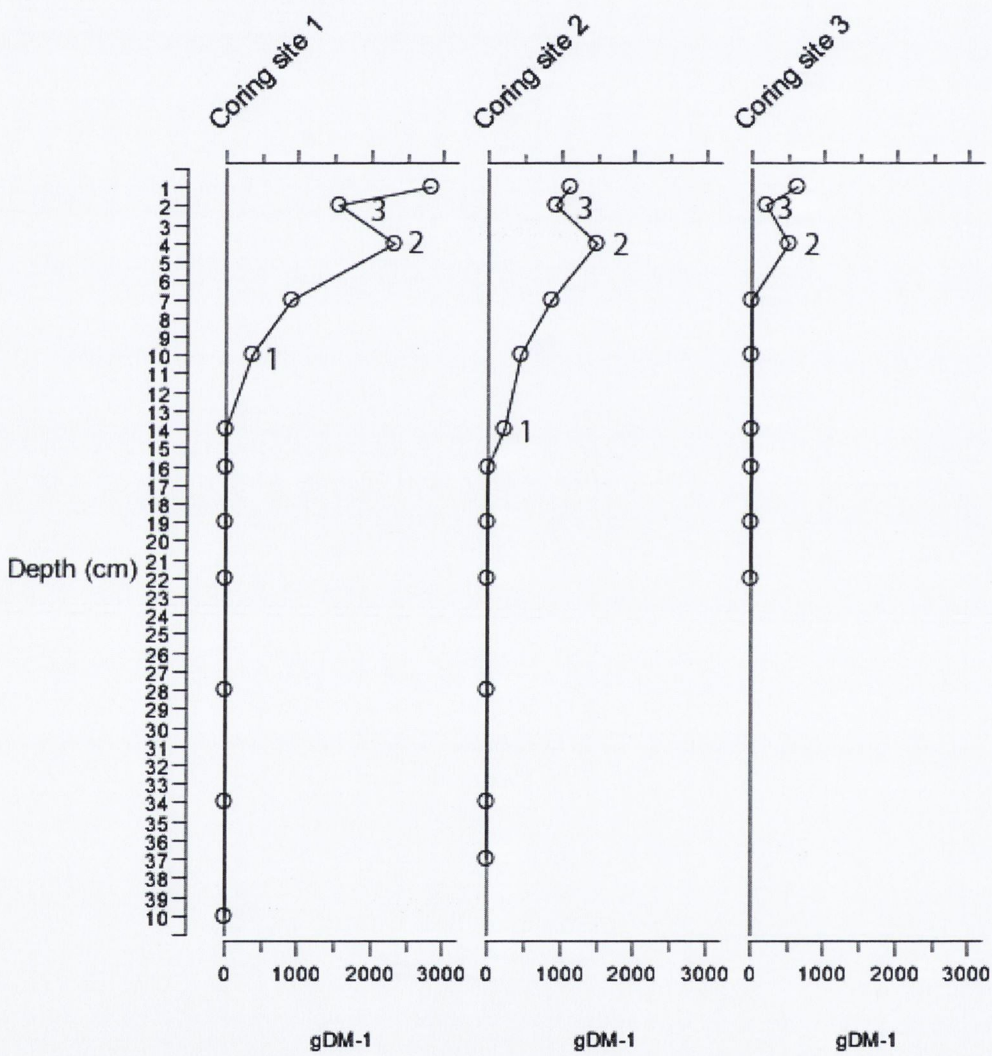


Figure 5.11: Up-core variations in SCP concentration at each Coring Site within Lough Currane and the markers used for cross-correlation. 1: the beginning of the SCP record, 2: the peak in SCP concentrations, 3: the decline in SCP concentrations

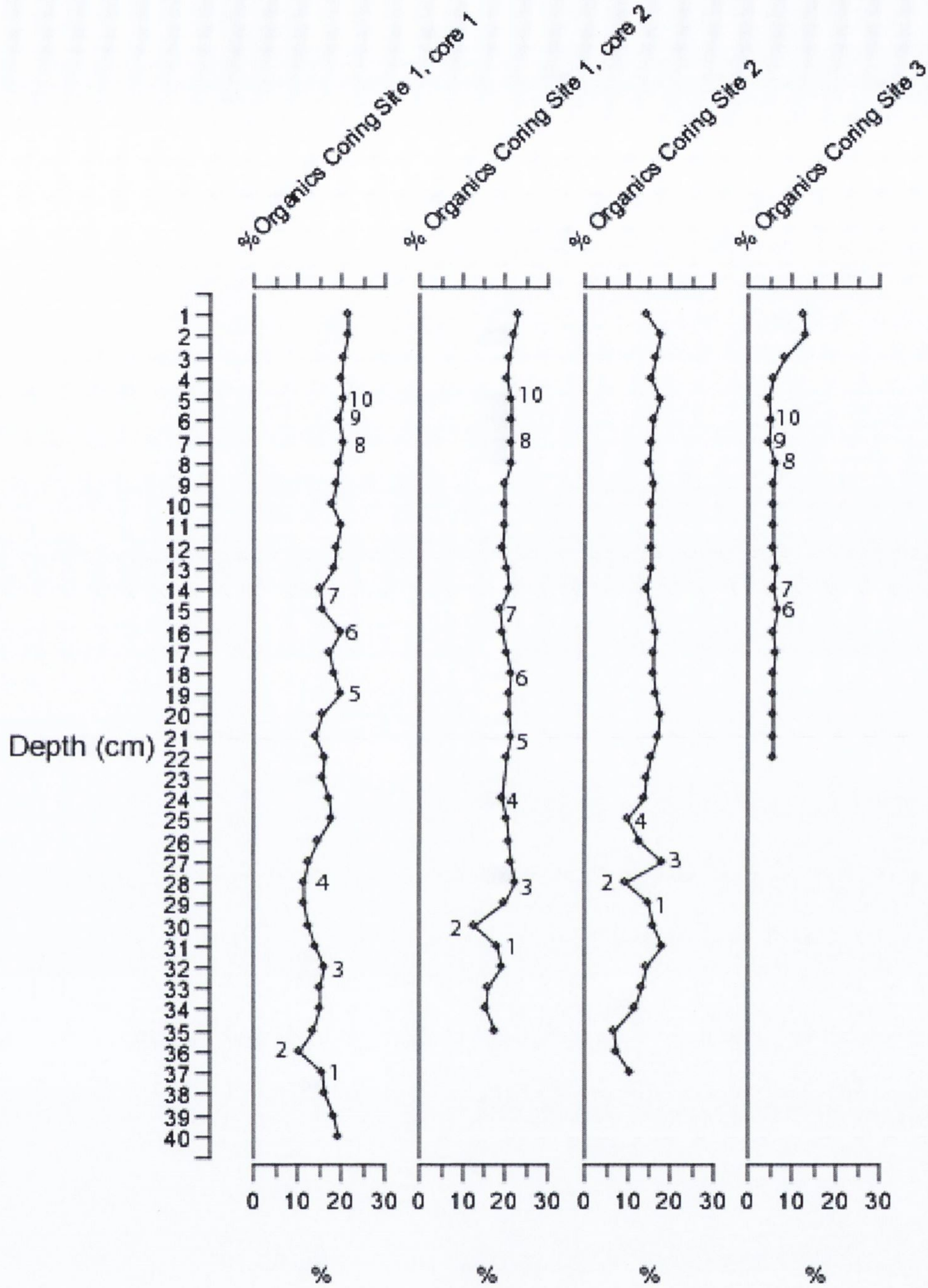


Figure 5.12: Up-core variations in % organic content at each coring site in Lough Currane and the markers used for inter-core correlation.

5.2.4.2 Chronology used for the current research

The chronology provided by the CRS model was successfully calibrated at Coring Site 1 via the analysis of ^{137}Cs and SCPs. Since the chronology provided by the CIC model at Coring Site 3 was not validated and since the SCP records at each site were almost identical, following cross-correlation the

CRS dates from Coring Site 1 were extended to the other two coring sites. The ^{14}C dates provided for Coring Site 2 show older material overlying younger material. These dates appear to be subject to large errors as outlined previously, and could not be used to provide a chronology for each 1 cm subsection in the core. The % organic content profile is similar in the lower half of the cores from Coring Sites 1 and 2 (Figure 5.12). Based on this similarity, ^{14}C dates for Coring Site 1 were also extended to Coring Sites 2 and 3, following inter-core correlation.

The depth-age graphs for each sediment core used for the analysis of sedimentary components are shown in Appendix G. Linear interpolation was used to provide a chronology for each 1 cm subsection between the measured ^{210}Pb and ^{14}C dates. The dates provided by the CRS model represent the period from 1822 AD to the present; while the dates provided by ^{14}C dating represent samples older than 184 years (c.1822 AD). All of the depth-age graphs display a substantial increase in the age of sediment subsections between the last measured ^{210}Pb date (c.1822 AD) and the first ^{14}C date (c.640 AD). This increase in sediment age is probably erroneously high due to the large errors associated with the ^{14}C dates. Due to the fact that the measured ^{14}C dates are likely to be erroneously old, dates for samples stated as older than 184 years (c.1822 AD) are also subject to large errors and should be treated with caution. Since the chronology provided by the CRS model was successfully validated, the dates provided for subsamples dated from c.1822 AD to the present were deemed to be relatively accurate.

5.3 Assessing catchment land use change

5.3.1 Pollen analysis

Up-core variations in the relative abundances of pollen and spores at the three coring sites within Lough Currane are shown in figures 5.13 to 5.15. High abundances of herbaceous pollen namely Poaceae, arboreal pollen such as *Alnus, Betula* and *Quercus* and spores from lower plants such as *Pteridium* characterise the profiles from each coring site.

5.3.1.1 Coring Site 1

A total number of 30 pollen and spore types were encountered in subsamples from Coring Site 1. Maximum and minimum pollen counts were respectively, 327 and 302. The maximum and minimum pollen concentration values were

428 and 89 grains x10^{-3} respectively. Damaged grains accounted for between 9% and 22% of the total pollen sum in all samples counted. Up-core variations in the relative abundance of pollen were apparent and the results of the numerical zonation identified two statistically significant pollen assemblage zones.

The lowermost zone, S1-1, from the base of the core to c.1840 AD is characterised by abundances of arboreal and herbaceous pollen such as *Alnus*, *Betula* and Poaceae. A peak in the abundance of *Betula* is apparent in c.380 AD coinciding with decreases in the abundance of pollen from shrubs namely *Calluna* and *Corylus* and in the aquatic *Isoetes*. Pollen concentrations begin to increase in c.380 AD also.

The uppermost zone, S1-2, from c.1830 AD to 2006 AD is characterised by a decrease in the abundance of Poaceae. The abundance of Poaceae increases sharply c.2000 AD however. *Alnus* reaches a peak in c.1840 AD but its abundance subsequently declines. In S1-2 there is also a slight increase in the abundance of pollen from lower plants, namely Polypodiaceae. There is also a gradual increase in the abundance of *Pinus* from c.1950 AD and its abundance peaks c.2000 AD. Pollen concentrations fluctuate in S1-2 and decrease from c.1980 AD to 2006 AD.

5.3.1.1 Coring Site 2

Twenty-seven pollen and spore types were encountered in subsamples from Coring Site 2. Counts ranged from 301 to 315. The maximum and minimum pollen concentration values were 224 and 61 grains x 10^{-3}, respectively. Damaged grains accounted for between 7 % and 13% of the total pollen sum in all subsamples counted. The numerical zonation of the assemblages from Coring Site 2 identified two statistically significant zones.

The lowermost zone, S2-1, from the base of the core to c.1930 AD, similar to site 1, is characterised by high abundances of arboreal and herbaceous pollen. Up-core variations in pollen, spores and pollen concentrations are minimal. Despite differences in the locations of assemblage zone markers, there are some similarities in the pollen assemblage profiles between Coring Site 1 and Coring Site 2. Both profiles display a decrease in the abundance of Poaceae in c.1840 AD and a decrease in the abundance of *Betula* between c.400 AD and c.500 AD.

The uppermost zone, S2-2, from c.1930 AD to the top of the core is characterised by an increase in herbaceous pollen, especially in the abundance of Poaceae. There is a decrease in arboreal pollen such as *Alnus* in c.1950 AD followed by a steady increase after this date. Pollen concentrations decrease from c.1920 AD to 2007 AD.

5.3.1.2 Coring Site 3

A total number of 18 pollen and spore types were encountered in subsamples from Coring Site 3, and maximum and minimum pollen counts were respectively, 309 and 3. There was virtually no pollen present from the base of the core to 7 cm. The maximum and minimum pollen concentration values were 125 and 0.75 grains x $10^{-3,}$ respectively. Damaged grains accounted for between 11% and 29% of the total pollen sum in all subsamples counted. No statistically significant zones were found in the assemblage from Coring Site 3.

High abundances of herbaceous pollen namely Poaceae, arboreal pollen such as *Alnus, Betula* and *Quercus* and spores from lower plants such as *Pteridium* characterise the profile. A steady increase in the abundance of arboreal pollen and a steady decrease in the abundances of lower plants occur from c.1950 AD to 2007 AD. Pollen concentrations are low from the base of the core to c.1950 AD, increasing after this date. The peak in pollen concentration at Coring Site 3 in c.2000 AD coincides with the peak in % organic content at the same date.

5.3 Temporal and spatial water quality variations at Lough Currane

5.3.1 Analysis of TP

Maps displaying TP levels in surface water samples obtained on April 29th 2010 and average TP recorded by Kerry County Council in the period from 2001 to 2009 are shown in Figure 5.16. Both maps show that highest TP readings have been found in the south-west section of the lake close to the outlet of the Currane River. Maximum and minimum TP levels recorded in April 2010 were, respectively, 172 µg l^{-1} and 5 µg l^{-1}. Overall lowest TP levels in the samples collected in April 2010 were in the south-east section of the lake close to the inlet from the Capall River. Low levels of TP were also found at mid-lake sites. The average TP results from Kerry County Council show high TP levels at the inflows from the Cummeragh and Capall Rivers and low TP levels at mid-lake sites.

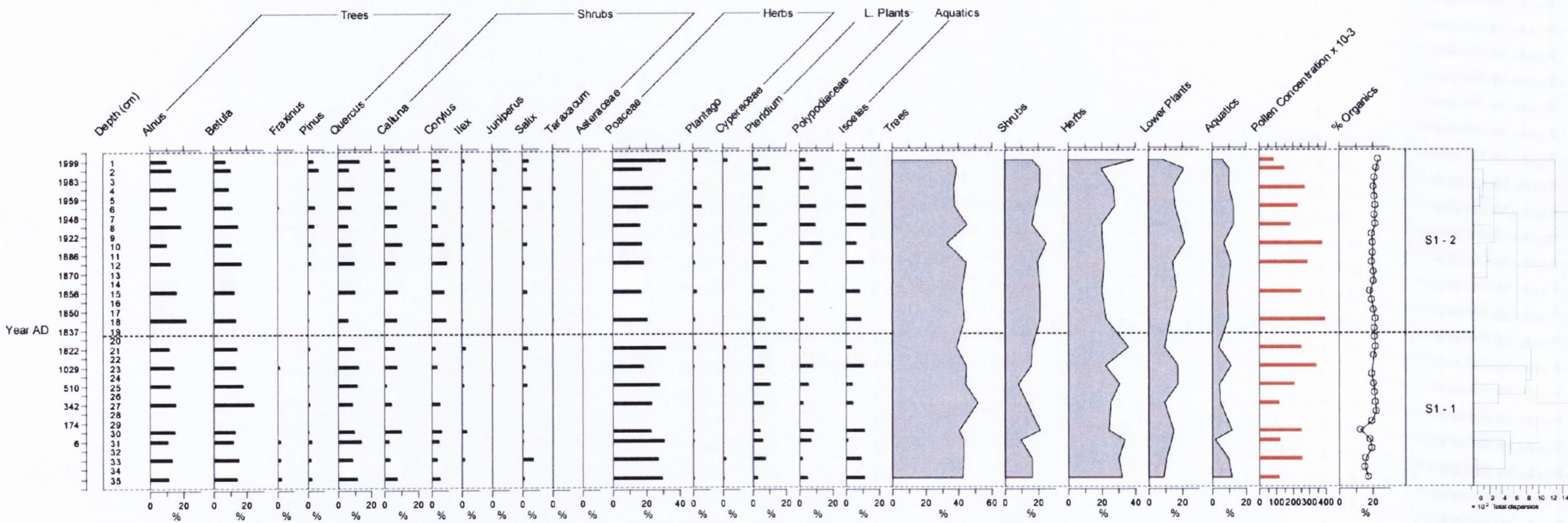


Figure 5.13: Relative abundances of pollen at Lough Currane Coring Site 1. Only taxa with relative abundances > 2 % are included in the diagram. Zones were obtained by CONISS

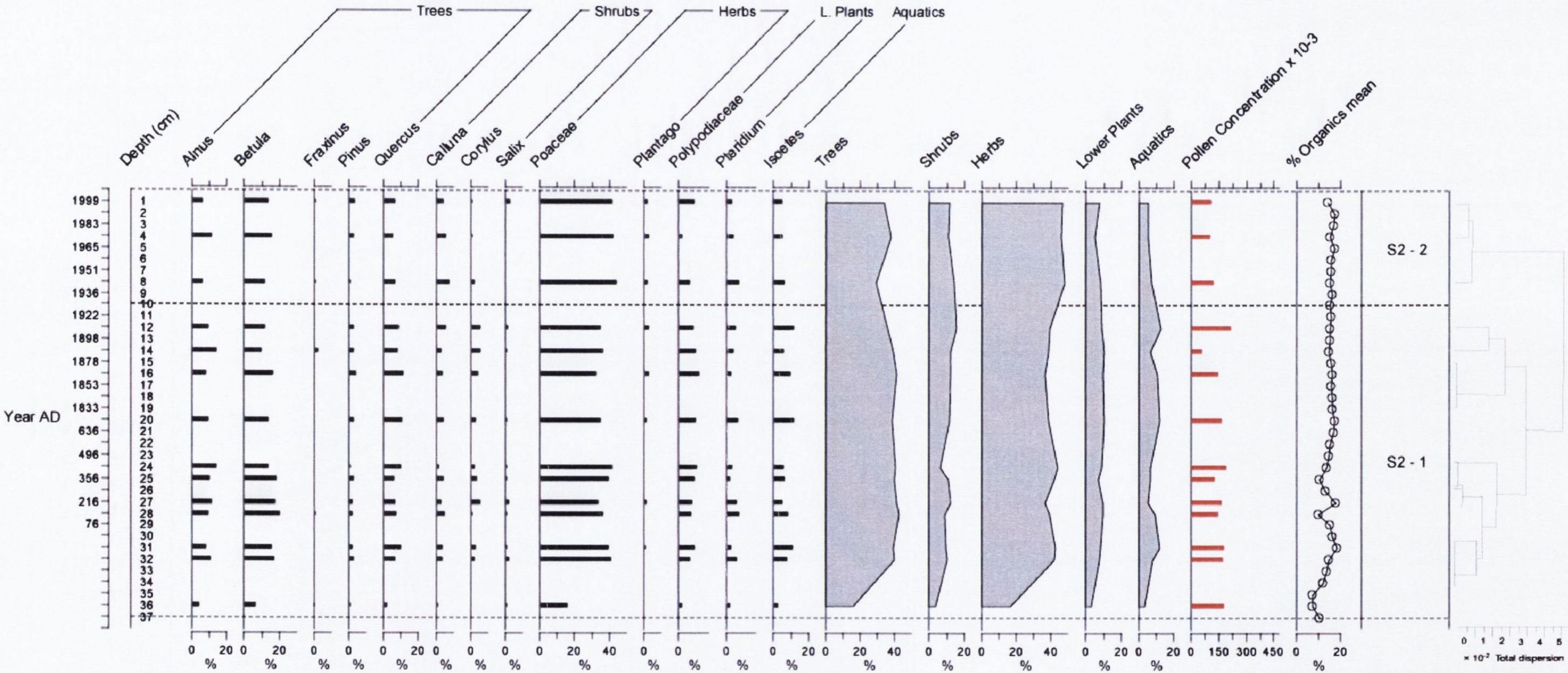


Figure 5.14: Relative abundances of pollen at Lough Currane Coring Site 2. Only taxa with relative abundances of > 2 % were included in the diagram. Zones were obtained by CONISS

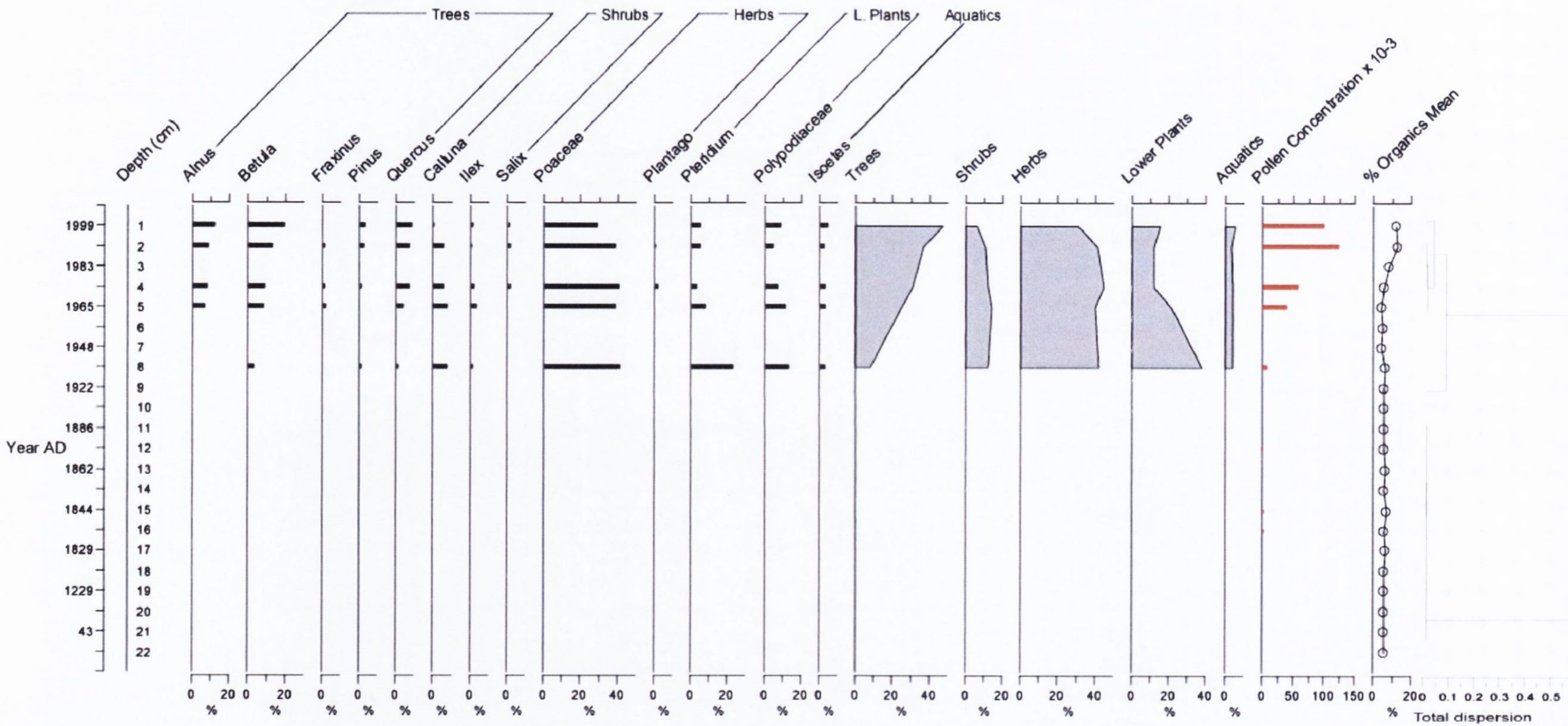
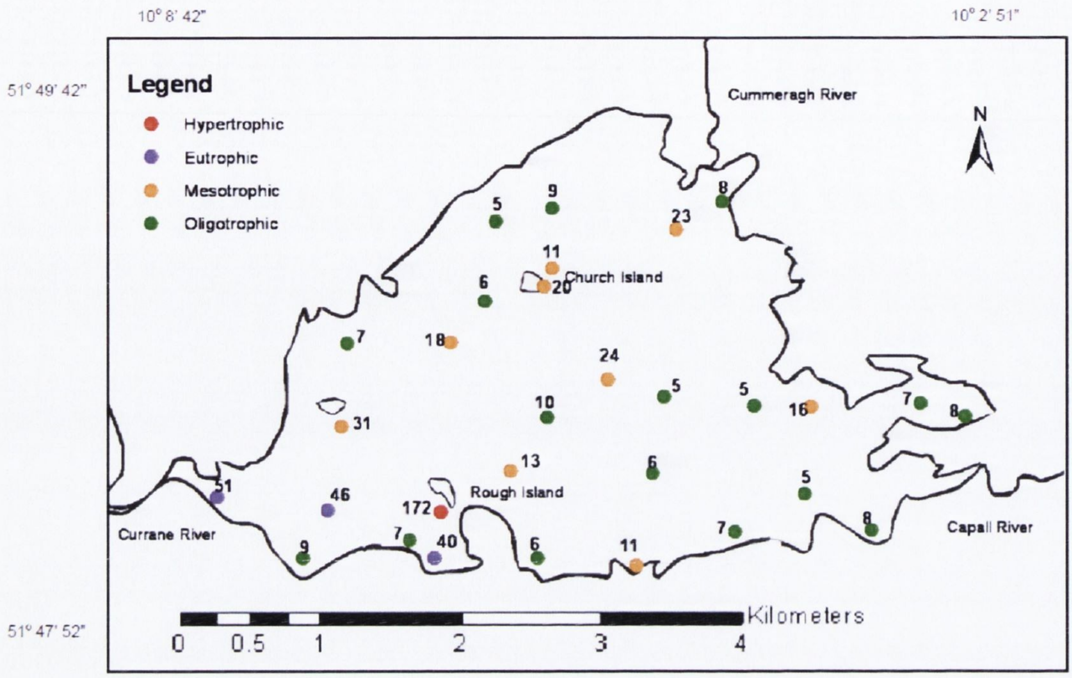


Figure 5.15: Relative abundances of pollen at Lough Currane Coring Site 3. Only taxa with relative abundances of > 2% were included in the diagram.

a.



b.

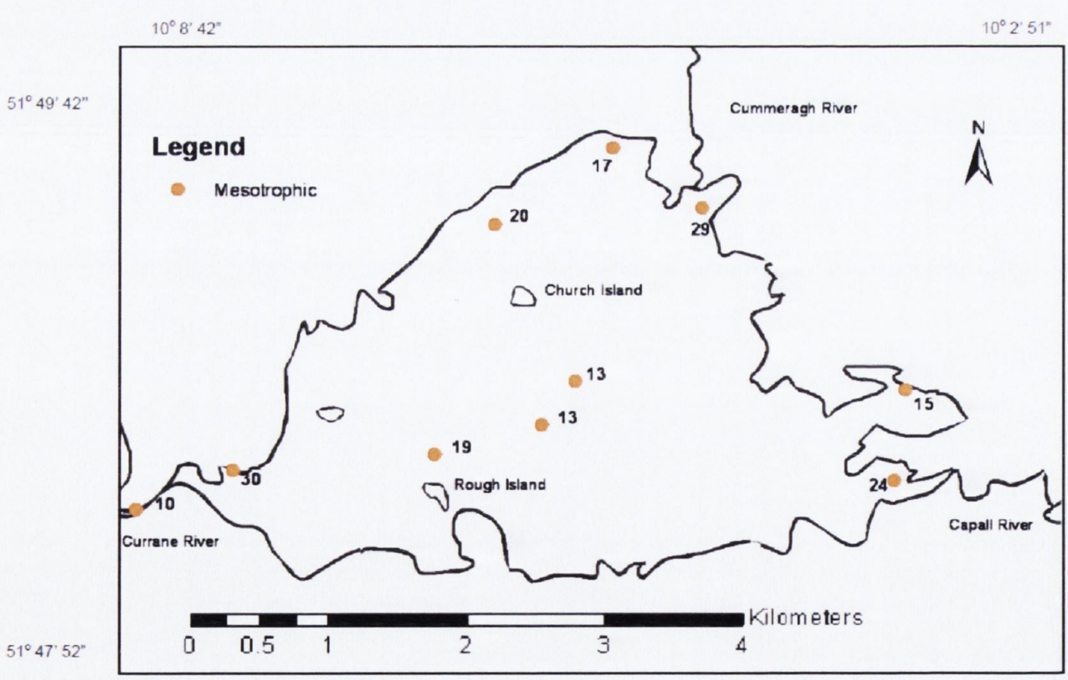


Figure 5.16: a.TP levels (µg l^{-1}) in surface water samples collected on April 29th 2010 from Lough Currane and b. Average TP levels (µg l^{-1}) measured by Kerry County Council from 2001 to 2009

5.3.2 Diatom assemblages

Photographs of some of the more abundant diatoms encountered in samples from Lough Currane are shown in Figure 5.17.

5.4.2.1 Surface sediment subsamples

A total of 125 diatom taxa were encountered in the surface sediment subsamples at Lough Currane. Maximum and minimum diatom counts were, respectively, 648 and 13. The abundances of the main diatom taxa encountered in the surface sediment subsamples are shown in Figure 5.18. Only taxa with a relative abundance of over 5 % were included in the diagram. High abundances of *Achnanthes minutissima*, *Cyclotella comensis* and *Cyclotella krammeri* characterise the assemblages. Maximum and minimum diatom concentrations were, respectively, 82 and 0.4 valves x 10^{-6}. Diatom concentrations were highest at mid-lake sites and close to the deepest point of the lake, while concentrations were lowest at sites located close to shore and at one mid-lake site (Figure 5.19).

5.4.2.2 Coring Sites 1 and 2

The diatom assemblage profiles from Coring Sites 1 and 2 display very similar trends and so will be dealt with together. A total number of 138 and 122 diatom taxa were encountered in core subsamples from respectively, Coring Sites 1 and 2. Maximum and minimum diatom counts were, respectively, 660 and 601 at Coring Site 1 and 663.5 and 601.5 at Coring Site 2. Variations in diatom abundance at Coring Site 1 and Coring Site 2 are shown in figures 5.20 and 5.21. Only taxa with a relative abundance of over 2 % were included in the diagrams. Relatively high abundances of planktonic diatoms characterise both profiles, particularly *Cyclotella comensis* and *Cyclotella krammeri.* The maximum and minimum diatom concentration values were, respectively, 247 and 51 valves x 10^{-6} for Coring Site 1 and 209 and 35 valves x 10^{-6} for Coring Site 2. Up-core variations in the relative abundances of diatoms from Coring Sites 1 and 2 were visually apparent. The broken stick model identified two statistically significant DAZ at each site.

The lowermost DAZ (S1-1 and S2-1) runs from the base of the cores to c.1980 AD in Coring Site 1 and c.1970 AD in Coring Site 2.

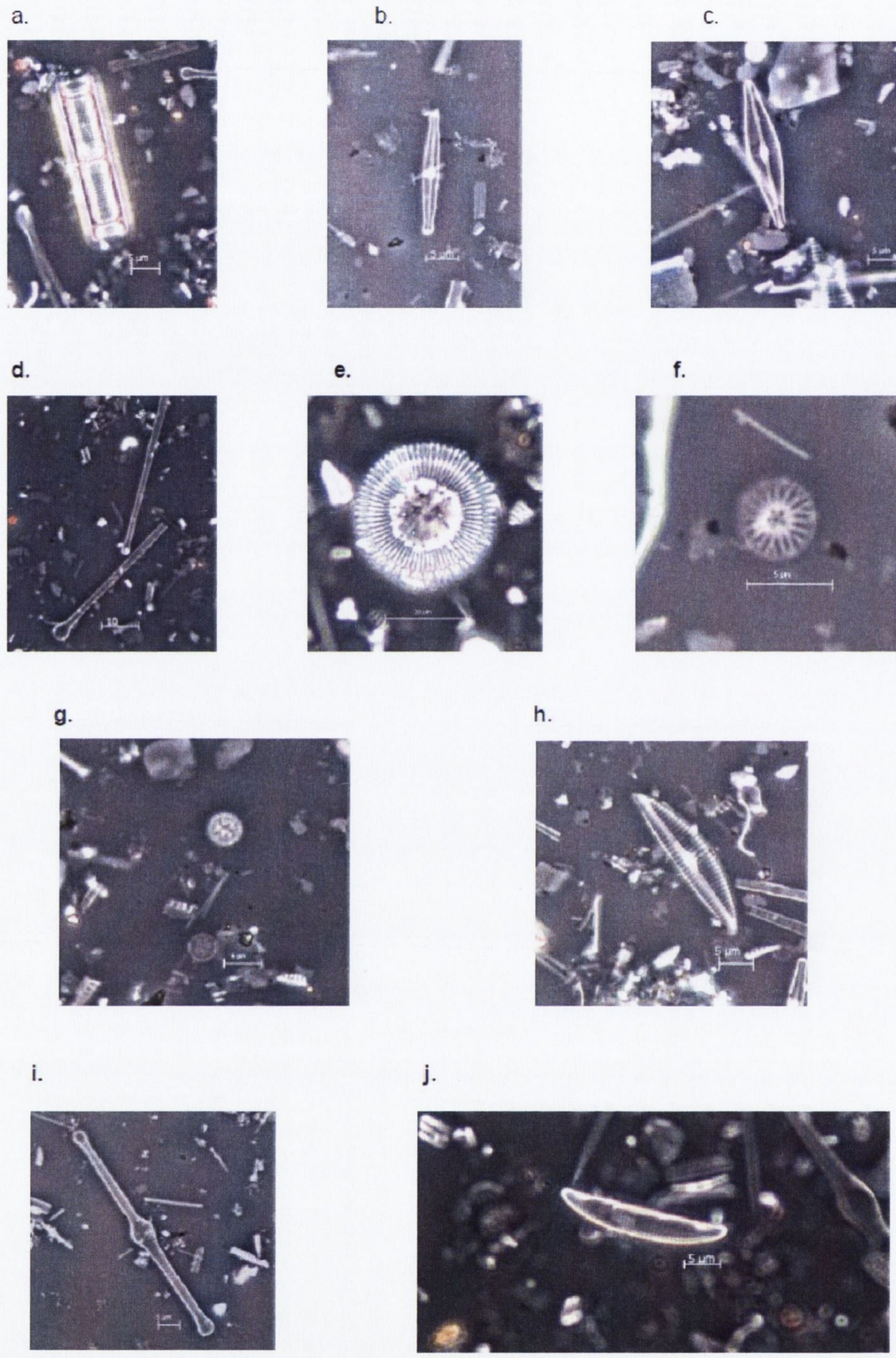


Figure 5.17: Photographs of diatoms encountered in samples from Lough Currane: (a) *Aulacoseira ambigua*, (b) *Achnanthes minutissima*, (c). *Anomoeoneis vitrea*, (d) *Asterionella formosa*, (e) *Cyclotella krammeri*, (f) *Cyclotella pseudostelligera*, (g) *Cyclotella comensis*, (h) *Cymbella gracilis*, (i) *Tabellaria flocculosa*, (j) *Eunotia incisa*

The zone is characterised by abundances of *Cyclotella comensis* and *Cyclotella krammeri* (maximum and minimum relative abundances of 34% and 40% respectively in S1-1 and 26% and 40% respectively in S2-1). Abundances of the oligotrophic to mesotrophic diatoms *Achnanthes minutissima, Anomoeoneis vitrea, Fragilaria exigua and Tabellaria flocculosa* (van Dam et al., 1994) all remain relatively stable. Taxa with preferences for mesotrophic to eutrophic water such as *Asterionella formosa*, *Aulacoseira ambigua* and *Cyclotella pseudostelligera* (van Dam et al., 1994; Lotter, 1998; Finney et al., 2000; Bigler et al., 2007), are present but at very low abundances. Diatom concentrations remain relatively stable apart from peaks at the base of the core (c. 120BC) (244 valves x 10^{-6}), c.510 AD (196 valves x 10^{-6}) and c.1959 AD (247 valves x 10^{-6}) in S1-1 and a peak at c.500 AD in S2-1 where concentrations reach 209 valves x 10^{-6}.

The uppermost DAZ (S1-2 and S2-2) running from respectively, c.1980 AD and c. 1970 AD to the top of each core, 2006 (Coring Site 1) and 2007 (Coring Site 2) is characterised by increases in taxa with preferences for mesotrophic to eutrophic water, namely, *Asterionella formosa, Aulacoseira ambigua* and *Cyclotella pseudostelligera.* These taxa reach abundances of 10 %, 5 % and 21% respectively in S1-2 and 9 %, 4 % and 16% respectively in S2-2. Taxa with a preference for oligotrophic to mesotrophic water, particularly *Cyclotella comensis* and *Cyclotella krammeri* (Round et al., 1990), are less abundant in this zone, as are *Anomoeoneis vitrea* and *Fragilaria exigua*. Diatom concentrations also decrease steadily in both cores.

5.4.2.2 Coring Site 3

A total number of 105 diatom species was encountered in core subsamples from Coring Site 3. Maximum and minimum diatom counts and concentrations were, respectively, 645 and 606 and 149 and 18 valves x 10^{-6}. Variations in diatom abundances at Coring Site 3 are shown in Figure 5.22. Only taxa that exceeded 2 % abundance were included in the diagram. Up-core variations in relative abundances of diatoms were apparent and the numerical zonation carried out on the assemblages from site 3 indicated that there were three statistically significant DAZ.

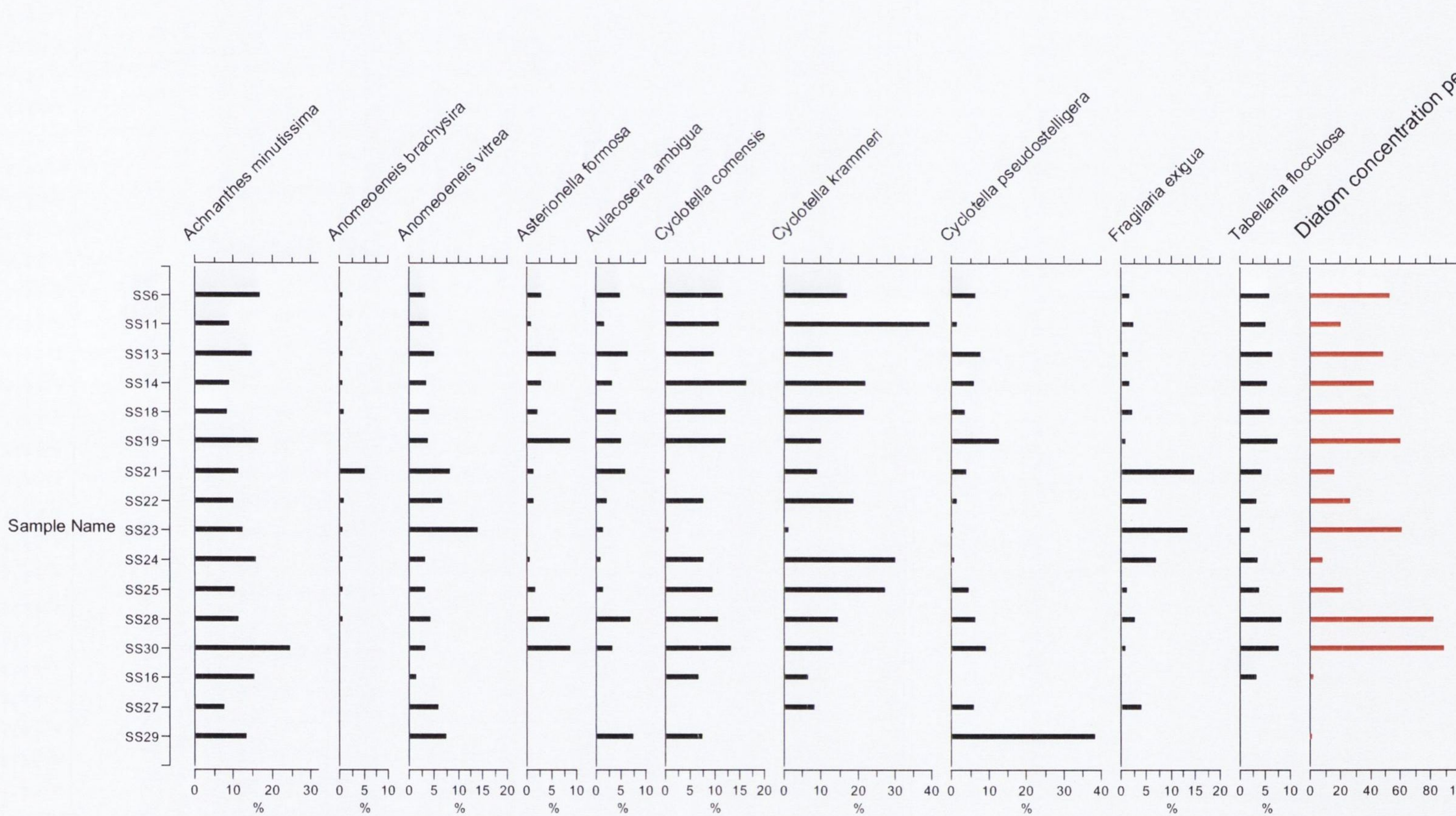


Figure 5.18: Diatom taxa with a relative abundance of > 5 % in the surface sediment subsamples at Lough Currane

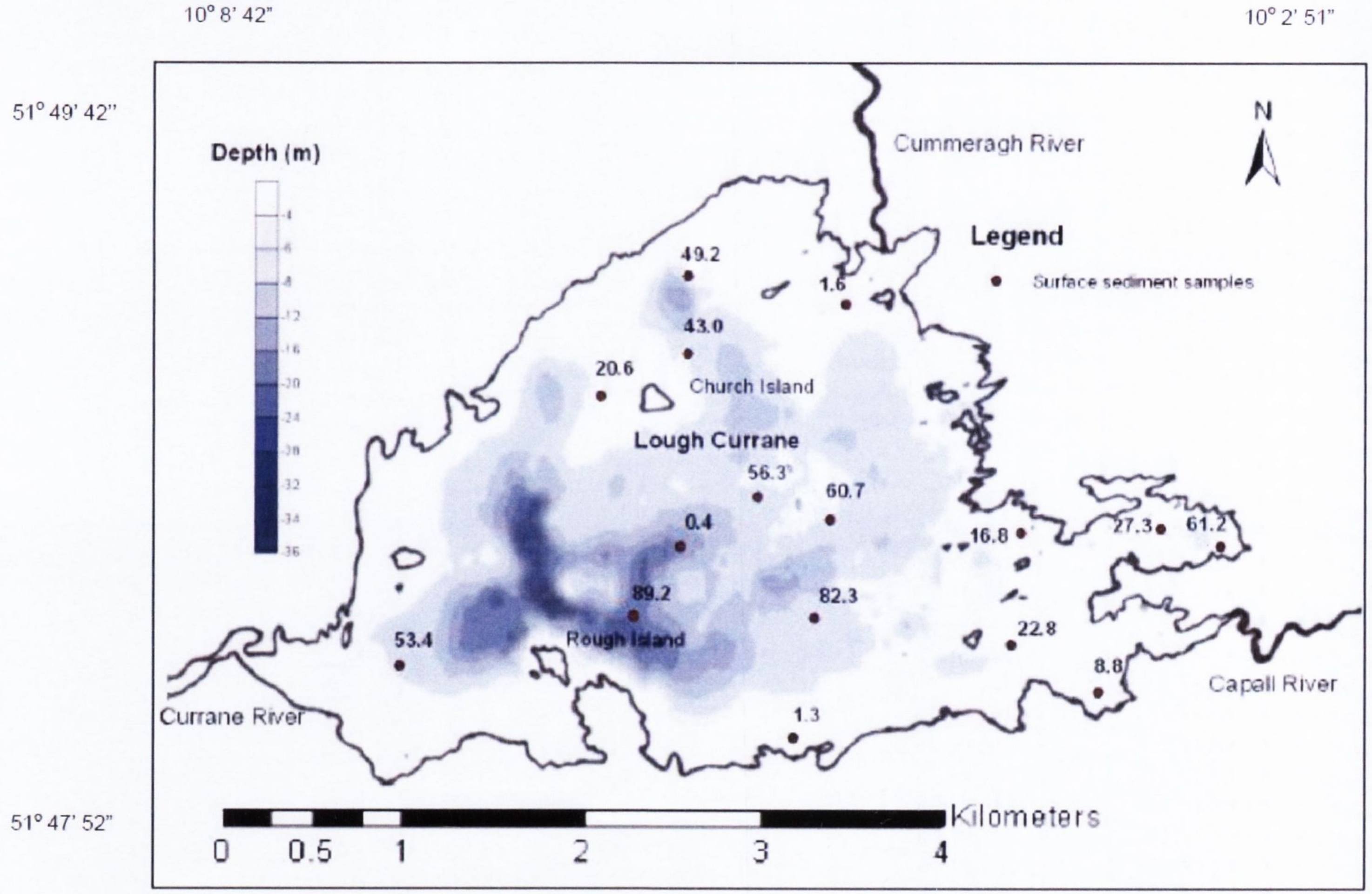


Figure 5.26: Diatom concentrations (valves x 10^{-6}) in the surface sediment subsamples at Lough Currane. The bathymetry of the lake is also shown.

The lowermost DAZ (S3-1) runs from the base of the core to c.1875 AD. The zone is characterised by an abundance of benthic diatoms that have preferences for oligotrophic to mesotrophic water, namely *Achnanthes minutissima, Anomoeoneis vitrea, Cymbella gracilis, Eunotia incisa, Eunotia paludosa* and *Fragilaria exigua,* (van Dam et al., 1994). There are also relatively high abundances of *Cyclotella comensis* and *Cyclotella krammeri* but their abundances are lower than at Coring Sites 1 and 2. Diatom concentration peaks in c.40 AD in S3-1.

DAZ S3-2, from c.1875 AD to c.1980 AD, is characterised by a marked decrease in *Achnanthes minutissima* and *Anomoeoneis vitrea,* and an increase in the planktonic *Cyclotella krammeri* and *Cyclotella radiosa*. Taxa with preferences for mesotrophic to eutrophic water, such as *Asterionella formosa* and *Cyclotella pseudostelligera* (van Dam et al., 1994; Lotter, 1998; Finney et al., 2000; Bigler et al., 2007), are present in S3-2, but at very low abundances. Diatom concentrations continue to decline to 25 valves x 10^{-6} in c.1950 AD.

The uppermost DAZ, S3-3, runs from c.1980 AD to 2007 AD. The zone is characterised by an increase in the abundances of taxa with preferences for mesotrophic to eutrophic water, such as *Asterionella formosa* and *Cyclotella pseudostelligera* (van Dam et al., 1994; Lotter, 1998; Finney et al., 2000; Bigler et al., 2007). There is also an increase and subsequent decrease after c.1990 AD in the abundance of *Cyclotella comensis* and decreases in the abundances of *Cyclotella krammeri* and *Cyclotella radiosa*. Levels of *Achnanthes minutissima* and *Anomoeoneis vitrea* increase, while those taxa with preferences for oligotrophic water, such as *Eunotia incisa, Eunotia paludosa* and *Fragilaria exigua* (van Dam et al., 1994), decrease. Diatom concentrations remain relatively stable in S3-3, apart from a decrease in c.1990 AD (18 valves x 10^{-6}).

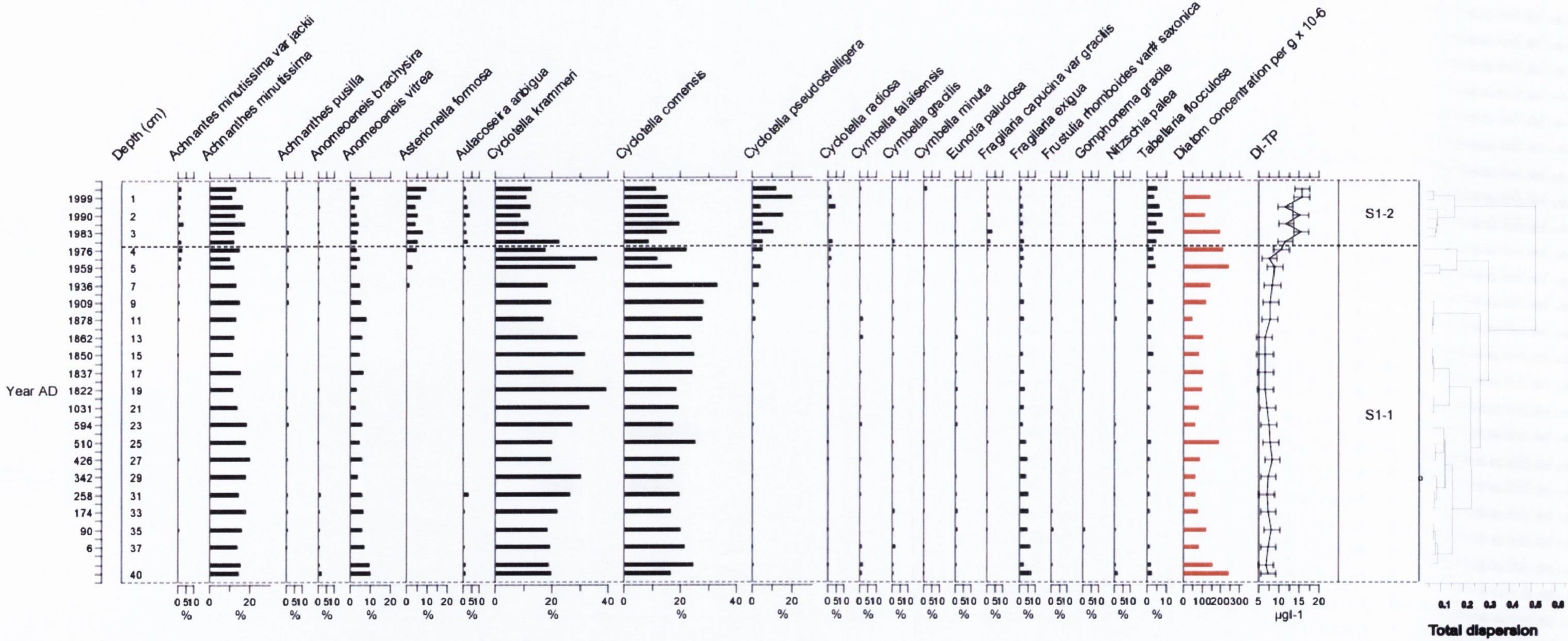


Figure 5.20: Diatom % abundance at Lough Currane Coring Site 1. Only taxa with relative abundance > 2 % are included in the diagram. Zones were obtained by CONISS.

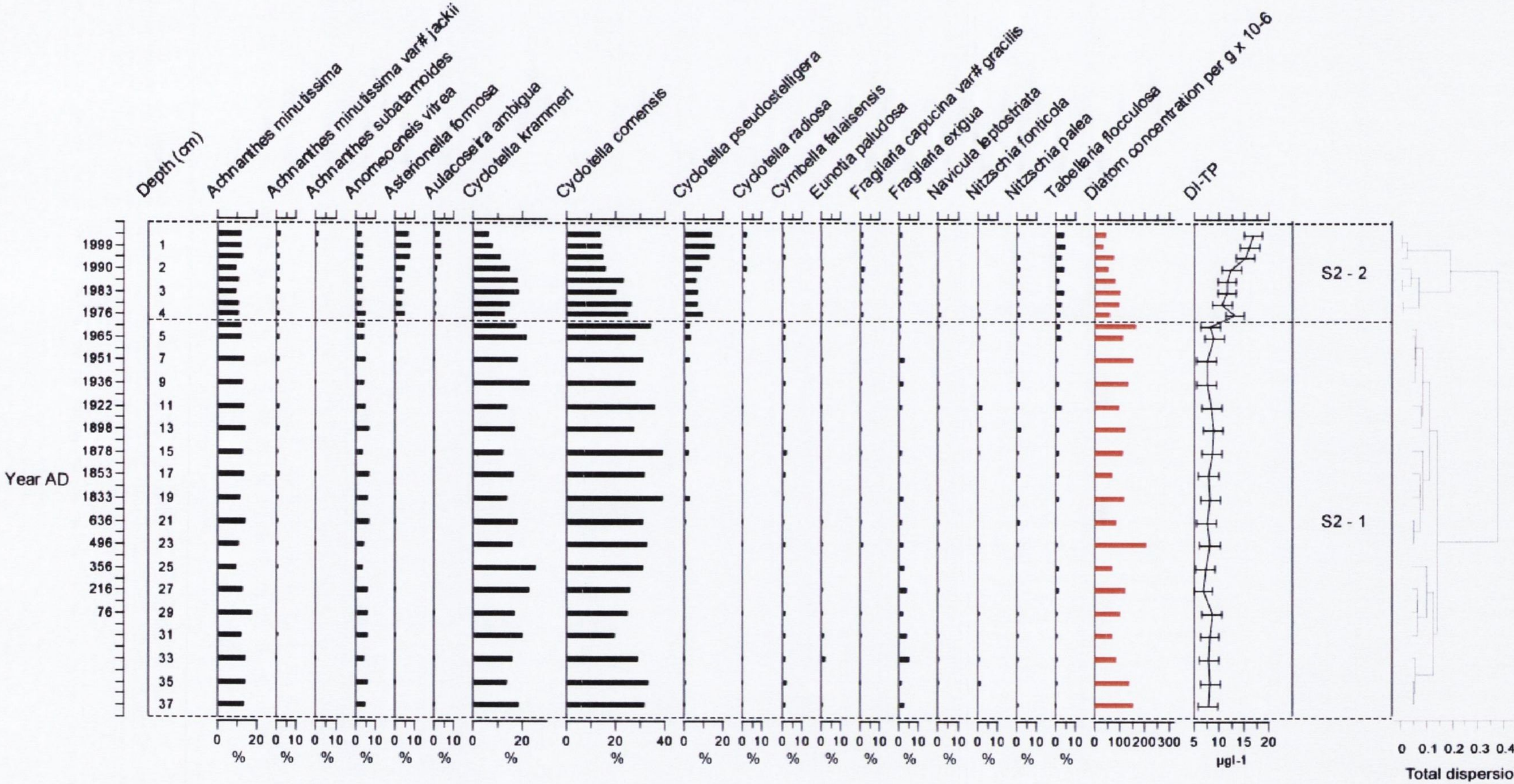


Figure 5.21: Diatom % abundance at Lough Currane Coring Site 2. Only taxa with relative abundance > 2 % are included in the diagram. Zones were obtained by CONISS

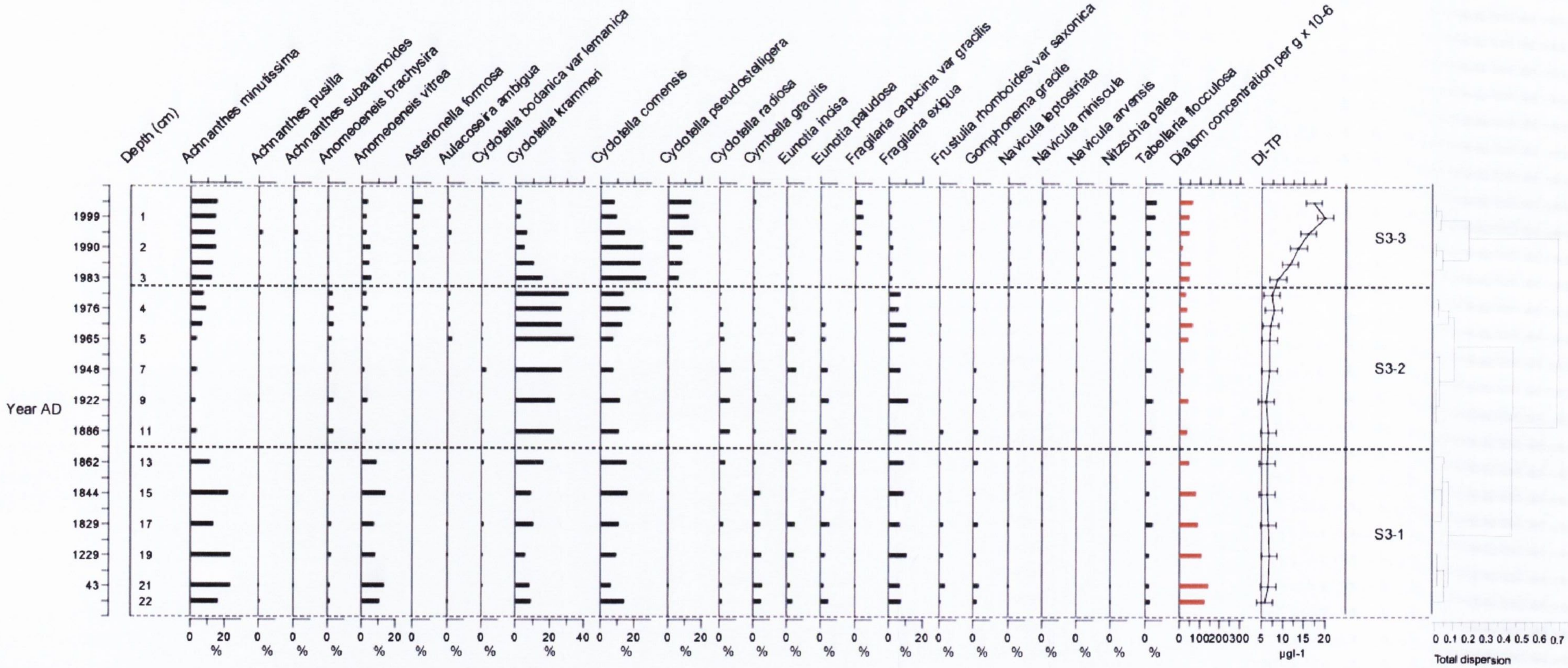


Figure 5.22: Diatom % abundance at Lough Currane Coring Site 3. Only taxa with relative abundance > 2 % are included in the diagram. Zones were obtained by CONISS

5.4.3 Transfer functions

5.4.3.1 Surface sediment subsamples

Transfer functions were performed on 13 out of the 16 surface sediment samples due to very low diatom concentrations in three samples. Mean measured TP and the DI-TP levels at each surface sediment sample are shown in Table 5.3. All of the training sets displayed DI-TP levels close to measured TP at different surface sediment sites (Table 5.3). However, both the north-west European and combined TP training sets provided the lowest range of minDC values as well as lowest mean minDC values as displayed in Table 5.4. Both training sets also displayed a high representation of fossil species from the surface samples in Lough Currane (Table 5.5). Of these two training sets, the north-west European training set provided the lowest RMSEP and highest jackR^2 values (see Table 5.6). For this reason, the north-west European training set was used for analysis on the surface sediment subsamples. DI-TP levels were relatively variable across the lake basin as shown in Figure 5.16 with highest DI-TP found at mid-lake sites, while lowest DI-TP was found close to the inlet from the Capall River.

Sample ID	Measured TP	DI-TP Irish Ecoregion	DI-TP North-west European	DI-TP Combined TP
SS 6	45.5	7.2	11.0	16.0
SS 11	6.3	6.1	7.3	16.0
SS 13	9.1	7.7	13.3	17.8
SS 14	10.8	6.9	11.1	16.2
SS 18	23.9	7.0	10.5	16.6
SS 19	5.3	9.4	16.2	19.0
SS 21	15.5	7.6	10.1	12.5
SS 22	7.1	6.9	10.2	15.5
SS 23	7.8	7.5	8.1	9.3
SS 24	7.9	6.3	8.0	14.6
SS 25	5.5	6.5	10.4	17.0
SS 28	6.2	9.7	12.5	17.6
SS 30	12.6	7.9	13.2	16.7

Table 5.3: Measured TP (µg l^{-1}) (April 2010) and reconstructed DI-TP (µg l^{-1}) for the surface sediment sampling sites used for environmental reconstructions

Sample ID	Irish Ecoregion	North-west European	Combined TP
SS 6	79.9	63.6	63.6
SS 11	66.6	54.3	54.8
SS 13	86.2	73.4	73.4
SS 14	70.6	58.8	58.8
SS 18	76.5	64.4	64.4
SS 19	94.4	68.6	68.8
SS 21	90.2	91.4	91.8
SS 22	83.9	80.1	80.1
SS 23	88.6	84.7	84.9
SS 24	79.4	67.7	68.3
SS 25	74.1	67.3	67.4
SS 28	86.4	71.8	71.8
SS 30	85.3	68.9	68.9
Mean	81.7	70.4	70.5

Table 5.4: minDC values for the surface samples used for the reconstruction of DI-TP at Lough Currane

Training Set	Number of fossil species in training set (%)	Sum of species in training set (%)
Irish Ecoregion	65.1	90.9
North-west European	72.6	91.2
Combined TP	77.1	92.2

Table 5.5: Mean % of the fossil diatom species present in the surface samples from Lough Currane that were represented in each of the training sets used for analysis in the current study.

	Irish Ecoregion	North-west European	Combined TP
jackR^2	0.74	0.73	0.64
RMSEP	0.21	0.26	0.33

Table 5.6: jackR^2 and RMSEP values for the training sets used for environmental reconstructions at Lough Currane.

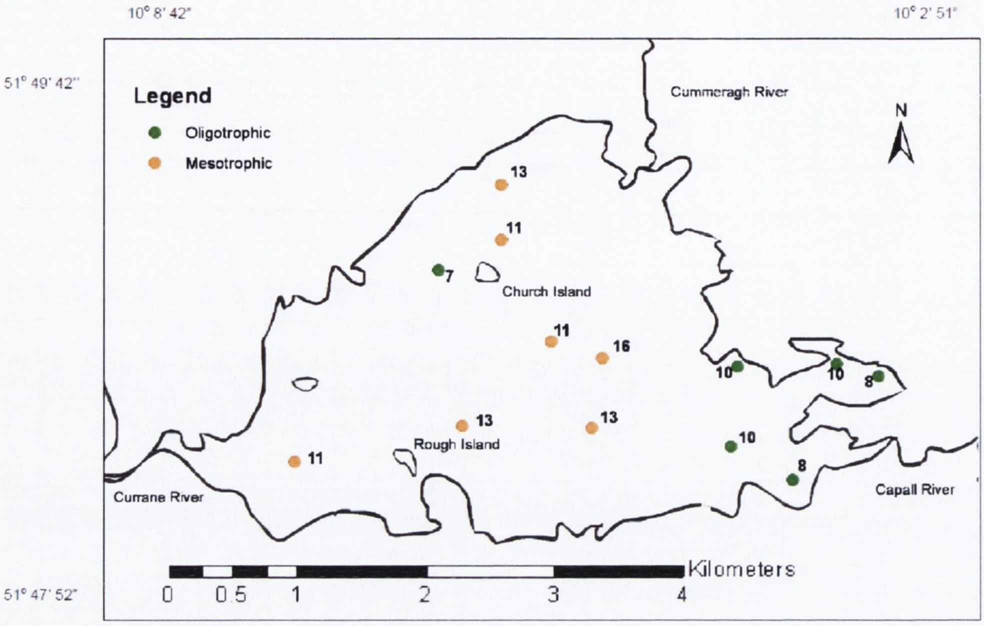


Figure 5.23: DI-TP (µg l^{-1}) in the surface sediment subsamples at Lough Currane. The north-west European training set was used for the reconstruction of DI-TP.

5.4.3.2 Coring sites

Transfer functions were performed on subsamples from each coring site using the Irish Ecoregion, north-west European and combined TP training sets. Mean measured TP and reconstructed DI-TP levels at each coring site are shown in Table 5.6. The north-west European and combined TP training sets provided the closest levels of reconstructed DI-TP to the average TP measured at each of the coring sites. While the Irish Ecoregion training set provided the lowest RMSEP and highest jackR^2 values (see Table 5.5); it provided DI-TP levels that were far lower than measured TP in the coring sites as shown in Table 5.6. The results of the MAT carried out on subsamples from each sediment core are shown in Table 5.7. The north-west European and combined TP training sets provided the lowest range of minDC values for the core samples. The minDC values for these two training sets are similar as both training sets are amalgamations of a number of the same smaller training sets (Table 4.3). Both training sets also displayed a high representation of fossil species from the core samples in Lough Currane (Table 5.9). Of these two training sets, the north-west European training set had the lowest RMSEP value and the highest jackR^2 value (see Table 5.6). As a result the north-west European environmental reconstruction was used for analysis on the subsamples at each coring site. At each coring site, levels of DI-TP were relatively stable, remaining in the oligotrophic range until c. 1975 AD at Coring

Site 2 (Figure 5.21), c.1980 AD at Coring Site 1 (Figure 5.20) and c.1985 AD at Coring Site 3 (Figure 5.22), increasing to mesotrophic after these dates.

Site ID	Measured TP	DI-TP Irish Ecoregion	DI-TP North-west European	DI-TP Combined TP
Coring site one	19	8	16	19
Coring site two	20	9	17	17
Coring site three	24	10	17	16

Table 5.7: Mean measured TP ($\mu g\ l^{-1}$) (Kerry County Council measurements 2001-2009) and reconstructed DI-TP ($\mu g\ l^{-1}$) for the coring sites at Lough Currane

		Irish Ecoregion	North-west European	Combined TP
Coring site one	minDC min	55.9	45.9	45.9
	minDC max	88.1	68.2	68.2
Coring site two	minDC min	55.0	47.1	47.1
	minDC max	87.6	67.9	67.8
Coring site three	minDC min	65.2	54.1	54.1
	minDC max	89.8	80.3	80.1

Table 5.8: The range of minDC values for the core samples in Lough Currane

Training Set	Number of fossil species in training set (%)	Sum of species in training set (%)
Irish Ecoregion	73.2	93.9
North-west European	75.5	93.8
Combined TP	82.2	95.4

Table 5.9: Mean % of the fossil diatom species present in the core samples from Lough Currane that are also present in each of the training sets used for analysis in the current study.

5.5 Gradient analysis

Ordination was used to address both of the research questions in this study.

5.5.1 Choice of response model

DCA was carried out on the datasets used for ordination using CANOCO for Windows version 4.5 software in order to determine the choice of response model for gradient analysis. The lengths of gradient for the ordination of both the diatom datasets and the diatom and DI-TP datasets are shown in tables

5.10 and 5.11. The lengths of gradients in all analyses were < 3. For this reason the linear methods PCA and RDA were for analyses.

Species Data	Co-variables	Model	Lengths of Gradient Axis 1	Axis 2	Axis 3	Axis 4
Diatoms: surface samples	N/A	DCA	1.32	0.76	0.42	0.61
Diatoms: Core samples	Sediment depth	DCA	1.33	0.90	0.67	0.48

Table 5.10: Lengths of gradient from the DCA carried out on the diatom datasets from surface and core samples at Lough Currane.

Species Data	Model	Lengths of Gradient Axis 1	Axis 2	Axis 3	Axis 4
DI-TP & Diatoms S1	DCA	0.62	0.47	0.47	0.46
DI-TP & Diatoms S2	DCA	0.55	0.18	0.18	0.14
DI-TP & Diatoms S3	DCA	1.07	0.51	0.55	0.51

Table 5.11: Lengths of gradient from the DCA carried out on the DI-TP and diatom data from the three coring sites in Lough Currane.

5.5.1 Analysing variability in the diatom assemblages

5.5.1.1 PCA

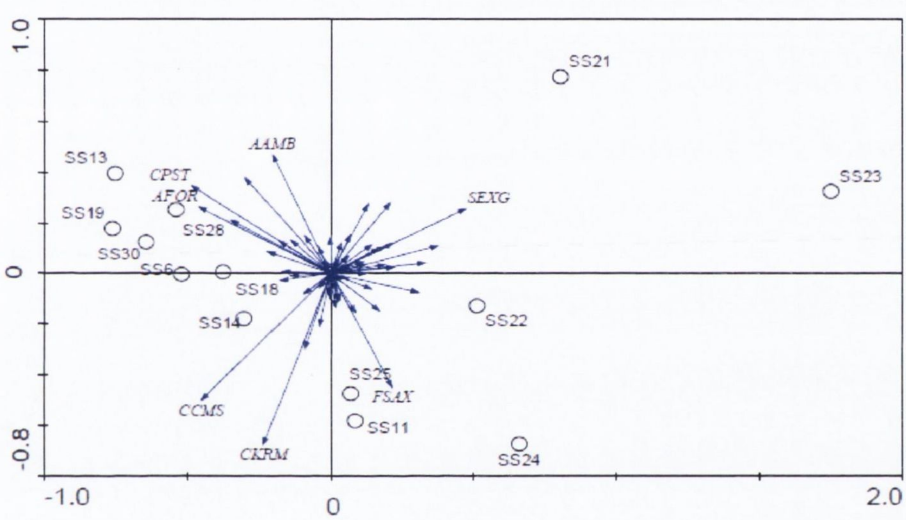
The results of the PCA carried out on diatom datasets from the surface sediment and core samples are shown in figures 5.24 and 5.25. Two main gradients were identified along the first two axes of PCA in both the surface sample dataset and core sample dataset. Cumulatively the first and second axes explained 68% of the variance in the surface sample dataset and 62% of the variance in the core sample dataset.

- **Surface samples**

The PCA bi-plot for the surface sample data is displayed in Figure 5.24. Samples SS21 and SS23 plot farthest from the origin and away from the other sampling sites. This indicates that the assemblages in these sites are dissimilar to the other surface samples.The samples SS13, SS19, SS30, SS6, SS28, SS18 and SS14 are located close together on the PCA bi-plot indicating the similarity of their diatom assemblages.

Samples scores or eigenvectors indicate the amount of variance in the dataset that can be explained by each sample. Samples SS23, SS21, SS19 and SS13 display the highest sample scores in the dataset indicating that they are most important for explaining inter-sample variation in the dataset (Table 5.12).

The taxa *Asterionella formosa* (AFOR), *Aulacoseira ambigua* (AAMB), *Cyclotella comensis* (CCMS), *Cyclotella krammeri* (CKRM), *Cyclotella pseudostelligera* (CPST) and *Fragilaria exigua* (SEXG) plot farthest from the origin, indicating their importance for explaining inter-sample variation in the dataset. These taxa have the highest species scores in the dataset, shown in Table 5.14, which confirms their importance.



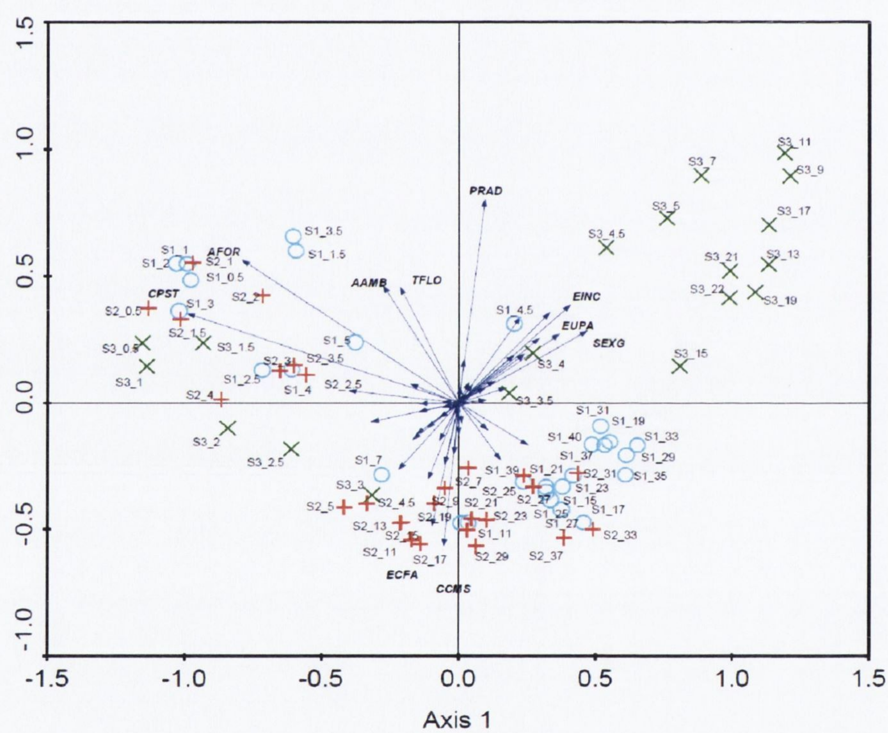
PCA Axis	1	2	3	4	Total Variance
Eigenvalue (λ)	0.52	0.16	0.08	0.05	1
Variance Explained (%)	52.2	15.7	8.2	4.8	
Cumulative Variance (%)	52.2	67.9	76	80.8	

Figure 5.24: PCA bi-plot and summary statistics for the diatom assemblages in the surface sediment subsamples at Lough Currane

- **Core samples**

The PCA bi-plot for the core sample data, displayed in Figure 5.25, shows a split between Coring Sites 1 and 2 and Coring Site 3. The samples from Coring Sites 1 and 2 plot close together on the bi-plot, while the majority of samples from Coring Site 3 plot farther apart. However, the uppermost samples from Coring Site 3, S3_0.5 to S3_3 (2007 AD to c.1980 AD), plot close to the uppermost samples in Coring Site 1 (S1_0.5 to S1_7 (2006 AD to c.1936 AD)) and Coring Site 2, S2_0.5 to S2_5 (2007 AD to c.1965 AD). The sample scores shown in Table 5.11 indicate that samples from 5 cm to 22cm (c.1965 AD to c.550 BC) in Coring Site 3 and the uppermost samples in each site are most important for explaining inter-sample variation in the dataset.

For the core sample data, the taxa *Asterionella formosa* (AFOR), *Cyclotella comensis* (CCMS), *Cyclotella pseudostelligera* (CPST), *Cyclotella radiosa* (PRAD), *Eunotia incisa* (EINC) and *Fragilaria exigua* (SEXG) plot farthest away from the origin, indicating their importance for explaining inter-sample variation in the dataset. These taxa have the highest species scores in the dataset (Table 5.14) which confirms their importance.



PCA Axis	1	2	3	4	Total Variance
Eigenvalue (λ)	0.43	0.18	0.06	0.05	1
Variance Explained (%)	43.4	18.3	6.3	5.1	
Cumulative Variance (%)	43.4	61.8	68.1	73.2	

Figure 5.25: PCA bi-plot and summary statistics carried out on diatom assemblages from core samples in Lough Currane. The blue circles correspond to samples from Coring Site 1, the red crosses to samples from Coring Site 2 and the green x's to samples from Coring Site 3.

Sample Code	λ Axis 1	Sample Code	λ Axis 2
SS23	1.75	SS21	0.77
SS21	0.81	SS13	0.39
SS24	0.66	SS23	0.32
SS22	0.52	SS28	0.25
SS11	0.09	SS19	0.18
SS25	0.07	SS30	0.12
SS14	-0.30	SS18	0.00
SS18	-0.37	SS6	0.00
SS6	-0.52	SS22	-0.13
SS28	-0.54	SS14	-0.18
SS30	-0.64	SS25	-0.48
SS13	-0.75	SS11	-0.58
SS19	-0.76	SS24	-0.68

Table 5.12: Sample scores from the PCA carried out on surface sediment samples from Lough Currane. Samples are listed in order of their sample score (λ) along either axis.

Sample Code	λ Axis 1	Sample Code	λ Axis 2
S3_9	1.21	S3_11	0.99
S3_11	1.19	S3_7	0.90
S3_17	1.13	S3_9	0.89
S3_13	1.13	S3_5	0.73
S3_19	1.08	S3_17	0.70
S3_21	0.99	S1_3.5	0.66
S3_22	0.99	S3_4.5	0.61
S3_7	0.89	S1_1.5	0.60
S3_15	0.81	S2_1	0.55
S3_5	0.76	S1_2	0.55
S3_1.5	-0.93	S1_17	-0.47
S2_1	-0.97	S2_13	-0.48
S1_0.5	-0.98	S1_11	-0.48
S1_1	-0.99	S1_9	-0.48
S2_1.5	-1.02	S2_33	-0.50
S1_3	-1.02	S2_29	-0.50
S1_2	-1.03	S2_37	-0.53
S2_0.5	-1.13	S2_11	-0.54
S3_1	-1.14	S2_17	-0.56
S3_0.5	-1.15	S2_35	-0.57

Table 5.13: Samples scores from the PCA carried out on core samples from Lough Currane. Samples are listed in order of their sample score (λ) along either axis.

a. Surface sediment samples

Code	Taxon	λ Axis 1	Code	Taxon	λ Axis 2
SEXG	*Fragilaria exigua*	2.39	AAMB	*Aulacoseira ambigua*	2.36
EINC	*Eunotia incisa*	1.91	PRAD	*Cyclotella radiosa*	1.9
ENNG	*Cymbella gracilis*	1.68	CPST	*Cyclotella pseudostelligera*	1.75
EPEC	*Eunotia pectinalis*	1.56	BVIT	*Anomoeoneis vitrea*	1.41
GGRA	*Gomphonema gracile*	1.13	BBRE	*Anomoeoneis brachysira*	1.38
CHME	*Navicula mediocris*	1.11	AFOR	*Asterionella formosa*	1.33
FSAX	*Frustulia rhomboides var. saxonica*	1.09	SEXG	*Fragilaria exigua*	1.29
BVIT	*Anomoeoneis vitrea*	1.05	FGRT	*Fragilaria capucina var. gracilis*	1.06
NAAN	*Navicula angusta*	0.96	ADMI	*Achnanthes minutissima var.minutissima*	0.77
NLST	*Navicula leptostriata*	0.95	ACNP	*Achnanthes pusilla*	0.75
FCVA	*Fragilaria capucina var vaucheriae*	-0.89	PSAT	*Achnanthes subatomoides*	-0.54
ENMI	*Cymbella minuta*	-0.91	GANT	*Gomphonema angustum*	-0.56
AAMB	*Aulacoseira ambigua*	-1.03	CCIS	*Cymbella cistula*	-0.68
TFLO	*Tabellaria flocculosa*	-1.11	FERI	*Fustulia rhomboides var viridula*	-0.75
CKRM	*Cyclotella krammeri*	-1.19	NSMU	*Navicula submuralis*	-0.78
PRAD	*Cyclotella radiosa*	-1.51	SNIA	*Stephanodiscus niagarae*	-1.06
FGRT	*Fragilaria capucina var. gracilis*	-1.75	ECFA	*Cymbella falaisensis*	-1.5
CCMS	*Cyclotella comensis*	-2.28	FSAX	*Frustulia rhomboides var. saxonica*	-2.26
AFOR	*Asterionella formosa*	-2.32	CCMS	*Cyclotella comensis*	-2.53
CPST	*Cyclotella pseudostelligera*	-2.45	CKRM	*Cyclotella krammeri*	-3.41

b. Core samples

Code	Taxon	λ Axis 1	Code	Taxon	λ Axis 2
SEXG	*Fragilaria exigua*	1.83	PRAD	*Cyclotella radiosa*	3.14
EINC	*Eunotia incisa*	1.58	AFOR	*Asterionella formosa*	2.20
EUPA	*Eunotia paludosa*	1.43	AAMB	*Aulacoseira ambigua*	1.81
BBRE	*Anomoeoneis brachysira*	1.29	TFLO	*Tabellaria flocculosa*	1.78
GGRA	*Gomphonema gracile*	1.15	EINC	*Eunotia incisa*	1.51
CKRM	*Cyclotella krammeri*	0.98	BBRE	*Anomeoeneis vitrea*	1.39
FSAX	*Frustulia rhomboides var. saxonica*	0.93	CPST	*Cyclotella pseudostelligera*	1.37
CBOL	*Cyclotella bodanica var. lemanica*	0.87	CBOL	*Cyclotella bodanica var. lemanica*	1.32
ENNG	*Cymbella gracilis*	0.79	SEXG	*Fragilaria exigua*	1.10
CCIS	*Cymbella cistula*	0.68	EUPA	*Eunotia paludosa*	1.06
ACNP	*Achnanthes pusilla*	-0.60	NARV	*Navicula arvensis*	-0.57
NARV	*Navicula arvensis*	-0.66	NLST	*Navicula leptostriata*	-0.58
PSAT	*Achnanthes subatomoides*	-0.69	CKRM	*Cyclotella krammeri*	-0.65
TFLO	*Tabellaria flocculosa*	-0.84	SCON	*Fragilaria construens*	-0.79
NPAL	*Nitzschia palea*	-0.85	BVIT	*Anomoeoneis vitrea*	-0.88
AAMB	*Aulacoseira ambigua*	-1.09	ADMI	*Achnanthes minutissima var.minutissima*	-0.95
AMJA	*Achnanthes minutissima var. jackii*	-1.25	NPAL	*Nitzschia palea*	-1.03
FGRT	*Fragilaria capucina var. gracilis*	-1.57	NFON	*Nitzschia fonticola*	-1.18
AFOR	*Asterionella formosa*	-3.10	ECFA	*Cymbella falaisensis*	-1.90
CPST	*Cyclotella pseudostelligera*	-3.88	CCMS	*Cyclotella comensis*	-2.22

Table 5.14: PCA species scores for Lough Currane a. diatom surface sample data and b. core sample data. Taxa with the highest species scores (both negative and positive) along the first 2 PCA axes are shown. Taxa are listed in order of their species score (λ) along either axis.

5.5.2.2 RDA

RDA was used in order to assess which morphometric parameters were important for explaining the variability in the diatom assemblages. Two main gradients were identified along the first two axes of RDA in the surface sample dataset. As shown in table 5.15, cumulatively the first and second axes accounted for 85% of the variance in the surface samples dataset

RDA Axis	1	2	3	4	Total Variance
Eigenvalue (λ)	0.88	0.81	0.85	0.95	0.57
Variance Explained (%)	68.7	16.1	9.6	5.6	
Cumulative Variance (%)	68.7	84.8	94.4	100	

Table 5.15: Summary statistics of RDA carried out on surface sample data from Lough Currane - Species environment correlation.

The results of Monte-Carlo permutation tests and the forward selection of environmental variables are shown in Table 5.16. The four environmental variables chosen, i) site depth, ii) distance to nearest shoreline (Shore), iii) distance to nearest inlet/river (Inlet) and iv) distance to nutrient source (P-Source), explained 0.57 of the variance for the surface sample data. Distance to shore (Shore) was the only statistically significant variable, explaining 0.32 of the variance with a p-value of 0.002 for the surface sample data.

Variable Name	Variance Explained	P
Shore	0.32	0.002
Site_Dep	0.10	0.094
P-source	0.09	0.162
Inlet	0.06	0.334
TotalVariance	0.57	

Table 5.16: RDA: Amount of variance explained and p-values from the Monte-Carlo permutation tests and forward selection of environmental variables carried on Lough Currane surface sample data.

5.5.3 Analysing the drivers of up-core variations in trophic status

5.5.3.1 RDA

RDA was used in order to aid in assessing which anthropogenic and climatic parameters were important in explaining variability in the DI-TP and diatom assemblage datasets at each coring site in Lough Currane. One main gradient was identified in the first RDA axis in the datasets from each coring site. As shown in Table 5.17, the first axis explained 91% of the variance at Coring Site 1, 95% of the variance at Coring Site 2 and 94% of the variance at Coring Site 3.

a.

RDA Axis	1	2	3	4	Total variance
Eigenvalue (λ)	0.98	0.80	0.45	0.63	0.84
Variance explained (%)	90.8	6.8	1.7	0.6	
Cumulative variance (%)	90.8	97.6	99.3	99.9	

b.

RDA Axis	1	2	3	4	Total variance
Eigenvalue (λ)	0.95	0.87	0.60	0.39	0.85
Variance explained (%)	95.3	2.8	1.1	0.4	
Cumulative variance (%)	95.4	98.2	99.3	99.7	

c.

RDA Axis	1	2	3	4	Total variance
Eigenvalue (λ)	0.98	0.71	0.69	0.69	0.90
Variance explained (%)	94.2	2.9	2.2	0.6	
Cumulative variance (%)	94.2	97.1	99.3	99.9	

Table 5.17: Summary statistics of RDA carried out on DI-TP and diatom data at Lough Currane a. Coring Site 1, b. Coring Site 2 and c. Coring Site 3

RDA bi-plots showing species and environmental variables for each coring site are shown in Figure 5.26. At coring each site the environmental variables Sheep, Temperature, Precipitation and Storms are located close to taxa with preferences for mesotrophic to eutrophic water, *Asterionella Formosa* (AFOR) and *Cyclotella pseudostelligera* (CPST) as well as DI-TP, indicating a positive correlation between these environmental variables and taxa. Of these environmental variables, Sheep is located farthest from the origin, indicating its importance for explaining inter-sample differences. The environmental variables Population and Houses also plot far from the origin but the arrows for these variables point in the opposite direction to the arrows for the mesotrophic to eutrophic taxa, indicating that they are negatively correlated.

The results of the Monte-Carlo permutation tests and the forward selection of environmental variables are shown in Table 5.18. The seven environmental variables chosen explained 0.84 of the variance at Coring Site 1, 0.85 of the variance at Coring Site 2 and 0.90 of the variance at Coring Site 3. The environmental variables Sheep, Houses, Population and Cattle were deemed statistically significant at each coring site; however, Sheep density (Sheep) explained the vast majority of the variance at each site. The climatic variables Precipitation, Temperature and Storms explained a very small proportion of the variance at each site indicating that they are not significant in explaining inter-sample variation in each dataset.

5.6 Eutrophication of Lough Currane

The analysis of TP and DI-TP in the surface samples from Lough Currane showed that nutrient levels are spatially variable throughout the lake. Highest TP values were found in the south-east section of the lake and at the inlets to the two inflowing rivers. Both TP and DI-TP were lowest in the south-west section of the lake and at mid-lake sites.

Diatoms were used to track changes in trophic status at the three coring sites in Lough Currane. The results of the PCA carried out on the relative abundances of diatoms showed that Coring Sites 1 and 2 had similar diatom assemblages while the assemblages at site 3 differed. Diatom concentrations differed throughout each of the coring sites. Distance from shore was deemed to be significant in explaining inter-sample differences in the diatom assemblages. Each coring site responded in the same way to increased nutrient input. The diatom assemblages were characterised by an increase on *Asterionella formosa* and *Cyclotella pseudostelligera*, taxa with preferences for mesotrophic to eutrophic conditions. However, the timing of a change in trophic status differed between the three coring sites. Coring Site 2, located close to the Cummeragh River, displayed a change from oligotrophic to mesotrophic status in c.1970 AD; while the trophic status of Coring Site 1 and Coring Site 3 changed in, respectively c.1980 AD and c.1985 AD.

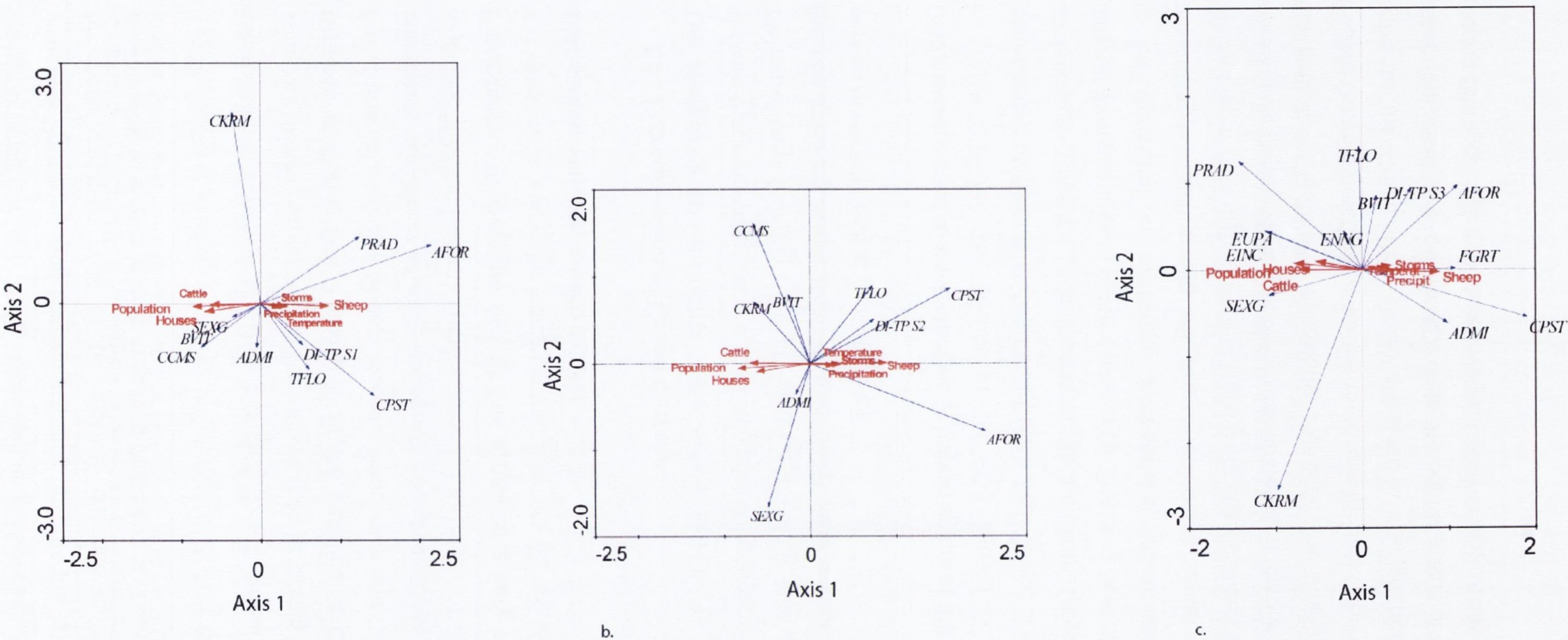


Figure 5.26: RDA bi-plots showing species and environmental variables at Lough Currane a. Coring Site 1, b. Coring Site 2 and c. Coring Site 3. The environmental variables that were used were Houses, Population, Cattle, Sheep, Precipitation, Temperature and Storms

Sheep density was deemed to be statistically significant in driving ecological change at each of the coring sites. The climatic variables were not deemed to be statistically significant at any of the coring sites. Data relating to the mink farm and the commercial forestry plantations were not included in the statistical analyses. However, their influence will be considered when making an overall assessment of the drivers of ecological change at the lake.

a.

Variable Name	Variance Explained	P
Sheep	0.730	0.002
Population	0.070	0.002
Cattle	0.010	0.002
Houses	0.010	0.002
Temperature	0.010	0.004
Precipitation	0.004	0.046
Storms	0.003	0.116
Total Variance	0.84	

b.

Variable Name	Variance Explained	P
Sheep	0.790	0.002
Houses	0.020	0.002
Cattle	0.020	0.002
Population	0.010	0.002
Temperature	0.003	0.06
Precipitation	0.002	0.200
Storms	0.001	0.19
Total Variance	0.85	

c.

Variable Name	Variance Explained	P
Sheep	0.780	0.002
Houses	0.070	0.002
Cattle	0.020	0.002
Population	0.020	0.002
Temperature	0.007	0.064
Storms	0.004	0.022
Precipitation	0.001	0.226
Total Variance	0.90	

Table 5.18: RDA: Amount of variance explained and p-values from the Monte-Carlo permutation tests and forward selection of environmental variables carried out DI-TP and diatom assemblage data at Lough Currane a. Coring Site 1, b. Coring Site 2 and c. Coring Site 3

Chapter Six: Discussion

This chapter provides a synthesis and discussion of the results presented in chapter five. The historical record of eutrophication at the test site, Lough Currane, is first addressed. The first research question: "To what extent is recent eutrophication caused by anthropogenic factors" is then discussed. The importance of the various point, intermediate and diffuse nutrient sources within the study catchment, as well as the influence of climatic variability, to the eutrophication of the test site is addressed. The results of the palaeolimnological methods utilised in the study are analysed and discussed in relation to the historical, documentary and climate records collected for the catchment of the lake.

The second research question: "To what extent does the response to increased nutrient loads vary spatially within a lake basin?" is then addressed. This is achieved through an examination of the within-lake variability in the response to increased nutrient loads. Current within-lake variability in water quality is first discussed by analysing the TP, DI-TP and diatom results obtained from the surface samples within the test site. The within-lake variability in the historical record of eutrophication is then discussed. The sedimentary patterns within the test site, determined via analyses of % organic content, microfossil concentrations, SCP concentration and PSA, are discussed in relation to the assumption that a sediment core collected from the deepest point of a lake is representative of overall limnological conditions. The up-core variations in the diatom assemblages and DI-TP are then addressed and are compared at each of the coring sites.

6.1 The historical record of eutrophication at the test site

The palaeolimnological results from Lough Currane suggest that the lake is not naturally enriched. The lake is entirely underlain by Devonian sandstones (Reynolds and Peterson, 2000) and the P content of sandstone is generally considered to be low (0.01%) (Stevenson and Cole, 1999). In addition, the results of the diatom analyses carried out on subsamples from the sediment cores collected at Lough Currane suggest that the lake remained oligotrophic for most of the time period recorded by the sediment cores (c.2000 years). This time period spans the periods from the Late Iron Age and Early Christian

Period (Aalen et al., 1997) and encompasses the entire Anthropocene, from the beginning of industrialisation to the present (Crutzen, 2002).

The historical records of water quality from Lough Currane suggest that eutrophication commenced between the mid 1950s and mid 1970s (Faran, 1947; Grainger, 1952; Went, 1971; Central Fisheries Board, 1985). The palaeolimnological analyses undertaken as part of the current research appear to confirm this suggestion. Based on the analysis of cores taken from three areas within the lake, the transition from oligotrophic to mesotrophic status occurred between c.1970 AD and c.1985 AD. Prior to the 1970s the diatom assemblages are characterised by taxa with preferences for oligotrophic water such as *Cyclotella comensis, Cyclotella krammeri* (Anderson et al., 1993; Reavie and Smol, 2001; Chen, 2006) and *Fragilaria exigua* (van Dam et al., 1994). With the transition to mesotrophic conditions, the diatom assemblages at each site are characterised by increases in taxa with preferences for mesotrophic to eutrophic water, *Asterionella formosa* and *Cyclotella pseudostelligera* (figures 5.20, 5.21 and 5.22). *Asterionella formosa* has been identified as an indicator of eutrophication in a number of studies (Findlay et al., 1998; Merilainen et al., 2000; Barker et al., 2005; Saros et al., 2005; St Jacques et al., 2005; Bigler et al., 2007) and has particular preferences for mesotrophic to eutrophic water (van Dam et al., 1994; Saros et al., 2005), while abundances of *Cyclotella pseudostelligera* have been known to increase with artificial fertilisation (Finney *et al.*, 2000). In Arctic climates *Cyclotella pseudostelligera* has been also associated with increased temperatures and longer ice-free conditions (Battarbee et al., 2002; Karst-Riddoch et al., 2005)

The timing of eutrophication at Lough Currane compares well with the timing of eutrophication at other lakes located in rural Ireland, confirming its suitability as a test site for the detailed study of the temporal and spatial variability of recent nutrient enrichment. For example, at lower Lough Erne, P concentrations rose steadily since the mid 1970s and were associated with diffuse agricultural sources (Zhou et al., 2000). In addition, Taylor et al. (2006) reported that five lakes (Loughs Ballybeg, Egish, Inchiquin, Mullagh and Sillan), located in predominantly agricultural catchments within the Irish Ecoregion, experienced accelerated enrichment after c.1980 AD while Dalton et al. (2010) stated that low nutrient levels prevailed at Bunaveela Lough in western Ireland until the 1980s. Catchment disturbance and nutrient enrichment were thought to be associated with afforestation and overgrazing.

6.2 Drivers of eutrophication at the test site

6.2.1 Sources of nutrients

6.2.1.1 Intermediate sources

- **Intensive agricultural production**

A mink fur farm, located in the study catchment, acts as an intermediate source of nutrients and palaeolimnological analyses suggest that the farm constitutes an important source of nutrients to the lake. The diatom assemblages identified for Coring Site 1 display a change from taxa with preferences for oligotrophic conditions to taxa with preferences for mesotrophic to eutrophic conditions in c.1970 AD, while the reconstructed DI-TP at Coring Site 2 suggests an almost immediate transition from oligotrophic to mesotrophic conditions with the establishment of the farm in 1969. Of the coring sites, Coring Site 2 is located closest to the inlet from the Cummeragh River and thus the mink farm (Figure 6.1). In general, intensive agricultural practices, including intensive livestock production, are regarded as high risk activities for P and N loss to surface waters (Jarvie et al., 2010). In the UK over the period 1925 to 1970, the largest P surpluses occurred in limited areas of arable soils receiving manure from intensive pig and poultry units (Withers et al., 2001), while in the southern plains of America, long term pig and poultry manure application increased P and N levels in surface soils by respectively, four and five times (Hooda et al., 2000). In the Guangdong region of China, pig waste is estimated to be a major source of N loading in aquatic ecosystems, contributing 72% of N loads to water systems (Gerber and Menzi, 2006) and at Lough Sheelin in Ireland, the establishment and development of intensive pig production facilities led to the gradual eutrophication of the lake (Keating and Dodd, 1975).

The mink farm is located very close to the Cummeragh River channel and the river's inflow to Lough Currane, as shown in Figure 6.1. The location of the farm may make it more susceptible to greater P loss to the Cummeragh River and eventually, Lough Currane, with P originating from livestock manure and farmyard waste.

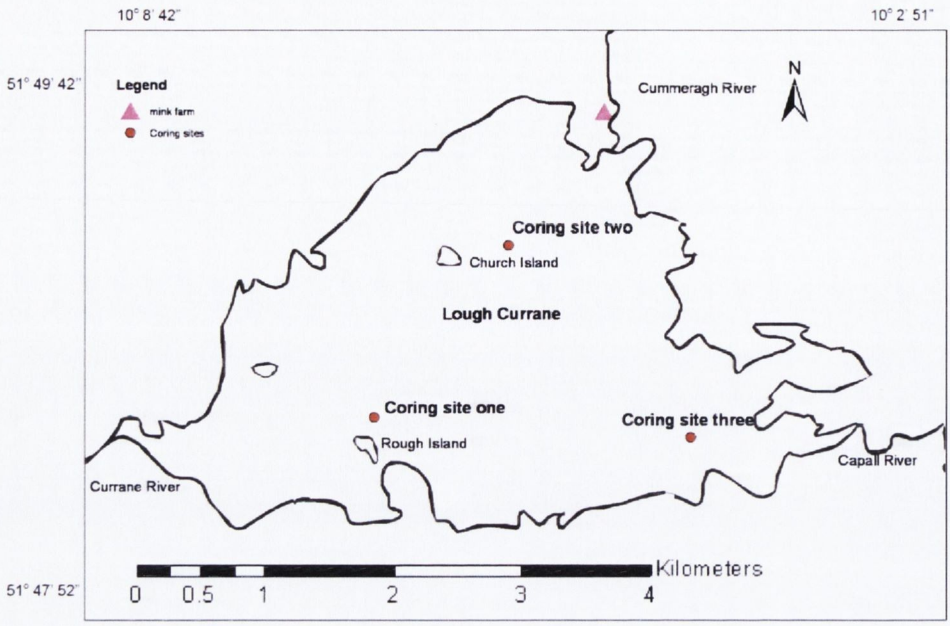


Figure 6.1: The location of the mink fur farm in the catchment of Lough Currrane, in relation to the coring sites within the lake.

There is widespread acknowledgment (e.g. Pionke et al., 2000; Weld et al., 2001; Heathwaite et al., 2001; Heathwaite et al., 2005; Hughes et al., 2005; Ulén and Jakobsson, 2005; Kleinman et al., 2006) that most of the P exported from agricultural watersheds generally comes from only a small part of the landscape. The CSA concept is widely used in nutrient management planning and describes an area where a particularly risky land use or land management activity is co-located with a high probability of a connection of those risks to the river system (Heathwaite, 2010). For example, Jarvie et al. (2010) stated that P and N loss to rivers from intensive agriculture may be exacerbated where high risk agricultural practices are located in close proximity to water courses, resulting in greater efficiency of the delivery of P and N to surface waters. They found that high winter stocking densities of cattle in barns and farmyards close to the stream channel resulted in the highly efficient delivery of livestock manure, farmyard waste and slurry to the stream channel throughout the year.

The spreading of manure, originating in the mink farm, on local land (Appendix A) may also contribute to the increased nutrient enrichment of the test site. Department of Agriculture inspector's reports state that the numbers of mink have not changed since the establishment of the farm, so it can be assumed that the same amount of manure has been spread since its establishment. In

1991, the Nitrates Directive (91/676/EEC) was unanimously adopted by EU member states. The Directive aimed at reducing and preventing water pollution caused by nitrate from agricultural sources. Under the Directive, the maximum amount of animal manure that could be applied was the amount containing 170 kg of N ha^{-1} $year^{-1}$ (Brouwer and Hellegers, 1996). In 2004 the Irish government applied for a derogation for amounts of up to 250 kg N ha^{-1} $year^{-1}$ from livestock/animal manure based on an output of 85 kg of N dairy cow^{-1} (Department of Agriculture and Food, 2005). Due to the high protein diet of mink, their feed contains more N when compared to other animals, such as pigs. The increased N content of mink feed results in an increased amount of N excreted in their faeces (Glem-Hansen, 1980; Pedersen and Sandbol, 2002). Pedersen and Sandbol (2002) found that, mink excrete between 1.2 g and 1.4 g N $animal^{-1}$ day^{-1} at a temperature of 16°C. Based on these quantities and the reported 50,000 mink associated with the farm in the Lough Currane catchment, between 58 kg and 72 kg N is produced by the farm day^{-1} and between 21,170kg and 26,280kg N is produced by the farm $year^{-1}$. Peat soils predominate in the catchment of Lough Currane (Figure 3.4) and are vulnerable to significant nutrient loss due to their high water content and potential to create overland flow (Daly et al., 2001). Although controls have been in place since 1992 in relation to the spreading of manure, prior to the 1990s the uncontrolled spreading of large amounts of mink manure on largely peat soils may also have contributed to the increased nutrient levels in the lake following the establishment of the farm.

- **Housing**

On initial inspection, the impact of housing to the nutrient enrichment of Lough Currane seems to be negligible owing to the large decline in the permanent population of the catchment (Figure 3.8). The trends in population and housing in the catchment of Lough Currane, seen in figures 3.8 and 3.9 reflect the general trend seen in Ireland. The pre-famine era in Ireland saw a large increase in population due to the availability of cheap food, housing and fuel, with population increasing by over 100% between 1770 and 1841 (Freeman, 1957; Whelan, 1997). The advent of the famine in 1845 then saw 1000,000 die and a further 2000,000 emigrating (Whelan, 1997). The catchment of Lough Currane saw a large decline in population and in the number of occupied houses following the famine and the population has not recovered since then (figures 3.8 and 3.9).

Some rural Irish lakes have shown evidence of enrichment prior to the famine. For example, at Crans Lough, Northern Ireland, an increase in DI-TP concentration is evident, which dates to the early 1700s (Erdil, 2008) and was thought to be associated with the arrival of plantation settlers (Dalton et al., 2009), while Lough Carra, in western Ireland, saw a decrease in DI-TP associated with de-population in the ten years following the famine in Ireland (Donohue et al., 2010). The catchment of Lough Carra is comparable to that of Lough Currane. Both lakes are low-lying (altitudes of 30 m.a.s.l and 6 m.a.s.l respectively) and have similar catchment sizes (114km^2 and 104km^2 respectively) and surface areas (1560ha and 1000ha respectively). Both catchments are dominated by intermediate and diffuse nutrient sources. The pollen records at Lough Currane show some evidence of catchment change following the famine. Coring Sites 1 and 2 display a decline in the abundance of Poaceae and an increase in the abundance of lower plants from c.1850 AD to c.1950 AD (figures 5.13 and 5.14). Abundances of Poaceae are associated with grassland agriculture (Dalton et al., 2005) and the decline in Poaceae at Lough Currane is likely to have been associated with the depopulation of the area and the partial re-establishment of scrub vegetation. However, in contrast to Lough Carra, only the shallowest coring site at Lough Currane showed evidence of diatom assemblage change following de-population (Figure 6.1). Shallow lakes and the shallow areas in deep lakes are more responsive to changes in nutrient loads due to a diminished potential to dilute nutrients (Liu et al., 2010b). Moreover, increased re-suspension of sediments in shallow sites results in a greater availability of nutrients in the water column (Taranu and Gregory-Eaves, 2008). Coring Site 3 saw a decline in the abundance of *Achanthes minutissima,* a taxon that has been reported to respond positively to enrichment in lakes (Carrick et al., 1988), from c.1845 AD. There is also an increase in the abundance of *Cyclotella krammeri*, a taxon that exists in oligotrophic conditions (Anderson et al., 1993; Reavie and Smol, 2001; Chen et al., 2008), during the same time period (Figure 6.2). However, this ecological change following de-population is not reflected in the up-core variations in DI-TP. In contrast to Lough Carra, the DI-TP records at each coring site in Lough Currane show minimal temporal variations until the 1970s and 1980s. The overall morphometry and geology of Lough Currane may have acted as buffers to changing nutrient loads associated catchment change prior to the 1970s. For example, the low mean depth (2 m) and calcareous geology at Lough Carra may have made the lake more sensitive to changes in nutrient concentrations. Marl lakes tend to be strongly P limited due to the co-precipitation of PO_4^{3-} with calcite (Hamilton et al., 2009). The sandstone geology and relatively high mean depth (6 m) of Lough Currane may have made the lake, especially the profundal zones, more resistant to changes in nutrient levels prior to the 1970s and 1980s, after which multiple stressors on the water quality of the lake emerged.

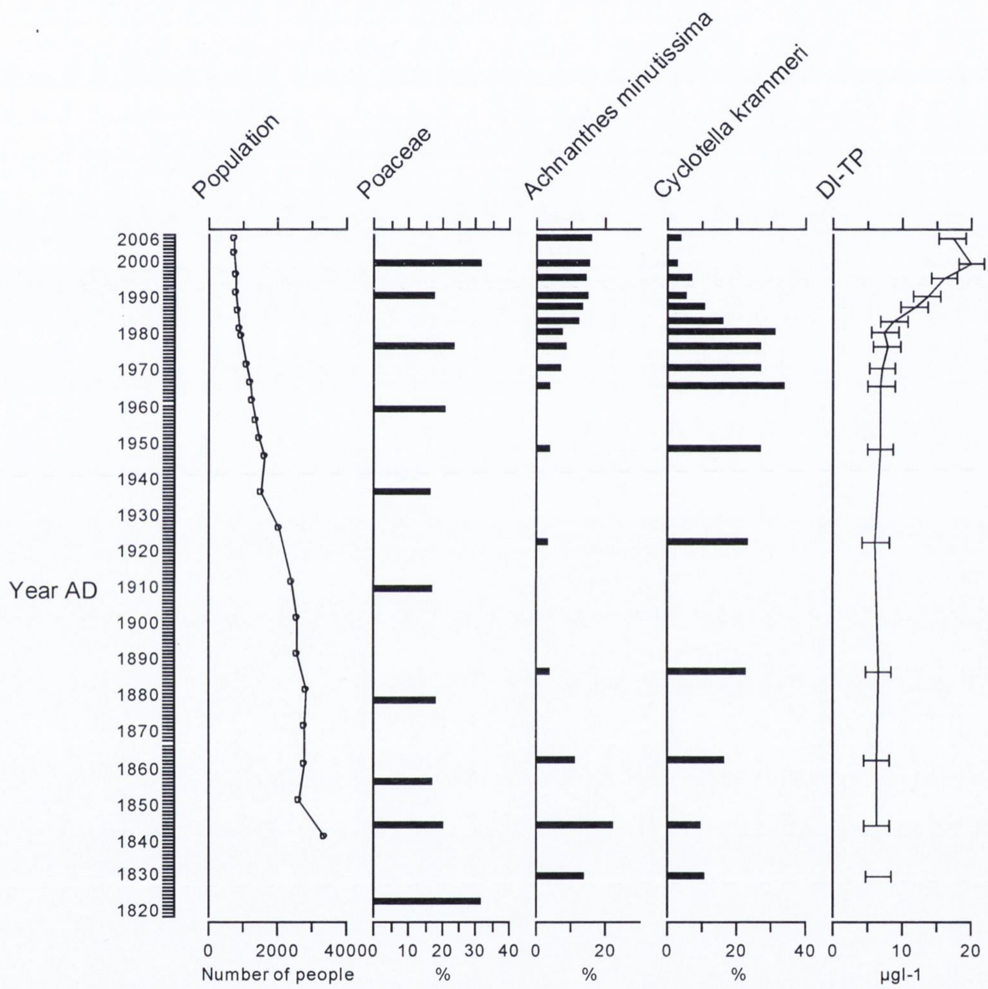


Figure 6.2: Temporal variations in population in the study catchment as well as in the sedimentary abundances of Poaceae (Coring Site 1), *Achnanthes minutissima*, *Cyclotella krammeri* and reconstructed levels of DI-TP at Coring Site 3 (Note that temporal variations in the abundance of Poaceae refer to sedimentary data collected from Lough Currane Coring Site 1).

Until the 1960s and 1970s, rural housing was almost exclusively associated with farming. The growth of towns and cities in the 1960s and 1970s led to increased levels of construction of houses in rural areas and the development of the one-off non-farm dwelling house accessible to a town. In addition, the size of rural dwellings increased. For example, the number of dwellings with eight rooms or more showed strongest growth over the period from 1991 to 2002 (Corcoran et al., 2007). According to the census of 2006, in rural Ireland 27% of houses are one-off houses, defined as detached houses with an individual septic tank or treatment system (Central Statistics Office, 2009). In the catchment of Lough Currane this proportion increases to c.80% (Table 3.7). In 2010, a NPPR was implemented on second homes in Ireland. The highest numbers of second homes were recorded in counties with high tourist numbers such as Donegal and Kerry, where 15,596 second homes were declared based on the NPPR (Healy, 2010). Lough Currane is situated on the Ring of Kerry route, a popular tourist destination in Ireland. An average of 3,156,000 tourists visited the south-west region of Ireland between 2002 and 2006, with 13% of visitors staying in rented accommodation (Fáilte Ireland, 2009). The study catchment contains over 100 (26%) unoccupied houses. This figure is based upon a comparison of the number of occupied houses in the catchment stated in the 2006 census and the number of houses counted by the author in 2008 as part of the current research.

The population in the Lough Currane catchment is likely to be substantially higher in summer than at other times of the year, and it is highly probable that a large number of the unoccupied houses in the catchment are used as holiday homes for the summer months. As a result, the septic systems within these houses may act as a seasonal source of nutrients to the lake. Bigler et al. (2007) found that nutrient levels in Lej de San Murezzan in the Swiss Alps first increased with the exploitation of St. Moritz as a tourist resort at the beginning of the 20th century. In addition, Koster et al. (2005) stated that a large summer population at Walden Pond, Massachusetts, USA, contributed to approximately 27% of the annual P load and 64% of the annual N load to the lake. Highest nutrient levels in Lough Currane were found in the south-west section of the lake as seen in Figure 6.3. These elevated nutrient levels may be associated with storm related runoff from a cluster of one-off houses located close to the shores of the lake. Storm conditions (> 10 mm of rain in 24hours (Heathwaite and Dils, 2000)) preceded the measurement date for these samples in April 2010 and will be discussed in more detail later (See section 6.2.2). Pla et al. (2005) suggested that local factors, such as shoreline development, may have had an important impact on increasing nutrient levels in some isolated bays in Lake of the Woods, Ontario and while this may be the case in the south-west section of Lough Currane, housing is unlikely to be a major contributor to the enrichment of the lake as a whole. Although the population of the catchment may increase substantially during the summer months of the year, oligotrophic conditions prevailed when the population was 78% higher in 1841. Moreover, the number of houses in the catchment has not increased since 1851 and so the catchment did not experience an increase in the building of one-off houses associated with the change in rural living which occurred throughout Ireland in the 1960s and 1970s.

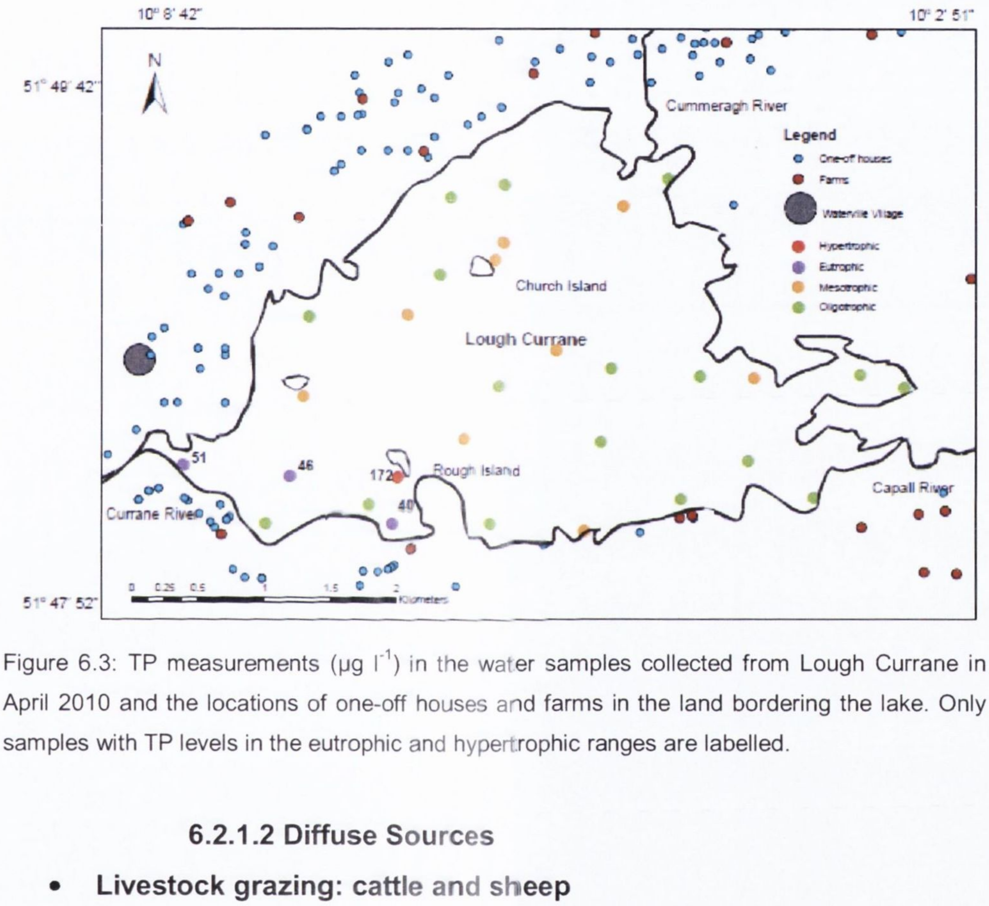


Figure 6.3: TP measurements (μg l^{-1}) in the water samples collected from Lough Currane in April 2010 and the locations of one-off houses and farms in the land bordering the lake. Only samples with TP levels in the eutrophic and hypertrophic ranges are labelled.

6.2.1.2 Diffuse Sources

- **Livestock grazing: cattle and sheep**

Most environmental concerns associated with grazing animals are in relation to high animal densities (Hubbard et al., 2004). The results of the RDA carried out on the diatom and DI-TP datasets indicate that an increasing density of sheep was statistically significant in explaining up-core increases in DI-TP, and in the abundances of mesotrophic to eutrophic diatom species, throughout the 3 coring sites at Lough Currane. In the intensive livestock farming areas of England, average livestock densities are 1.8 to 2.5 LU ha^{-1}. At these densities the accumulation of P in the soil is in excess of 20 kg ha^{-1} $year^{-1}$ (Ulén et al., 2007). The calculation of LUs is based on the food requirements of the animals such that a cow weighing 600 kg is equal to 1 LU, while five sheep are equivalent to 1 LU (European Commission, 2010). In Ireland, the average livestock density in the most intensively grazed areas is 1.5 LU ha^{-1} (Ulén et al., 2007). In the Cahersiveen rural district, which encompasses the catchment of Lough Currane, the density of livestock (cattle and sheep) was lower than the average of the most intensively grazed areas in Ireland from 1871 to 1981 (Figure 6.4.) In contrast, in 1991, the livestock density in the Cahersiveen rural district was greater than average, and probably reflects increased sheep numbers.

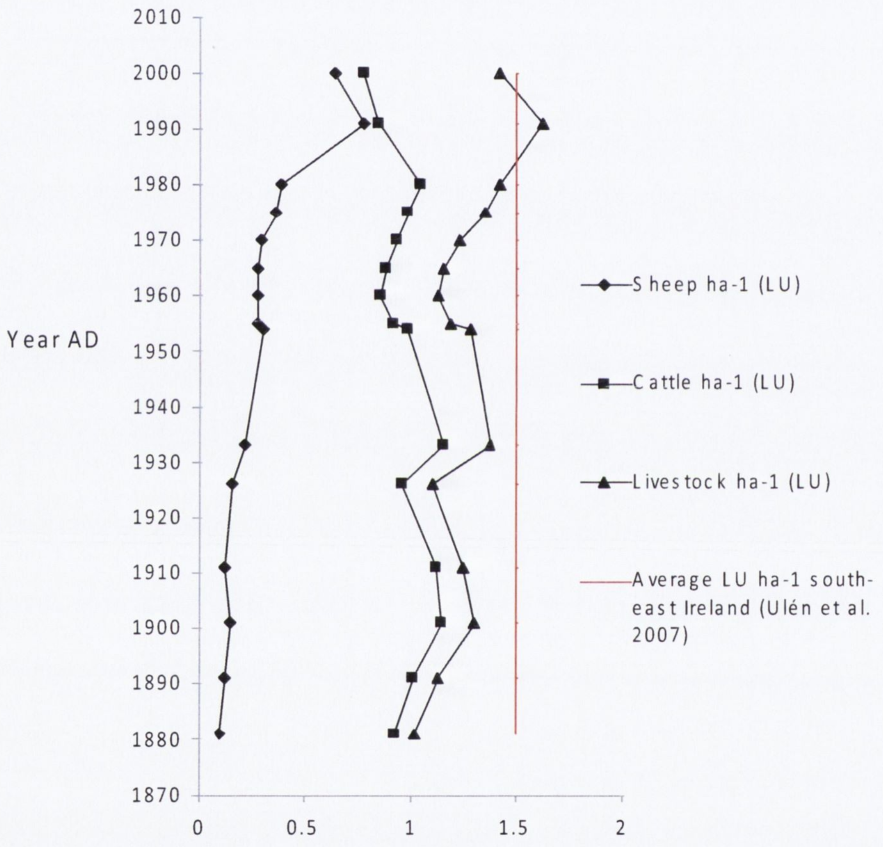


Figure 6.4: Livestock density in the Cahersiveen rural district as well as the average livestock density in the south-east of Ireland, reported by Ulén et al. (2007).

Most of the catchment of Lough Currane has a livestock carrying capacity of 0.2 to 0.6 LU ha^{-1} (Kerry County Committee of Agriculture, 1972). This carrying capacity is associated with the peat soils in the catchment (Figure 3.4). However, in the lowland areas around the shores of the lake, the livestock carrying capacity is 1.2 to 2.2 LU ha^{-1} (Kerry County Committee of

Agriculture, 1972). According to the census of agriculture 2000, the most intensively grazed DEDs in the catchment were Lough Currane and Mastergeehy (Table 6.1). Sheep density is highest in Mastergeehy, which is mostly upland and comprises mostly peat soils, while cattle density is highest in Lough Currane which is low-lying and comprises mostly brown earth and podzolic soils. The stocking density of sheep in Mastergeehy exceeds the maximum carrying capacity of the peat soils. Figure 6.5 shows the historical variations in the stocking density of livestock in the Cahersiveen rural district as well as the livestock carrying capacity of the various soils in the study catchment. On the peat soils, the stocking density of livestock was far higher than the carrying capacity from 1881 to 2000, while the stocking density of sheep only exceeded carrying capacity in 1991. The stocking density of livestock did not exceed carrying capacity on the brown earth or podzolic soils around the lake (Figure 6.5). On peat soils, increased stocking densities of sheep can lead to erosion problems (May et al., 2005). The increase in livestock stocking density coincides with an increase in the sediment accumulation rate and an increase in DI-TP in the lake (Figure 6.6.), which compares well with other sites. For example, an increase in sheep stocking density led to accelerated sedimentation at Blelham Tarn in the English Lake District (van der Post et al., 1997) and at Ballydoo Lough in Connemara, Western Ireland (Huang and O'Connell, 2000).

DED	Number of sheep	Sheep $LUha^{-1}$	Number of cattle	Cattle $LUha^{-1}$	$LUha^{-1}$
Ballybrack	5628	0.58	372	0.19	0.77
Derriana	14686	0.47	1027	0.16	0.63
Loughcurrane	2379	0.43	849	0.77	1.20
Mastergeehy	4900	0.76	618	0.48	1.23

Table 6.1: Number, density and % of livestock in the 4 DEDs that comprise the catchment of Lough Currane for the census of agriculture 2000.

The impact of the increased stocking of livestock, primarily sheep, to the deterioration of water quality at Lough Currane is confirmed when the lake is compared to Lough Cloonaghlin, whose catchment is dominated by diffuse nutrient sources (Figure 3.6). The diatom assemblages at Lough Cloonaghlin displayed similar floristic changes in comparison to those identified for Lough Currane. The floristic change was primarily due to a large increase in

Cyclotella pseudostelligera. This taxon is seen in far higher abundances in the surface sample from Lough Cloonaghlin compared to Lough Currane as shown in Figure 6.7. The taxon's abundance reaches c.55% while its abundance in Lough Currane reaches close to 20%.

Lough Cloonaghlin is located on the border between the DEDs, Derriana and Mastergeehy as seen in Figure 3.7. Based on the results from the census of agriculture for 2000, the number of livestock grazed in Derriana is far greater than in any of the other DEDs of which the study catchment is comprised, while the stocking density of livestock is highest in Mastergeehy as seen in Table 6.1. The correspondence between increased stocking density of livestock and floristic change in both Lough Currane and Lough Cloonaghlin suggest that increased livestock numbers, especially sheep, contributed substantially to the nutrient enrichment of both lakes.

- **Forestry**

The establishment of the coniferous forestry plantations in the study catchment, beginning in 1969, also coincides with the increase in DI-TP for the lake. The plantations consist primarily of lodgepole pine and sitka spruce. However, while the pollen profile at Coring Site 1 displays an increase in the abundance of *Pinus* from c.1950 AD, the proportion of *Pinus* found in all of the coring sites is very low. Pine and spruce trees have very high pollen productivity and dispersibility relative to other tree taxa (Jackson and Smith, 1994). Once produced by the plant, pine pollen becomes airborne and has been known to traverse great distances (Campbell et al., 1999). The scarcity of pine pollen in the sediment cores may be explained by the south-westerly prevailing wind in the area with airborne pollen being directed away from the lake.

One of the coniferous forestry plantations in the study catchment, Cloghvoola, is located close to the shores of Lough Currane and to Coring Site 3 as shown in Figure 6.8.

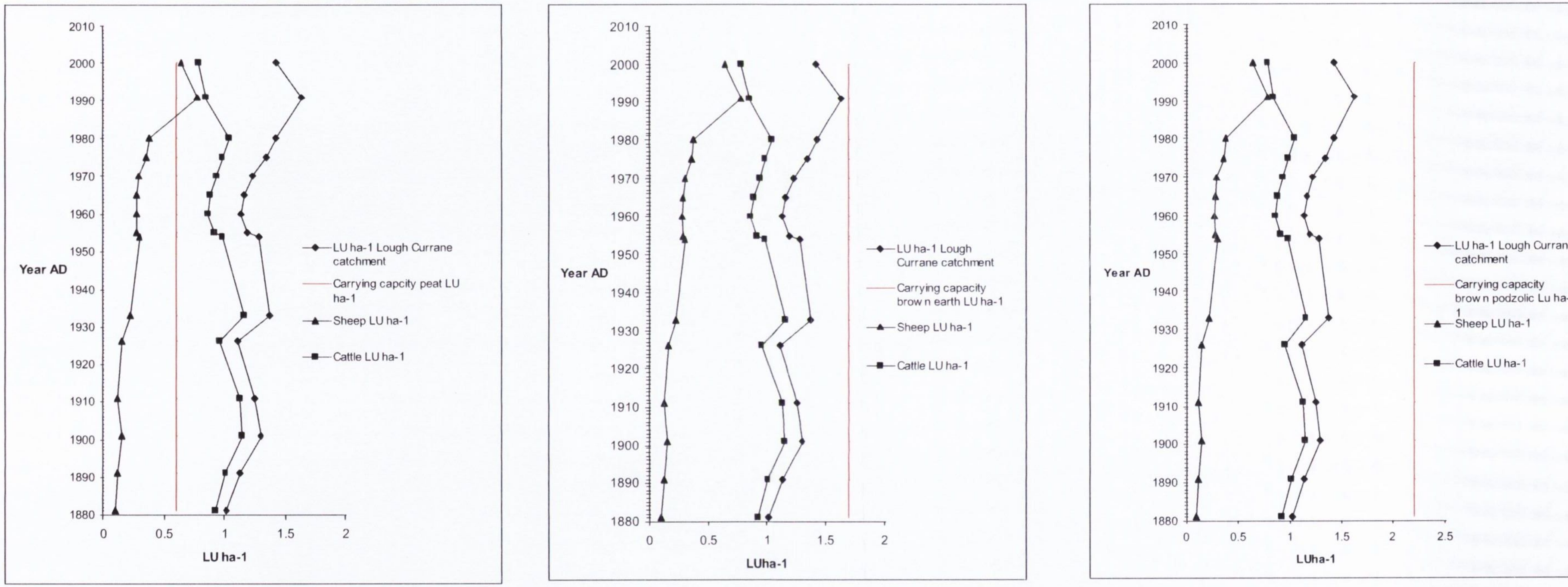


Figure 6.5: Temporal variations in the stocking density of livestock (cattle and sheep) in the Cahersiveen rural district and the carrying capacity of the soils found in the Lough Currane catchment (Kerry County Committee of Agriculture, 1972).

This plantation was established between 1971 and 1972 and clearfelling began in 1992 (Table 3.8). Planting and clearfelling operations are often associated with soil disturbance, sediment in-wash and the release of nutrients to water bodies (Neal et al., 2004). The increase in the % organic matter content and in the % of total sand at Coring Site 3, beginning in c.1970 AD and peaking in c.1990 AD coincides with the establishment of a coniferous plantation in close proximity to the lake, as shown in Figure 6.9. Coring Site 3 saw the largest increase in DI-TP when compared to the other two coring sites (Figure 5.22). Indeed the change in trophic status and the peak in DI-TP at Coring Site 3 follows, respectively, the establishment and harvesting of Cloghvoola, as shown in Figure 6.9. While the increase in livestock numbers is the main driving force behind the eutrophication of Lough Currane, the establishment of this coniferous plantation has probably had an impact in increasing the input of nutrients to the south-east section of the lake, thus exacerbating the effect of nutrient enrichment at Coring Site 3.

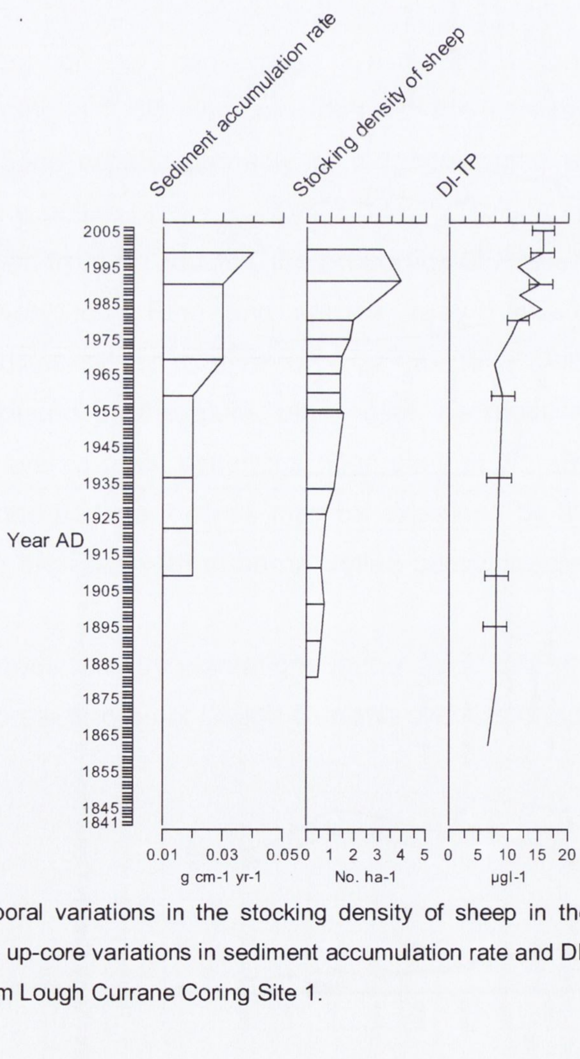


Figure 6.6: Temporal variations in the stocking density of sheep in the Cahersiveen rural district, as well as up-core variations in sediment accumulation rate and DI-TP recorded for the core collected from Lough Currane Coring Site 1.

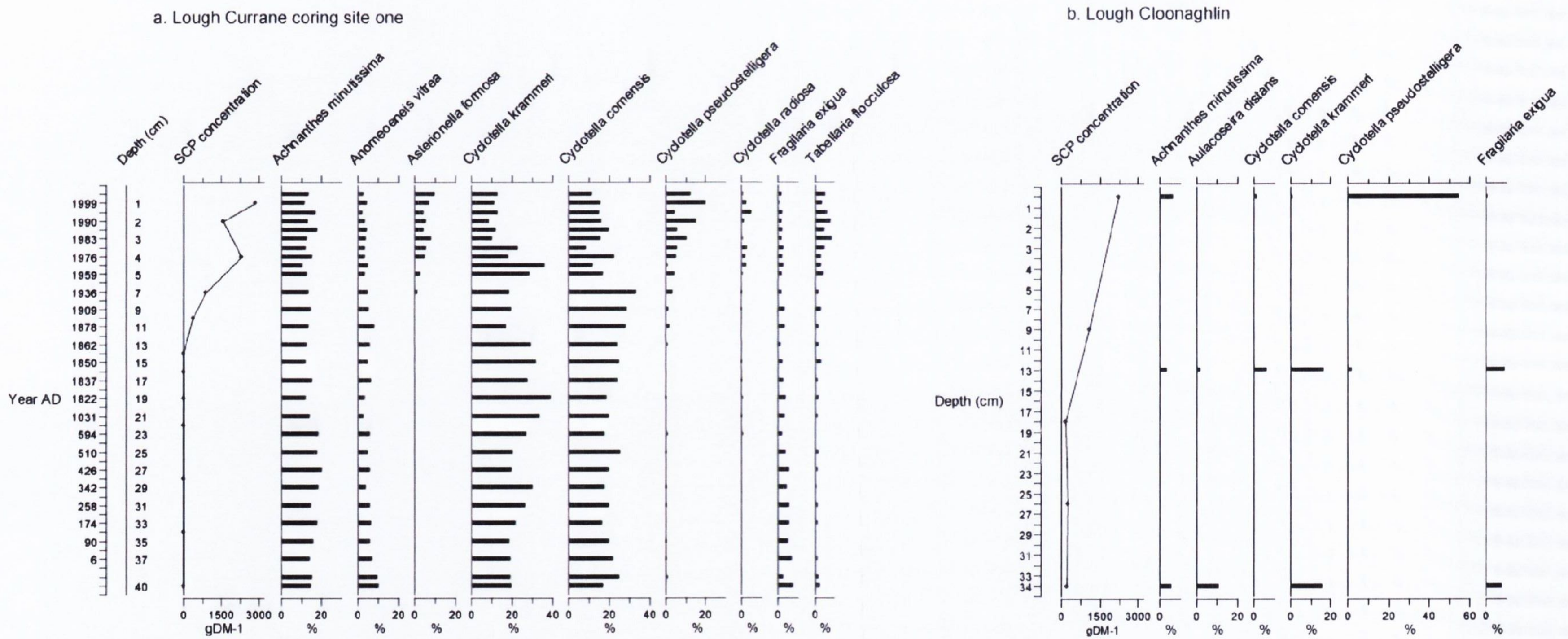


Figure 6.7: Diatom taxa with a minimum of 5% relative abundance at a. Lough Currane Coring Site 1 and b. Lough Cloonaghlin. Diatom records for Lough Cloonaghlin were obtained from Manel Leira, University of A Coruña, Spain.

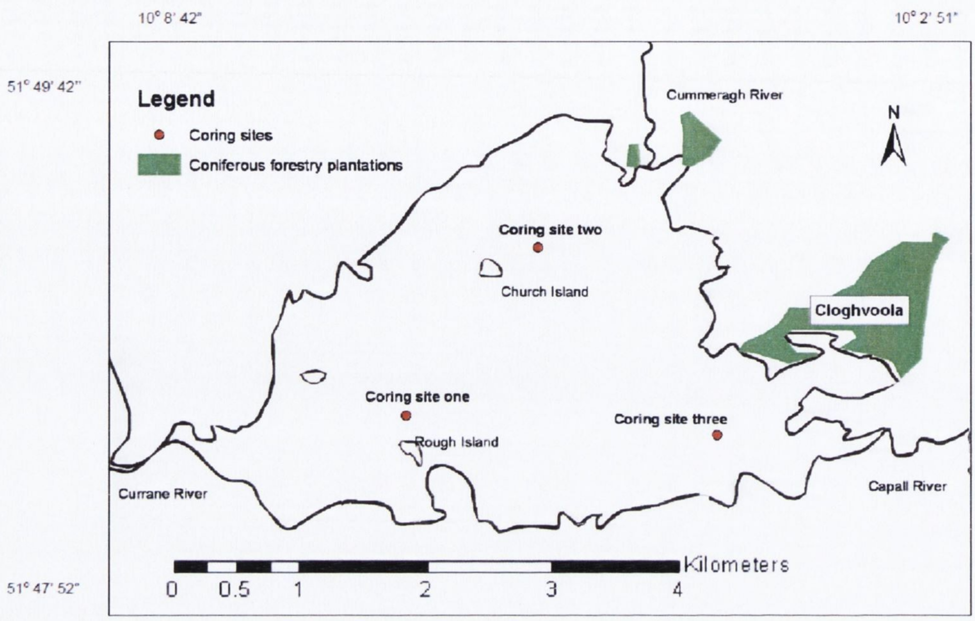


Figure 6.8: The location of Cloghvoola, a coniferous plantation, situated in close proximity to the shore of Lough Currane. The coring sites are also shown

6.2.2 The contribution of climatic factors to eutrophication

Aquatic environments are highly sensitive to ocean circulation patterns and lakes situated on the Atlantic seaboard provide ideal locations for the study of climatic fluctuations, particularly fluctuations in precipitation (Holmes et al., 2010). Lough Currane is located close to the south-west coast of Ireland and to the Valentia weather reporting station which aids the study of climatic fluctuations and their effect on lake water quality. The major control on inter-annual climate variations over the north Atlantic, together with western and central Europe is the NAO, an index of atmospheric pressure differences between Iceland and the Azores (Holmes et al., 2010). High NAO index values have been linked to winter climatic variations in Britain and Ireland, including the occurrence of westerly winds and increased air temperature (Jennings et al., 2000).

Figure 6.10 shows that increasing temperatures at Valentia from the 1980s to 2009 coincide with highly positive NAO index values. Temporal fluctuaions in temperature were not deemed to be significant in explaining variability in the diatom and DI-TP datasets (Table 5.18). However, of the three coring sites, DI-TP at Coring Site 3 increased by the largest proportion, by over 15 µg l^{-1} between c.1970 AD and c.2000 AD (Figure 5.22). This increase in DI-TP coincided with increases in annual mean temperature at Valentia (Figure 6.10). Increases in temperature can lead to the increased recycling of P (Ulén and Weyhenmeyer, 2007) and the enhanced growth of phytoplankton and macrophytes, especially in shallow sites (Elliott et al., 2006). However, the pollen profile at Coring Site 3 (Figure 5.22), and at the other coring sites (figures 5.13 and 5.14), shows minimal up-core variation in the abundance of aquatic pollen types (Figure 5.15). The increased DI-TP at Coring Site 3 is more likely to be due to nutrient transfers associated with clearfelling operations at Cloghvoola.

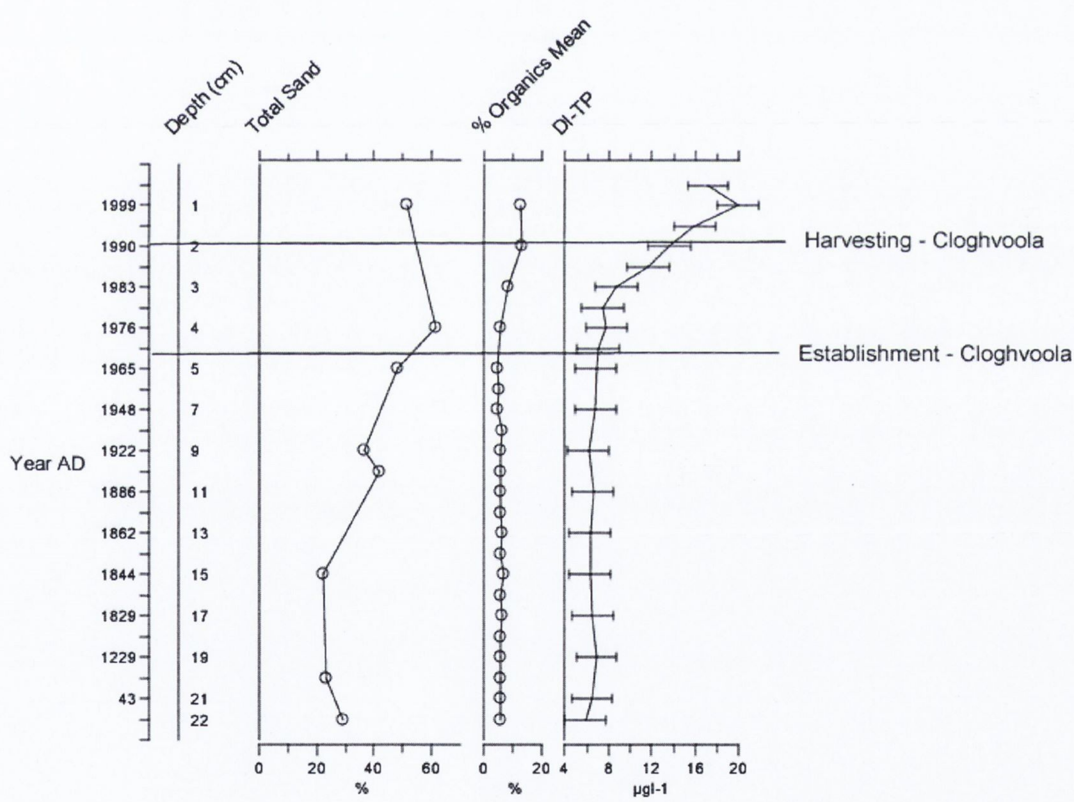


Figure 6.9: Up-core variations in DI-TP, % organic content and in the % of total sand at Lough Currane Coring Site 3. The dates for the establishment and the beginning of harvesting of the coniferous plantation, Cloghvoola are also shown.

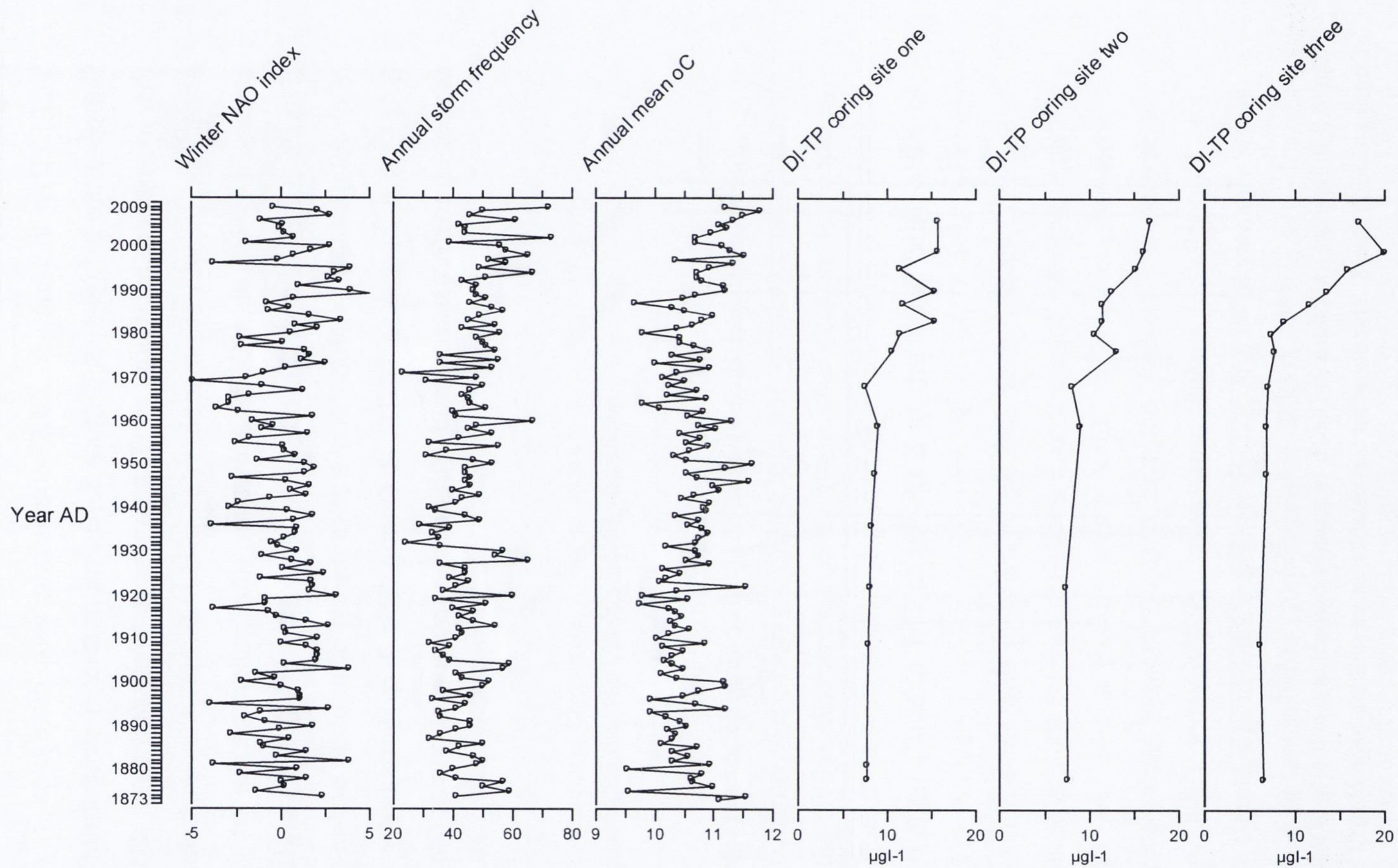


Figure 6.10: Historical variations in winter NAO index values, annual storm frequency and annual mean temperature recorded for Valentia from1873 to 2009, and DI-TP at each coring site from 1873 to 2006. NAO index values were obtained from (www.cgd.ucar.edu, 2011).

Winter precipitation in Ireland has also been shown to be above average when NAO index values are highly positive (Jennings et al., 2000). Figure 6.10 shows NAO index values and the annual frequency of storms at Valentia from 1871 to 2009. The early 1960s and early 1970s display negative NAO index values and relatively lower storm frequencies compared to the subsequent decades. The mink fur farm in the catchment of Lough Currane, which displays some of the characteristics of point sources, was established during this period. Point sources are largely storm independent and deliver high concentrations of P during low flows (Arnscheidt et al., 2007; Withers and Jarvie, 2008). Coring Site 2, the most proximate site to the fur farm, displayed an almost immediate change in trophic status associated with the establishment of the farm. The rapid change in the trophic status of Coring Site 2 corresponds well with the establishment of the mink farm in the study catchment. The low river flows associated with low precipitation in the years preceding and following the establishment of the farm are likely to have led to a sudden transfer of highly concentrated P from this same source to the north-east section of the lake, in which Coring Site 2 is located.

The years 1990 to 2000 displayed highly positive NAO index values, which are reflected in a generally higher frequency of storms during this period. The period from 1973 to 1990 also displayed positive NAO index values, reflected in a gradual increase in the annual frequency of storms at Valentia. A large number of studies have reported that storm runoff is significant in delivering the vast majority of annual P loads from intermediate (e.g. Edwards and Hooda, 2008; Edwards et al., 2008, Edwards and Withers, 2008; Withers and Jarvie, 2008) and diffuse (e.g. Jordan et al., 2005a; Douglas et al., 2007; Jordan et al., 2007; Bowes et al., 2008; Withers and Jarvie, 2008) sources to surface water. The results at Lough Currane compare well with these studies. While precipitation and storm frequency were not deemed to be statistically significant in explaining variability in the diatom assemblages associated with nutrient enrichment, there is evidence to show that high rainfall events have led to the increased delivery of nutrients to the lake and an exacerbation of nutrient enrichment within the lake. Table 6.2 shows the sampling dates when water samples containing over 100 $\mu g\ l^{-1}$ TP were collected, both by Kerry County Council and by the author, as well as the associated rainfall events prior to sampling. A storm event (> 10 mm rain in 24 hours (Heathwaite and Dils, 2000)) preceded all of the dates when TP exceeded 100 µg l^{-1} at Lough Currane since 2003. The extremely high TP measurements in water samples collected in October 2005 followed a storm event on October 17th 2005. Storm transfers are known to be most effective in transferring P to surface waters after a dry period (Simard et al., 2000; Jennings et al., 2003) and this is evident in the test site. Prior to the storm event in October 2005, there had been no precipitation for five days. While a storm event did not immediately precede the high TP values in water samples collected in November 2005; in the period prior to the 17th of November 2005 there were 31 consecutive days of rainfall including seven storm events. These events would have been important in creating saturation excess runoff and delivering P to the lake. Figure 6.10 shows an increasing frequency of storms from 1970 to 1990 and from 1990 to 2000. The increased frequency of storms from the 1970s to the 2009 coincided with increased DI-TP associated with excessive livestock grazing in Lough Currane. The evidence described here suggests that high rainfall events are likely to have contributed to the increased delivery of nutrients from diffuse sources to Lough Currane from c.1973 AD to 2006.

Location	Sample date	TP µgl^{-1}	Rainfall mm	Rainfall Date
1km NE of Church Island	11-Jun-03	195	42	09-Jun-03
Mouth Of Capall River	11-Jun-03	124	42	09-Jun-03
1km NE of Church Island	27-Apr-05	180	28	27-Apr-05
Mouth of Currane River	27-Apr-05	132	28	27-Apr-05
Mouth Of Capall river	19-Oct-05	440	14*	17-Oct-05
Mouth of Currane River	19-Oct-05	875	14*	17-Oct-05
1km NE of Church Island	17-Nov-05	165	15**	04-Nov-05
100m NE of Rough Island	17-Nov-05	153	15**	04-Nov-05
SS2	29-Apr-10	172	22	27-Apr-10

* There was no rain for five days prior to this date

** There was rain for 31 consecutive days prior to 16-Nov-05. Total 243mm

Table 6.2: TP (µg l^{-1}) measured in Lough Currane and the storm events that preceded the dates of sample collection. Storm conditions are defined as > 10 mm rain in a 24 hour period (Heathwaite and Dils, 2000)

6.2.3 Summary: Assessing the extent to which recent eutrophication is caused by anthropogenic factors

The first research question that this research sought to answer was "to what extent is recent eutrophication caused by anthropogenic factors?" The results of the palaeolimnological analyses carried out on the test site, Lough Currane, along with the analysis of historical documentary and climate records indicate that overall, recent eutrophication (c.1970s AD) is caused by increasing livestock numbers associated with intensive livestock production and excessive livestock grazing. The nutrient enrichment of lakes associated with excessive livestock grazing, especially in excess of the carrying capacity of peat soils, is well documented and the results at Lough Currane compare well with other lakes in Ireland (e.g. Huang and O'Connell, 2000; Dalton et al., 2010; Donohue et al., 2010) and Europe (e.g. van der Post et al., 1997; Ulén et al., 2007). The location of the test site aided in the study of the impacts of climatic change, associated with variations in oceanic circulation, on the nutrient enrichment of lakes. Variations in oceanic circulation associated with the NAO were deemed to be important in controlling precipitation patterns at Valentia while high precipitation events associated with highly positive NAO index values are likely to have been important in delivering nutrients from diffuse and intermediate sources to the lake. For example, the grazing of livestock in excess of the carrying capacity of the land, combined with an increase in the number of storms probably led to increased runoff from the catchment and an increase in the sediment accumulation rate and levels of reconstructed DI-TP for the test site.

While mink farming is not widely practiced in Ireland, the mink farm, located in the catchment of the test site, shows some characteristics of an agricultural point source. The results from this research show that point sources, located in CSAs, can substantially affect the nutrient loading of lakes. In addition, this research shows that periods of low precipitation, associated with negative NAO index values, combined with increased P from a point source can lead to rapid eutrophication. However, different areas within the test site did not respond equally to increased nutrient loads.

6.3 Within-lake variability in the response to increased nutrient loads

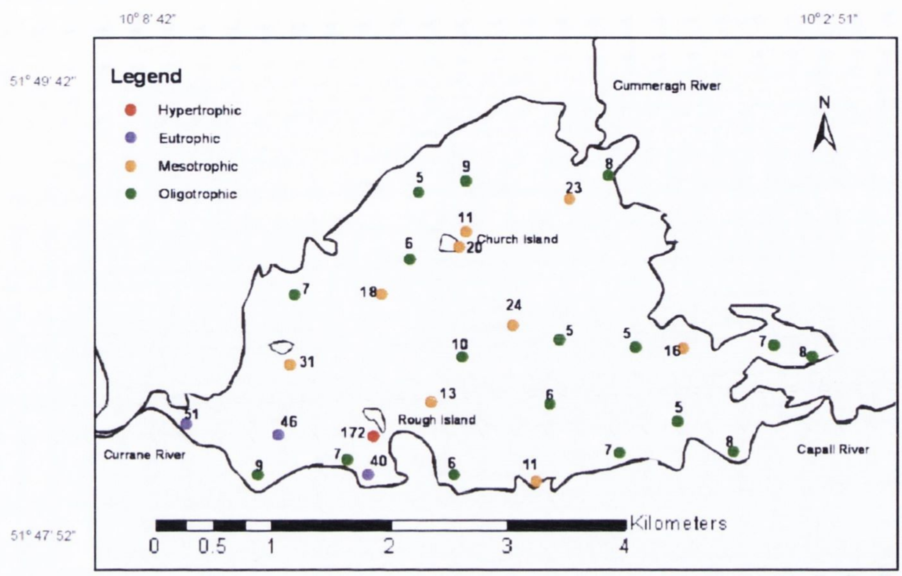
6.3.1 Current within-lake variability in water quality

Analysis of surface water samples collected from Lough Currane in April 2009 indicated that levels of TP varied spatially throughout the lake basin. However, these observed TP levels only provide a snapshot of the spatial variability at the time of sampling. In order to obtain a longer term view of spatial variability in water quality, levels of DI-TP were estimated, from diatom remains preserved in the surface sediment samples collected in April 2010. Overall, the DI-TP values for the surface sediments are lower than measured levels of TP for Lough Currane. While the errors associated with estimates on P concentrations inferred from sedimentary diatoms can be relatively large (Sayer, 2001), the DI-TP levels in the surface sediment samples display the same spatial trends seen in the surface water samples, as shown in Figure 6.11. Lowest TP and DI-TP were found in the south-east section of the lake, close to the Capall River, while higher values were found at a mid-lake site (TP 24 μg l^{-1}, DI-TP 16 μg l^{-1}). Similar values were also found around Church Island and Rough Island.

Within-lake variability in the diatom assemblages identified for the surface sediment samples are influenced by the morphometry of the lake basin. Sites SS21 to SS24 are characterised by high abundances of the benthic taxa *Achnanthes minutissima* and *Anomoeoneis vitrea* and relatively low abundances of the planktonic taxa *Cyclotella comensis* and *Cyclotella krammeri* (Figure 5.18). Phytoplankton assemblages in lakes often show clear differences associated with water depth. Studies carried out on the within-lake spatial variability of diatom assemblages (e.g. Anderson, 1990, 1998; Moos et al., 2005; Laird and Cumming 2008, 2009) have found that the relative abundances of planktonic taxa are generally lower in littoral areas compared to profundal or deeper areas within a lake. There is generally increased habitat availability for non-planktonic species in near shore and shallower water. In these areas sand, stones, mud and macrophytes act as habitats for non-planktonic diatoms, whereas in open water areas habitat availability is diminished owing to an abundance of planktonic taxa (Moos et al., 2005). Water depth has been found to be the main determinant of variability in the distribution of diatom taxa (e.g. Thayer et al. 1983; Anderson 1990, 1998; Moos et al. 2005; Adler and Hübener 2007; Laird and Cumming

2008, 2009), with distance to shore also being an important factor (Thayer et al., 1983; Anderson, 1998).

a.



b.

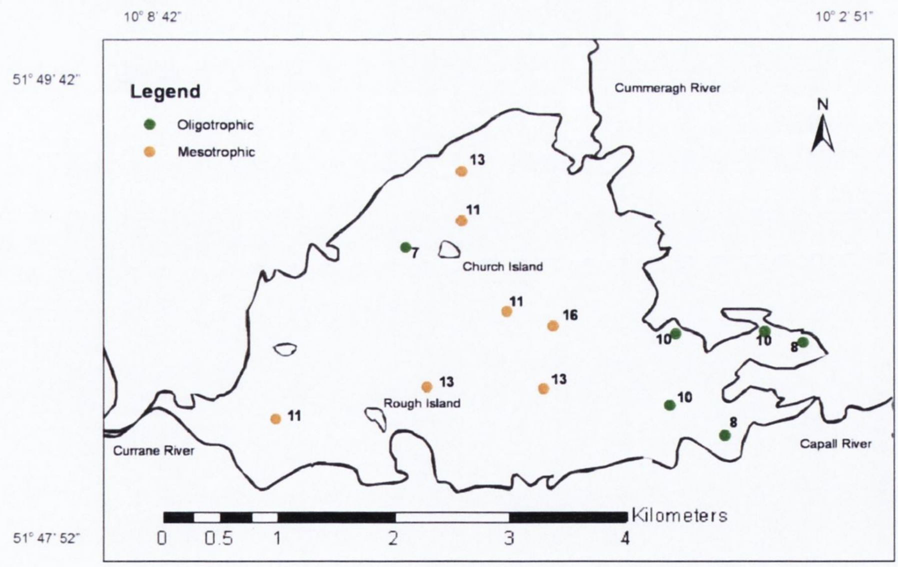


Figure 6.11: a. TP levels (µg l^{-1}) measured in water samples collected from Lough Currane on April 29th 2010 and b. DI-TP levels (µg l^{-1}) reconstructed for surface sediment samples collected from Lough Currane on April 29th 2010.

At Lough Currane distance to shore was identified as the main determinant of inter-sample variability in the diatom assemblages (Table 5.16). Sites located close to shore displayed different assemblages than those located in open water areas. However, all of the sites that were important in explaining inter-sample variability (SS21 to SS24) in the lake were located in littoral areas at depths of < 4 m as shown in Figure 6.12, indicating that water depth and distance to shore may be auto-correlated and both variables may be important in explaining inter-sample variability.

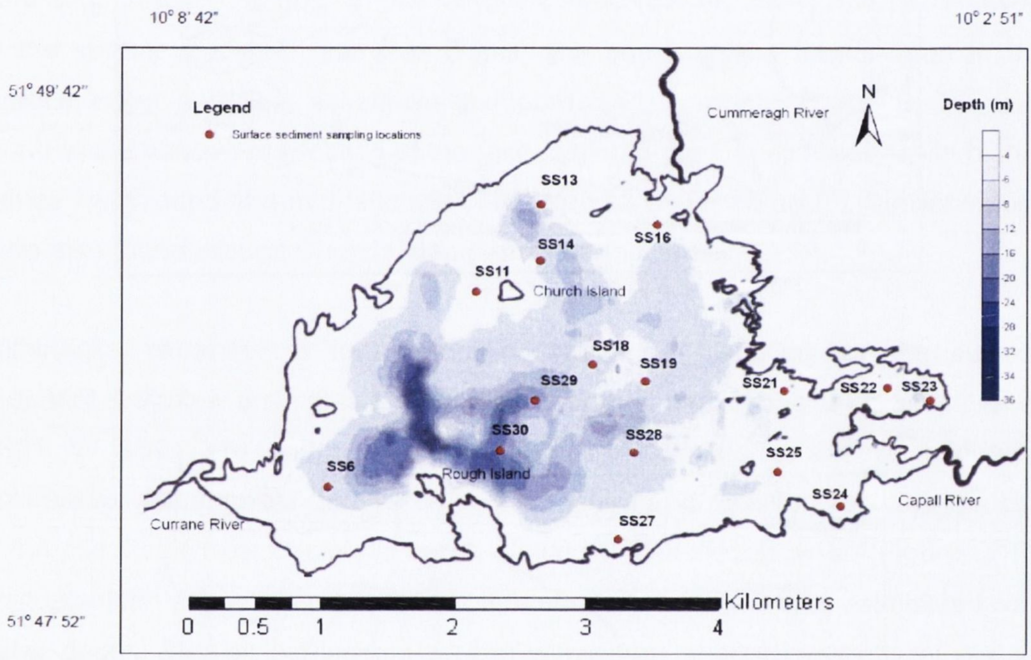


Figure 6.12: The surface sediment sampling locations at Lough Currane and the bathymetric map of the lake

Morphometric parameters such as distance to shore and water depth are important in explaining the variability in the diatom assemblages in relation to their life-form categories in Lough Currane. However, both the TP and DI-TP readings indicate that the proximity to the inflowing rivers and nutrient sources may be more important with regard to the spatial variability in the response to increased nutrient loads at the lake. Highest TP measurements in the samples collected in April 2009 were found in the south-west section of the lake both by the author and by Kerry County council (Figure 6.11). However, these values appear to be related to storm runoff as shown in Table 6.2 and may be related to one-off housing and shoreline development. The high average TP measurement for this part of the lake recorded by Kerry county council is due to one measurement of 875 $\mu g\ l^{-1}$ in October 2005, following a storm event (Table 6.2). If this measurement was excluded the average TP at the outlet of the lake would be 20 $\mu g\ l^{-1}$. Due to the shallow water depth and presence of rocks, the collection of surface sediment samples from this part of the lake was not possible. As a result the area is under-represented by the surface sediment samples. The DI-TP value at SS6 does not reflect the high TP values found in the south-west section of the lake (Figure 6.11). Moreover, the diatom assemblages at SS6 do not show high abundances of mesotrophic to eutrophic species (Figure 5.18). Further work is needed to ascertain if the spatial pattern of TP is maintained throughout the year and to determine if the south-west section of the lake displays consistently high TP values.

Within lakes, TP can be high close to nutrient sources, usually associated with inflowing rivers (Pla et al., 2005; Steinman et al., 2009). At Lough Currane, the main inflowing rivers are the Cummeragh and the Capall and relatively high TP values were reported at their inflows by Kerry County Council during the period from 2001 to 2009 (Figure 5.23). As described in chapter three, the majority of the potential anthropogenic nutrient sources to Lough Currane are located in the catchment of the Cummeragh River, with the catchment of the Capall River displaying fewer nutrient sources (Figure 3.6). The south-east section of the lake displayed the lowest TP and reconstructed DI-TP values of the samples collected in April 2009. This section of the lake is influenced by the inflow from the Capall River as shown in Figure 6.11. These sites also display low proportions of the mesotrophic to eutrophic species *Asterionella formosa* and *Cyclotella pseudostelligera* (Figure 5.18).

6.3.2 Within–lake variability in the stratigraphic record of eutrophication

6.3.2.1 Sedimentary patterns at Lough Currane

The process of sediment focussing, where sediment is transported to and accumulates in the deeper zones of a lake (Blais and Kalff, 1995), underpins the assumption that sediment cores collected from the deepest point of a lake basin are representative of overall limnological conditions (Anderson, 1998; Bindler et al., 2001). According to the process of sediment focussing, grain size distributions are mainly affected by the energy level of the water with finer particles reaching deeper water and coarser particles dropping out in shallower zones (Wang et al., 2009). Erosional zones and shallower areas are characterised by coarser non-cohesive sediments (Blais and Kalff, 1995; Punning et al., 2005). Maximum accumulation of fine grained material including organic matter (Bindler et al., 2001; Shuman, 2003) and microfossils (Anderson, 1990; Beaudoin and Reasoner, 1992; Anderson, 1998) are thought to take place in the deepest zones of a lake; while, due to the processes of sediment deposition, the largest variations in sedimentological properties should occur close to shore and close to river inflows (Punning et al., 2004; Kumke et al., 2005).

At Lough Currane, the deposition of organic matter, microfossils (diatoms and pollen) and SCPs also appear to follow the process of sediment focussing. Analysis of the surface sediment samples show that sites with the highest organic matter content and highest concentrations of diatoms were located at mid-lake sites and in the deeper zones of the lake (Figures 5.2 and 5.19). The coring sites also display this pattern. The deepest point of the lake (Coring Site 1) contained the highest concentrations of diatoms, pollen and SCPs and the highest organic matter content as shown in Figure 6.13. The most peripheral coring site (Coring Site 3) contained the lowest concentrations of these same proxies (Figure 6.13). A comparison of the up-core variations in organic matter (Figure 5.1), grain size (Figure 5.5) and the relative abundances of diatoms (Figures 5.20, 5.21 and 5.22) and pollen (Figures 5.13, 5.14 and 5.15) indicate that the coring sites in the profundal areas of the lake (Coring Sites 1 and 2) display similar stratigraphic records while most variation is accounted for by the most peripheral coring site (Coring Site 3).

Rose et al. (1999) found that ten cores, collected from Loch Coire nan Arr in north-west Scotland, showed similar overall up-core variations in concentrations of SCPs and concluded that a single core gives a reasonable representation of the major depositional changes in SCPs. However, all of the cores were collected from the deeper parts of the basin at Loch Coire nan Arr. The coring sites at Lough Currane, although located at varying depths and distances to shore in the lake basin, display the same trend as seen in the comparison of the cores at Loch Coire nan Arr. Although highest SCP concentrations were found in the deepest parts of the lake, following the mechanisms of sediment focussing, each coring site recorded a similar pattern of SCP deposition. In this way, the deepest point was deemed to be representative of all the coring sites within the lake.

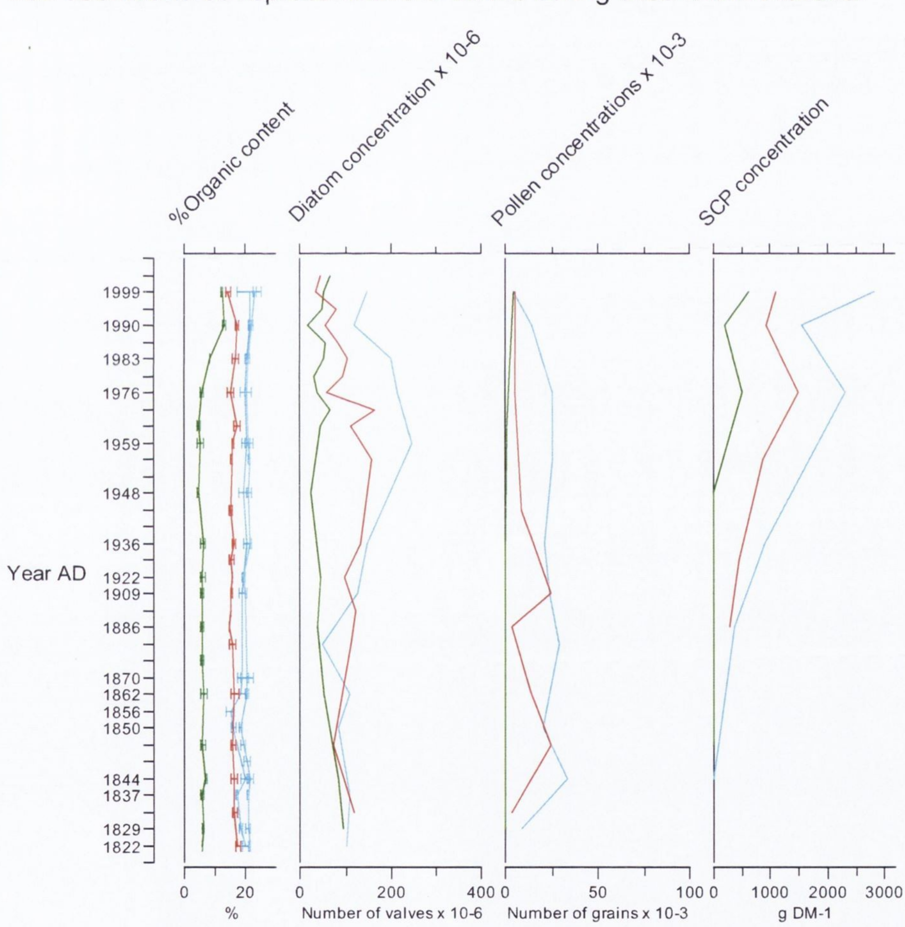


Figure 6.13: Up-core variations in % organic content, and concentrations of diatoms, pollen and SCPs from each of the coring sites at Lough Currane. Site 1: blue, site 2 :red, site 3: green. Samples from c.1822 AD to the present were used, as the chronology is most reliable for this portion of the cores. Coring Site 1 displays 2 % organic content graphs; this is because 2 sediment cores were analysed for Coring Site 1.

The deposition of organic matter, microfossils (diatoms and pollen) and SCPs appears to follow the process of sediment focussing at Lough Currane however; the grain size distributions in the surface sediment samples appear to deviate from the expected pattern associated with sediment focussing. Analyses of the surface sediments indicate that highest mean grain size was found at shallow sites located close to shore however, lowest mean grain size was found at mid-lake sites rather than in the deeper zones of the lake (Figure 5.3). A statistically significant negative correlation existed between mean grain size and distance to shore in the surface samples at Lough Currane (Table 5.1). The core samples display a similar trend, with highest mean grain size occurring at the deepest point of the lake and lowest mean grain size occurring at the most peripheral site (Figure 5.5). The process of sediment focussing also assumes that sediment accumulating in the deepest zone of a lake will be well sorted (Blais and Kalff, 1995; Bindler et al., 2001). The grain size results at Lough Currane also contradict this assumption. The most well sorted sediments were located at mid-lake sites (Figure 5.5), while the deepest point contained the most poorly sorted sediment of the coring sites (Figure 5.5).

The trend seen in the grain size results at Lough Currane, where the deepest point did not display lowest mean grain size and the most well sorted sediment may be specific to the morphometry of the lake. A similar trend was found by Wang et al. (2009) at Lake Pumoyum, Co. Tibet, China and was attributed to the location of the deepest point, close to a river inlet. The deepest point at Lough Currane is located almost 3 km from a river inlet but is located relatively close to shore, as shown in Figure 4.5, which may have contributed to the increased deposition of coarse grained material at the deepest point. Despite the unusual pattern of grain size distribution at Lough Currane, each coring site displayed similar up-core variations in grain size (Figure 5.5). In this way, the deepest point provided a representative record of up-core variations in grain size at Lough Currane.

6.3.2.2 Spatial variability in historical water quality inferred from diatoms.

Nutrient levels have been measured frequently in Lough Currane since 2001. Due to the lack of long term water quality data, diatoms were used in the current study to track temporal changes in the trophic status of the test site and to assess the within-lake variability in the response to increased nutrient loads. The results of the PCA carried out on diatom assemblages from the core samples in Lough Currane reflect the variability found in the surface sediment samples in the lake. Samples from Coring Site 3, which is located close to shore and in the south-east section of the lake, were deemed to be the most important in explaining inter-sample variation in the dataset (Figure 5.25).

The up-core variations in diatom assemblages are different at Coring Site 3 compared to the other 2 coring sites (Figures 5.20, 5.21 and 5.22). Similar to the surface sampling sites, these differences are related to the morphometry of the lake basin and the differences between assemblages located in littoral and profundal zones. In addition, while Coring Sites 1 and 2 comprise two DAZ, three zones are apparent at Coring Site 3. Coring Site 3, due to its water depth, was deemed to be more sensitive to changes in nutrient levels following de-population associated with the famine. The up-core changes in the diatom assemblages reflect this sensitivity and display a decrease in abundances of *Achnanthes minutissima* and an increase in the abundance of the oligotrophic taxon *Cyclotella krammeri*. The reconstructed DI-TP at Coring Site 3 also displays a decrease from c.2000 AD. Moreover, the south-east section of the lake displayed the lowest levels of DI-TP and TP in the surface samples collected throughout the lake. These results, in addition to the evidence of oligotrophication at Coring Site 3 following the famine, indicate that shallow water may be more sensitive to changes in the nutrient levels and may respond more rapidly to decreases in nutrient loads. The other cores, located in profundal zones, do not show these trends, indicating that they are less sensitive to changes in nutrient loading.

While many lakes have shown within-lake spatial variability in phytoplankton assemblages, multiple cores taken from those lakes all show similar up-core variations in assemblages associated with increased nutrient loading (e.g.

Anderson, 1990, 1998; Ginn et al., 2007; Selby and Brown, 2007). This pattern is also apparent at Lough Currane. Despite differences between littoral and open water sites, the uppermost samples in each of the coring sites have very similar diatom assemblages and respond in a similar way to increased nutrient levels within the lake. However, the timing of eutrophication varies between the three coring sites. Similar to the results found in the surface samples, the influences of the proximity to nutrient sources is seen in the variability of the timing of eutrophication in Lough Currane. This influence appears to overshadow the influence of morphometry on the water quality of the lake. The diatom assemblages identified for Coring Sites 1 and 2 display a change from taxa with preferences for oligotrophic conditions to taxa with preferences for mesotrophic to eutrophic conditions in c.1970 AD. However the transition from oligotrophic to mesotrophic status occurs almost immediately at Coring Site 2, the most proximal coring site to the Cummeragh river and the mink farm, while the transition from oligotrophic to mesotrophic status is delayed until c.1980 AD at Coring Site 1 (Figure 6.14). At Coring Site 3, which is located close to the Capall River, the change from oligotrophic to mesotrophic diatom taxa occurs in c.1980 (Figure 5.22) while the transition to mesotrophic status occurs five years later in c.1985 (Figure 6.14). While Coring Site 3 is probably affected to some extent by the input of nutrients from the Cummeragh River, the nutrient enrichment of the coring site appears to be associated with shoreline activity and the establishment and harvesting of a coniferous plantation. This difference at Coring Site 3 suggests that while the response to increased nutrient loads is similar throughout the lake, the sources that are important in delivering nutrients to different parts of a lake may vary.

6.3.3 Summary: Assessing the extent to which the response to increased nutrient loads varies spatially within the test site

The second research question that this research sought to answer was "to what extent does the response to increased nutrient loads vary spatially within a lake basin?" Diatoms were used as a proxy for water quality variations and the diatom assemblages, both in the surface and core samples, displayed the same distributional pattern seen in other studies of the within-lake variability in diatom assemblages (e.g. Anderson, 1998; Moos et al., 2005; Adler and Hübener, 2007;

Laird and Cumming, 2008, 2009). The assemblages showed a split between deeper water and littoral zones. The morphometric parameters, water depth and distance to shore were deemed to be important in driving variability in the diatom assemblages but this variability was due to differences in habitat preferences between planktonic and benthic species.

Each coring site within the test site displayed the same response to nutrient enrichment and the analysis of pollen and diatom concentrations, % organic content and PSA indicate that, in general, the deepest point is representative of overall limnological conditions. However, the timing of eutrophication differed between the three coring sites. The results of the limnological analyses carried out at the test site indicated that water quality, represented by TP and DI-TP, varied spatially within the lake. Proximity to nutrient source was deemed to be important in driving the variability in levels of TP and DI-TP in the surface samples and the variability in the timing of eutrophication at the coring sites.

Sites in locations associated with riverine inputs of P and sites located close to sources associated with the shorelines of the lake, responded more rapidly to increased nutrient loads within the lake. Coring Site 2, located closest to the main source of nutrients to the lake, the Cummeragh River, responded rapidly to increased nutrient loads while Coring Site 3, located farthest from the Cummeragh River, showed a delayed response to nutrient enrichment. However, the establishment and clearfelling of a coniferous plantation close to Coring Site 3 exacerbated the nutrient enrichment at this part of the lake. The study of multiple coring and surface sites proved useful in identifying both the primary sources of nutrients to the lake and the local sources that can exacerbate nutrient enrichment in lakes. If only one point was sampled and studied within the lake, the impact of local sources may not have been apparent in the palaeolimnological record. The study of multiple sites, also displayed that shallow sites appear to be more sensitive to changes in nutrient loading, allowing possible oligotrophication effects, for example associated with de-population to be realised.

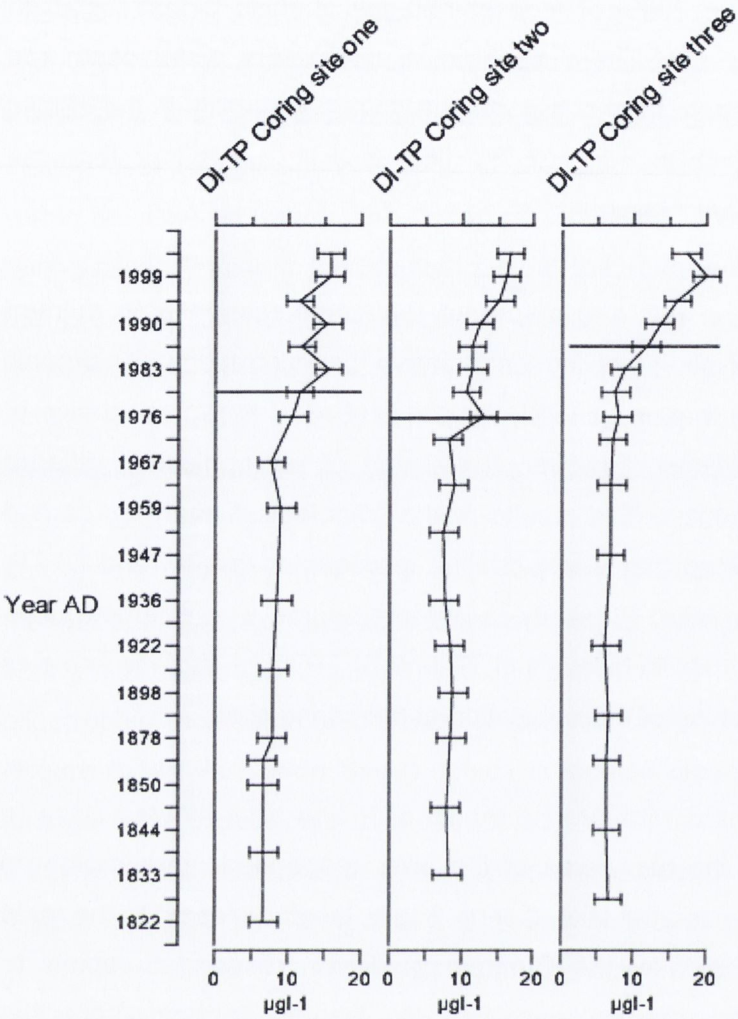


Figure 6.14: Up-core variations in DI-TP at each of the coring sites in Lough Currane. The horizontal bars that dissect the y axes denote the transition from oligotrophic to mesotrophic conditions.

6.4 Overall findings and contribution to existing knowledge

This research acts as a case study of temporal and spatial variability of recent eutrophication, with an emphasis on the Irish Ecoregion and sought to provide a link between the various pressures and effects of water quality deterioration in lakes. With regard to the pressures affecting eutrophication in lakes, this research contributes to a suite of research on the eutrophication of lakes including the work of Foy et al. (1995, 2003); Foy and Lennox (2000); Jordan et al. (2002, 2005); Jordan and Rippey (2001, 2003); Donohue et al. (2005, 2006, 2010); Taylor et al. (2006) and Dalton et al. (2010) in the Irish Ecoregion and Bowes et al. (2005, 2008); Bertahas et al. (2006); Bigler et al. (2007); Ulén et al. (2007) and Torrent et al. (2007) globally. Through the analysis of limnological, palaeolimnological as well as historical documentary and climate records, the findings of the current research support the notion that eutrophication effects in freshwater lakes are predominantly human-induced. However, climatic fluctuations, particularly associated with variations in oceanic circulation patterns, can enhance both the delivery of nutrients to lakes and the effects of increased nutrient loads in lakes. Positive NAO index values have been linked to increased water temperatures in lakes (e.g. George et al., 2004; Bleckner et al., 2007) however, lakes situated on the western European seaboard are thought to be more susceptible to increased precipitation associated with positive NAO index values (George et al., 2010). The findings from this research support this notion and indicate that increased precipitation can enhance the delivery of nutrients to lakes.

The palaeolimnological study of eutrophication is often limited to analyses of cores collected from a single site within a lake basin (e.g. Bennion et al., 2004; Ekdahl et al., 2004; Miettinen et al., 2005; Finsinger et al., 2006; Taylor et al., 2006; Bigler et al., 2007; Bjerring et al., 2008). The current research provides a contribution to the discipline of palaeolimnology and to the study of spatial variability of water quality in lakes. The findings of this research indicate that, when analysing the pressures and effects of eutrophication in lakes, a within-lake multi-site (including multi-coring site) sampling approach is preferable to a sampling approach based on a single sample/coring site. The findings related to the study of spatial variability of water quality carried out as part of the current research indicate that the study of multiple sites within a lake allows the effects of individual nutrient sources on the water quality of both the entire lake and individual areas to be determined. This is of value in the management of lakes and their watersheds and aids in mitigating against further water quality deterioration. If a single sampling site is used, the contribution of local sources of nutrients to the nutrient enrichment of a lake may not be seen in the stratigraphic record. A within-lake multi-site approach also accommodates for variations in assemblages and their response to increased nutrient loads according to morphometric parameters such as water depth and distance to shore.

Chapter Seven: Conclusion

The primary aim of this thesis was to examine the factors that influence eutrophication in lakes. Palaeolimnological techniques, in addition to the use of historical documentary and climate records, were used to separate the anthropogenic signals from natural and climatically induced variability in the palaeolimnological record of eutrophication. A combination of limnological and palaeolimnological techniques as well as G.I.S was used to determine the extent to which the response to increased nutrient loads varies spatially within a lake basin. This chapter presents a summary of the research results and findings, outlines the limitations of the study and concludes with suggestions for future study.

7.1 Research findings

7.1.1 Research question one: To what extent is recent eutrophication caused by anthropogenic factors?

This research question sought to separate the effects of different anthropogenic signals in the palaeolimnological record of eutrophication from each other and from natural and climatically induced variability. Two key findings emerged from this case study in relation to the first research question.

- **Eutrophication effects in freshwater lakes are predominantly anthropogenically induced**

The results of the analyses of the palaeolimnological records obtained for each coring site, combined with the analysis of historical, documentary and climate records for the study catchment indicate that increasing livestock numbers, related to both point and diffuse sources, were primarily responsible for the recent nutrient enrichment (c.1970s AD) of the test site. Point source pollution and a sudden delivery of concentrated P following the establishment of a mink farm in a CSA led to an almost immediate change in the diatom assemblages identified for two out of the three coring sites. The diatom assemblages displayed a transition from abundances of taxa with preferences for oligotrophic water to abundances of taxa with preferences for mesotrophic to eutrophic water. Moreover, the most proximal coring site to farm experienced an almost immediate change in trophic status following its establishment

An increase in the stocking density of livestock, especially sheep, probably in response to increased headage payments under CAP was deemed to be a significant driver of diatom assemblage and trophic change at each of the coring sites. The impact of excessive livestock grazing was confirmed when the diatom assemblages at the test site were compared to those at a lake, located in the study catchment, that was not influenced by point sources of nutrients.

Intermediate sources associated with housing were not deemed to be important to the nutrient enrichment of the test site as a whole, owing to the large decline in the population of the study catchment following the famine in Ireland. However intermediate sources may be important as local sources of nutrients to some areas of the test site.

- **Climatic fluctuations can enhance the effects of nutrient enrichment in lakes**

The location of the test site, close to the south-west Irish coast, aided the study of climatic fluctuations and their effect on lake water quality. Lakes situated on the western European seaboard are more susceptible to increased precipitation associated with variations in oceanic circulation (George et al., 2010). The results of the limnological and palaeolimnological analyses used in conjunction with the analysis of historical climate records indicate that precipitation patterns at the Valentia weather reporting station were influenced by the NAO. These precipitation patterns then had an effect on the delivery of nutrients to the test site, Lough Currane. Periods of low precipitation, associated with negative NAO index values, combined with increased levels of P, associated with a new point/intermediate source (mink farm) in the study catchment, appear to have led to rapid diatom assemblage change at two out of the three coring sites and a rapid change in trophic status at the most proximal coring site to the mink farm. In contrast, analysis of temporal changes in levels of TP and storm frequency indicate that high precipitation events led to elevated levels of TP in the test site. Highly positive NAO index values corresponded to an increase in the frequency of storms at Valentia. These high precipitation events are likely to have been important in delivering nutrients from diffuse and intermediate sources to the test site.

High NAO index values also corresponded to increased temperatures at Valentia from the 1980s to 2009. However the influence of temperature to the nutrient enrichment at the test site was not determined. The coring site located at the shallowest water depth displayed a more pronounced response to increased nutrient loads when compared to the other two coring sites, but this response was deemed to be due to increased nutrient loading associated with the establishment and harvesting of a coniferous forestry plantation.

7.1.2 Research question two: To what extent does the response to increased nutrient loads vary spatially within a lake basin?

This research question sought to determine the extent to which the response to increased nutrient loads varied spatially within a lake basin and to determine what parameters were important in influencing that variability. Through the use of a multi-site (including multi-coring site) sampling strategy and the analysis of limnological and palaeolimnological techniques as well as the use of G.I.S., two key findings emerged.

- **The response to increased nutrient loads is similar throughout a lake basin, but the timing and extent of that response can vary.**

The diatom assemblages identified for both surface sediment and core subsamples displayed a split between deeper water and littoral zones within the test site, with distance to shore and water depth deemed to be significant in driving that variability. However, this spatial variability in the diatom assemblages appeared to be due to differences in the habitat preferences between planktonic and benthic species. In relation to nutrient enrichment, each coring site displayed a similar response to increased nutrient loads. The diatom assemblages at all three coring sites displayed a transition from assemblages characterised by taxa with preferences for oligotrophic conditions such as *Cyclotella comensis*, *Cyclotella krammeri* and *Fragilaria exigua* to assemblages characterised by taxa that thrive in mesotrophic to eutrophic water, namely *Asterionella formosa* and

Cyclotella pseudostelligera. In addition, the analysis of pollen and diatom concentrations, % organic content and PSA indicate that, in general, the deepest point is representative of overall limnological conditions. However, the timing and extent of the response to increased nutrient loads varied throughout the three coring sites. Coring Site 2 responded to increased nutrient loads first in c.1970 AD, while Coring Site 3 responded to increased nutrient loads c.10 years later in c.1980 AD. In addition, Coring Site 3 displayed a more pronounced response to increased nutrient loads when compared to the other two Coring Sites, with DI-TP levels at Coring Site 3 increasing by 15 $\mu g\ l^{-1}$ between c.1970 AD and c.2000 AD.

- **Variability in the response to increased nutrient loads is driven by proximity to nutrient sources and water depth.**

The results of the limnological analyses carried out on surface samples from the test site indicate that water quality, represented by TP and DI-TP, varies spatially within a lake. In addition, the results of the diatom analyses carried out on subsamples from the coring sites indicate that the timing and magnitude of the response to increased nutrient loading was also spatially variable. Proximity to nutrient source was deemed to be important in influencing variability in water quality throughout the lake. The lowest levels of TP and DI-TP occurred at locations situated close to the Capall River, whose catchment contained fewer nutrient sources than that of the Cummeragh River. Conversely, the coring site located closest to the Cummeragh River responded almost immediately to the increased delivery of nutrients from sources located within its catchment. Sampling sites located close to sources associated with the shorelines of the lake also showed a more pronounced response to increased nutrient loads. Elevated levels of TP were measured in the south-west section of the lake and these levels appeared to be linked to storm related inputs of nutrients from a cluster of one-off houses close to the lake shore. In addition, Coring Site 3 displayed a pronounced response to increased nutrient loads, apparently associated with the establishment and harvesting of a coniferous forestry plantation located close to the shore. The difference seen in the temporal record of eutrophication at Coring Site 3 suggests that while the response to increased nutrient loads is similar throughout the lake, the sources that are important in delivering nutrients to different parts of the lake can vary. The within-lake multi-site approach deployed in the current research allowed the effects of individual nutrient sources to the nutrient enrichment of both the entire lake and individual areas to be determined.

A multi-site sampling strategy also allowed for the examination of the influence of morphometric parameters, such as water depth, to the response to increased and decreased nutrient loads. For example, Coring Site 3, located at the shallowest water depth of the three coring sites, appeared to be more sensitive to changing nutrient levels than the coring sites located in the profundal zones of the lake. The diatom assemblages at Coring Site 3 appeared to respond to de-population following the famine in Ireland. The diatom assemblages appear to record a period of slight oligotrophication from c.1850 AD to c.1950 AD. Moreover, Coring Site 3 also displayed a decrease in reconstructed DI-TP from c.2000 AD to 2007 AD, while the surface samples collected in April 2010 displayed primarily oligotrophic levels of TP and DI-TP in this section of the lake. This suggests that another period of oligotrophication is being presently being recorded by the sediment in the shallower regions of the lake.

7.2 Limitations of the current research

The interpretation of the entire palaeolimnological record in the sediments collected from the test site was hampered due to problems associated with the accuracy of the dates provided by ^{14}C dating. Bulk sediment samples were analysed for ^{137}Cs at Coring Sites 1 and 2, as picking macrofossils from the sediment proved extremely difficult. ^{14}C analysis of bulk sediment samples is prone to large errors due to the reservoir effect, which refers to the input of old radiocarbon from lake catchments or hydrothermal activity (Shen, 2010). However, a relatively accurate chronology was provided by ^{210}Pb, ^{137}Cs and SCP analyses, allowing the major variations in the palaeolimnological record to be interpreted. This research was concerned with up-core changes in the trophic status of the individual coring sites. Since each coring site remained oligotrophic until the late 1970s to 1980s, the ^{210}Pb chronology provided for the lake was sufficient for the interpretation of changes in trophic status at the lake.

The spatial variability of TP in water samples collected in April 2010 was based on one sampling occasion. While the TP levels measured from these samples gave an indication of the spatial variability of TP in the lake, the temporal variability in nutrient levels across the basin was not seen. In order to combat this limitation and to give an indication of longer term variability in nutrient levels, diatoms were analysed in the surface sediment samples. However, the collection of surface sediment samples from each chosen surface sampling site proved difficult due to the morphometry of the lake. In the shallower parts of the lake, the collection of surface sediment was not possible due to the presence of rocks on the lake bed. As a result, the DI-TP levels in the surface sediment samples do not represent the entire surface area of the lake. The influence of the Cummeragh River is also not represented in the surface sediment samples.

Historical, documentary and climate records were used to assess the contribution of anthropogenic and climate records to nutrient enrichment. While these records are invaluable for tracking the causes of ecological change in lakes, they are difficult to use for statistical analyses. The nature of the some of historical records that were collected for the study catchment did not allow a complete statistical analysis to be carried out and so most of the interpretation of the palaeolimnological record is based on judgmental analyses. The statistical significance of some of the nutrient sources was not obtained and the significance of the climatic variables appears to be underestimated in the statistical analyses. In addition, the numbers of mink associated with the mink farm stated in this thesis are based on a suggestion that there are 50,000 animals associated with the farm and not on numbers reported in Department of Agriculture inspector's reports. The request for the numbers of mink housed at the farm was not granted on the grounds of privacy issues. The amount of manure generated by the farm is based on Department of Agriculture inspector's reports and although the actual numbers of mink at the farm are not known, the impact of the farm on the nutrient enrichment of the lake is clear.

Hydraulic residence time can be important in controlling the effects of nutrient loading in lakes (Elliott et al., 2009) and fluctuations in climate can affect the hydraulic residence time of lakes (Nöges, 2005). The hydraulic residence time of the test site is based on limited measurements and so judgements on the effect of hydraulic residence time to nutrient loading at the test site were not possible.

7.3 Future directions

The results of the analysis of surface water samples in the test site indicate that nutrient levels vary spatially within the lake. However, the analysis of spatial variability in TP is based on one sampling occasion and on average TP readings from only five frequently sampled locations within the lake basin. High rainfall events have been shown to be important in the delivery of high concentrations of TP to lakes in this research, as well as by other authors (e.g. Heathwaite and Dils, 2000; Simard et al., 2000; Jordan et al., 2007; Withers et al., 2009). Through the frequent collection of water samples from across a lake basin, combined with good climatological and hydrological data, a true estimation of the spatial variability in TP, the importance of individual local sources, such as those associated with one-off housing and individual farmyards as well as the influence of factors such as hydraulic residence time could be realised.

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Appendix A

Results of the FOI request sent to the Department of Agriculture

Letter sent to the Department of Agriculture

Elaine Treacy
Department of Geography
School of Natural Sciences
Trinity College
Dublin 2
01 896 2035 /0851460413
treacyel@tcd.ie

Freedom of Information Unit,
Department of Agriculture, Fisheries and Food
Pavilion B,
Grattan Business Centre
Dublin Road
Portlaoise
Co. Laois

Re: Request for information – under the Freedom of Information Act.

To Whom It May Concern:

I wish to submit a request for information to the Freedom of Information Unit, Department of Agriculture, Fisheries and Food under the provisions of the Freedom of Information Act 1997-2003.

I am currently undertaking doctoral research on water quality in Irish lakes over the past 200-1000 years using Lough Currane Co. Kerry as a test site. I am collecting data on potential nutrient sources to the lake such as: climate, population, forestry and animal numbers including mink. There is a mink farm located close to the lake: Willow Herb Mink Farm, Dromkeare, Waterville, Co. Kerry. The first planning permission for the building of the mink farm was granted in 1966. There was also a fish farm located at this site. I wish to submit a request for the following information under the Freedom of Information Act 1997-2003.

1. Copies of **all licenses to keep mink** granted to Willow Herb Mink Farm, Dromkeare, Waterville Co. Kerry or any mink farm listed at Dromkeare, Waterville, Co. Kerry.
2. Copies of **all inspectors reports on mink premises re application/renewal of license (see template attached)** relating to Willow Herb Mink farm, Dromkeare, Waterville, Co. Kerry or any mink farm listed at Dromkeare, Waterville, Co. Kerry.
3. Copies of **all licenses granted in relation to a fish farm** located at Dromkeare, Waterville, Co. Kerry.

I enclose the €15 request fee and look forward to your response to the above request at your earliest convenience.

Regards,

____

Elaine Treacy
Technical Officer/PhD Research Student

Letter in reply to the FOI request

27th May 2009

Department of
Agriculture, Fisheries and Food
An Roinn
Talmhaíochta, Iascaigh agus Bia

FOI Ref: FOI/09/076

Ms Elaine Treacy
Department of Geography
School of Natural Sciences
Trinity College
Dublin 2

Re: Your request for information under the Freedom of Information Acts 1997-2003.

Dear Ms Treacy,

I refer to the request that you made under the Freedom of Information Acts 1997 and 2003 for records held by this Department for the following information:

1. *Copies of **all licenses to keep mink** granted to Willow Herb Mink Farm, Dromkeare, Waterville, Co. Kerry or any mink farm listed at Dromkeare, Waterville, Co. Kerry.*
2. *Copies of **all inspectors reports on mink premises re application/renewal of license (see template attached)** relating to Willow Herb Mink farm, Dromkeare, Waterville, Co. Kerry or any mink farm listed at Dromkeare, Waterville, Co. Kerry.*
3. *Copies of **ail licenses granted in relation to a fish farm** located at Dromkeare, Waterville, Co. Kerry.*

As already communicated to you, I am the decision maker with regard to points 1 and 2 of your request. I have made a final decision today to part-grant your request from 1998 to date by granting you access to those parts of the approval letters and reports of the inspections undertaken as part of the process of licensing premises under the Musk Rats Act 1933 (Application to mink) Order, 1965, which do not contain commercially sensitive information and/or names of Department Inspectors and farm management.

I am refusing you access to the information I have available with regard to the

- Name of Dept Inspector. (Privacy issues)
- Name of Manager of fur farm (Privacy issues)
- Number of breeding animals and total number of mink (commercial sensitive)
- Any other commercially sensitive information, such as the cost of pelts, works carried out at the premises, etc.

The reasons why I am refusing to grant the above information are explained further below.

1. **Schedule of records**
   Schedules A, B and C detail the conditions attached to licences issued to the premises mentioned in your request, in accordance with the Musk Rats Act, 1933 (Application to Mink) Order, 1965. The conditions applicable on 21st April 1998 are detailed in Schedule A (document 22). The conditions applicable to licences issued to this farm from 1 January 2001 to 30 June 2006 are detailed in Schedule B (document 23) and the conditions applicable since 1 July 2006 are attached at Schedule C (document 24). These documents are being released in full.

   The Schedule, attached, shows the documents that this Department considers relevant to your request. It also gives you a summary and overview of the decision as a whole. The schedule describes each document, and indicates whether the document is released in full, released with deletions or not released. The schedule refers to the sections of the FOI Act, which apply to prevent release. As to these documents, the schedule also provides brief reasons for the decision, which are meant to supplement the fuller and more detailed explanation given under heading 2 below.

2. **Findings, particulars and reasons for decisions to deny access.**
My decision is to grant you part access to all records relating to inspections and full access to licences (except for name of manager for privacy reasons) and to refuse you access to part of each inspection report under sections 6, 23, 27 and 28 of the Freedom of Information Acts, as appropriate.

Section 6 of the Freedom of Information Act states that the right of access to non-personal records applies to records created on or after 21 April 1998 unless otherwise prescribed by the Minister. Therefore, the records created between 1965 and 20th April 1998 do not come under the ambit of the Freedom of Information Act. Consequently, the only records to which a right of access applies are those pertaining to your request created on or after the 21 April 1998. I have, however, provided you with a copy of the conditions applicable to licences on 21st April 1998 and the licence in force on that date although these records were created before 21st April 1998.

In my opinion, the management of mink farms and livestock numbers are personal, confidential and commercially sensitive information. The records that I am denying you access to consist of the following – details of the management operating the mink farm, and the numbers of animals on the farm at the time of inspection.

Section 27 (1) (b*)* states that *"a head shall refuse to grant a request under section 7 if the record concerned contains financial, commercial, scientific or technical or other information whose disclosure could reasonably be expected to result in a material financial loss or gain to the person to whom the information relates, or could prejudice the competitive position of that person in the conduct of his or her profession or business or otherwise in his or her occupation, or*

Section 28(1) states - *"Subject to the provisions of this section, a head shall refuse to grant a request under Section 7 if, in the opinion of the head, access to the records concerned would involve the disclosure of personal information (including personal information relation to a deceased individual).*

Personal information is defined in Section 2 of the Freedom of Information Act, 1997 as:
Information about an identifiable individual that -
(a) would, in the ordinary course of events, be known only to the individual or members of the family, or friends, of the individual, or
(b) is held by a public body on the understanding that it would be treated by it as confidential……

The definition of personal information also specifically includes information relating to the financial affairs of the individual, including information relating to the employment or employment history of the individual, and also includes information relating to property of the individual (including the nature of the individual's title to any property).

Deletions have been made to parts of records in accordance with the provisions of sections 13(1) of the Act; therefore I have edited records to delete the commercial information on the inspection reports and details that are unrelated to the request therefore these records do not purport to be a complete record to which section 7 of the Act relates.

Section 13(1) states that

"Where a request under Section 7 would fall to be granted but for the fact that it relates to a record that is an exempt record, by reason of the inclusion in it, with other matter, of particular matter, the head of the public body concerned, shall, if it is practicable to do so, prepare a copy, in such form as he or she considers appropriate, of so much of the record as does not consist of the particular matter aforesaid and the request shall be granted by offering the requester access to the copy"

3. **Public interest considerations**

   Where an exemption under sections 23(1), 27(1) and 28(1) is invoked consideration must be given to the public interest aspect of the decision under Section 23(3)(b), 27(3) and 28(5) of the Act. It is my view that the public interest, in this case, does not warrant the release of the names and commercial information contained on the documentation. I am satisfied that there is an understanding that the information being denied, should be treated by the Department as confidential.

   I believe that on balance, the public interest is best served in this case by refusing to release the records requested. I believe that members of the public are entitled to a degree of personal privacy when dealing with government departments. Consequently, the over-riding public interest in this case favours the right of privacy of the individual over the public interest. Therefore the public interest is best served by protecting personal, confidential and financial information of the persons involved in the fur farming business.

4. **Rights of appeal**

   You may appeal this decision. Please note, that a fee of €75 applies for an appeal for all non-personal records. In the event that you need to make such an appeal, you can do so by writing to the Freedom of Information Unit, Department of Agriculture, Fisheries and Food, Grattan House, Grattan Business Centre, Dublin Road, Portlaoise, Co. Laois enclosing the appropriate fee. Payment should be made by way of bank draft, money order, postal order or personal cheque made payable to the Department of Agriculture, Fisheries and Food. You should make your appeal within 4 weeks (20 working days) from the date of this notification; however, the making of a late appeal may be permitted in appropriate circumstances. The appeal will involve a complete reconsideration of the matter by a more senior member of the staff of this Department/Body.

If you have any queries regarding this correspondence you can contact me by telephone at 01-5058767 and I will seek to answer any queries you may have.

Yours sincerely

Róisín O'Connell
Livestock, Beef and Sheepmeat Division
1st Floor Administration Building,
Backweston Campus,
Stacumny Lane
Celbridge,
Co Kildare

Inspectors report on mink premises 2006

MUSK RATS ACT ANNUAL REPORT FORM

NAME: Willow Herd Ltd.

ADDRESS: Dromkeane, Waterville,
Co Kerry.

PHONE NUMBER

NAME OF MANAGER: [redacted]
Assist. Mngr.: [redacted]

LOCATION OF MINK FARM: [redacted]

Area of compound: 2.86 Ha. approx

NUMBER OF BREEDING MINK: [redacted] females [redacted]males

TOTAL NUMBER OF MINK: [redacted]approx

TYPE OF PRODUCTION

Breeding Only

Breeding and Processing: Breeding & pelting

WASTE DISPOSAL

QUANTITY PRODUCED /ANNUM

DROPPINGS	250	TONNES
CARCASES	} 60	TONNES
OFFAL (ETC)	}	TONNES

METHOD OF DISPOSAL

DROPPINGS __per Nutrient Management plan on local farm spreadlands in agreement with Kerry County Council

OFFAL etc. __to rendering plant in Nobber Co Meath

PRESENT STATE OF FENCING AND SECURITY

Excellent. Box profile coated galvanise sheeting forms the fence. Fence is embedded in mass concrete base. The galvanised sheets are in addition topped with 5 strand mains electric security fence. Entrance and exit gates are escape proof. Culvert drains are gridded to prevent escape.

OTHERS OBSERVATION

The manager [redacted] is due to depart in about 2 months. [redacted] is due to take on his managerial responsibilities. [redacted] has said that plans are a foot to replace all the existing old buildings which house the mink over the next two years. This is seen as a means of upgrading manure handling on site also. All cages in the mean time are also being upgraded to keep ahead of the EU cage size requirements. All but two sheds are expected to be upgraded in this respect by the end of 2007.

I recommend that we seek a meeting with the owners in conjunction with the new manager early in 2007 to examine the proposed redevelopment program.

I also recommend that this mink farms licence be renewed.

SIGNED [redacted]

DATE 19/12/06

Inspectors report on mink premises 2003

AN ROINN TALMHAIOCHTA AGUS BIA
Musk Rats Act, 1933 (Application to Mink) Order, 1965

Inspector's Report on Mink Premises re. Application/Renewal of Licence

Name of Applicant [redacted] Manager

Company Name (e.g. T/A etc.) Willow Herb Ltd, Waterville Mink Farm, Waterville, Co. Kerry.

Date of Inspection: 22/12/03

Location of mink farm (in built-up area, near river, etc.) Dromkeane, Waterville, Co. Kerry.

Approximate area of mink compound 7 Acres

~~No. of mink on farm at time of visit~~ [redacted] males.

No. of breeding mink for coming season [redacted]

Total no. of mink at peak for coming season [redacted]

Is farm enclosed by a guard fence, if so state type (wire, concrete, etc.)? Box profile galv. fence, based in mass concrete, supported at 4/5 ?? entry/exits secure locking.

Are cages escape-proof? yes

Are trees, shrubs or undergrowth close to the guard fence? Cut well back no overhang.

Are rat holes, drainage channels effectively blocked or guarded? Yes N.B. in case of those leading out/in under the fence.

Do the gates in the guard fence close satisfactorily? yes.

Any other observations Propose to further improve cage size of any remaining small cages but subject to getting planning permission for two extra houses.

Recommendation:- Should advise owners on position regarding building of two extra houses.

Note: Licence renewal is recommended.

Signed [redacted]
District Inspector

Date 22/12/03.

Note: Two extra houses are to allow cage size be improved. Total No.s of mink will remain the same

Report on Inspection of Willow Herb Ltd, Mink Farm at Dromkeare, Waterville, Co. Kerry, on 17th January, 2003.

The District Inspector [redacted] inspected this mink farm on 11th December 2002 and in his report highlighted shortcomings with regard to the perimeter (safety) fence on the farm.

This mink farm was founded some 40 years ago by Mr. [redacted] The farm, which currently provides permanent employment for [redacted] local people, has an annual output of [redacted] mink pelts and is controlled by [redacted] This company has [redacted] other mink farms in [redacted] During the inspection visit of the 11/12/02 the then manager explained to [redacted] that he was leaving the management of the mink farm later that month and that a new manager was due to take up appointment in January.

I forwarded [redacted] inspection report to Livestock Breeding Division, Cavan on the 30/12/02 with a covering minute in which I proposed meeting the [redacted] Director and the new manager on-site as early as possible in January.
On 17th January accompanied by [redacted] by prior arrangement we met [redacted] Director of [redacted] and M [redacted], the new manager, on- site at Waterville.

In the course of discussion, Mr [redacted] pointed out that in [redacted] a major additional emphasis had now been placed in making sure that farmed mink would not be released to the wild from mink farms by objectors. It would appear that this possibility is a cause for significant concern in [redacted] where there are currently some 200 mink farms in operation.

We inspected the mink farm and saw the newly erected east perimeter/ boundary fence, which is 250 metres in length. I was very impressed with what the Director described as a newly designed specialist **Activist Secure Fence** of box steel construction, measuring 1.6 metres in height and anchored in 60 centimetres of concrete. The fence is supported lengthwise with galvanised tubular steel (stabiliser function plus wind precaution). The gates for ingress/egress to/from the mink compound are constructed of galvanised sheet steel and incorporating a special automatic double door feature, which is designed to prevent the accidental escape to the wild of any loose mink from within the compound. Following completion of our inspection tour of the premises, [redacted] **undertook** to erect an Activist Secure Fence to the same standard on the North side of the compound and also on that section of the West facing perimeter/boundary fence which was recently damaged by high gales and replaced by a secure temporary specification fence. [redacted] **also undertook** to have this section of the work **completed before the end of June 2003,** and the remainder of the West facing perimeter/boundary fence and the Northern perimeter/boundary fence **to be secured before the end of this year**. The total cost of of the completed and planned perimeter/boundary fence improvement works is estimated by [redacted]

In the course of conversation [redacted] seemed satisfied with the financial returns accruing from his company's mink farming activities. The average market price realised per pelt in the past production year wa[redacted]while the average feed cost per mink i[redacted]per pelt to cover labour, depreciation, machinery maintenance and profit. The current world demand for mink pelts is 25 million pelts per annum[redacted]

Recommendation

Having regard to the commitment displayed by the high standard of the modernisation/improvement works which are being undertaken on this mink compound by the Director/New Management, I recommend that Willow Herb Ltd mink farm at Dromkeare, Waterville, Co. Kerry, be granted a temporary licence for six months up to the end of June 2003 and that this farm be then re-inspected.

[redacted]
Livestock, Beef and Sheepmeat Division,
31st January, 2003.

Appendix B

List of diatoms encountered in samples from Lough Currane

- *Achnanthes distincta Messikommer*
- *Achnanthes flexella (Kutzing)Brun var. flexella*
- *Achnanthes helvetica (Hustedt) Lange-Bertalot, Kusber & Metzeltin*
- *Achnanthes holsatica Hustedt in Schmidt et al.*
- *Achnanthes kuelbsii Lange-Bertalot*
- *Achnanthes lacus-vulcani Lange-Bertalot*
- *Achnanthes laterostrata Hustedt*
- *Achnanthes minutissima Kutzing v.minutissima Kutzing (Achnanthidium)*
- *Achnanthes minutissima Kutzing var.jackii(Rabenhorst) Lange-Bertalot*
- *Achnanthes nodosa A.Cleve*
- *Achnanthes oblongella Oestrup*
- *Achnanthes pseudoswazi Carter*
- *Achnanthes pusilla (Grunow)De Toni*
- *Achnanthes rossii Hustedt*
- *Achnanthes stewartii Patrick*
- *Achnanthes subatomoides (Hustedt) Lange-Bertalot et Archibald*
- *Achnanthes ventralis (Krasske) Lange-Bertalot*
- *Amphipleura pellucida Kutzing*
- *Amphora inariensis Krammer*
- *Amphora veneta Kutzing*

- *Anomoeoneis brachysira(Brebisson in Rabenhorst) Grunow in Cleve*
- *Anomoeoneis styriaca (Grunow) Hustedt*
- *Anomoeoneis vitrea (Grunow) Ross*
- *Asterionella formosa Hassall*
- *Aulacoseira ambigua (Grun.) Simonsen*
- *Caloneis bacillum (Grunow) Cleve*
- *Caloneis silicula (Ehr.)Cleve*
- *Caloneis tenuis (Gregory) Krammer*
- *Caloneis undulata (Gregory) Krammer*
- *Cocconeis neodiminuta Krammer*
- *Cocconeis placentula Ehrenberg var.euglypta (Ehr.)Grunow*
- *Cocconeis placentula Ehrenberg var.lineata (Ehr.)Van Heurck*
- *Cyclotella bodanica Grunow var.lemanica (O.Muller ex Schroter) Bachman*
- *Cyclotella comensis Grunow in Van Heurck*
- *Cyclotella krammeri HÅkansson*
- *Cyclotella meneghiniana Kutzing*
- *Cyclotella pseudostelligera Hustedt*
- *Cyclotella radiosa (Grunow) Lemmermann*
- *Cymbella aspera(Ehrenberg) H.Peragallo*
- *Cymbella cesatii (Rabh.)Grunow*
- *Cymbella cistula(Ehrenberg)Kirchner*
- *Cymbella delicatula Kutzing*
- *Cymbella elginensis Krammer*

- *Cymbella falaisensis (Grunow) Krammer et Lange-Bertalot*
- *Cymbella gaeumannii Meister*
- *Cymbella minuta Hilse ex Rabenhorst (Encyonema)*
- *Cymbella perpusilla A.Cleve*
- *Cymbella proxima Reimer in Patrick & Reimer var. proxima*
- *Cymbella silesiaca Bleisch in Rabenhorst (Encyonema)*
- *Cymbella subaequalis Grunow*
- *Denticula kuetzingii Grunow var.kuetzingii*
- *Denticula mesolepta (Grunow in Van Heurck) Meister*
- *Diatoma mesodon (Ehrenberg) Kutzing*
- *Diatoma moniliformis Kutzing*
- *Diatoma tenuis Agardh*
- *Diploneis elliptica (Kutzing) Cleve*
- *Diploneis oblongella (Naegeli) Cleve-Euler*
- *Diploneis parma Cleve*
- *Diploneis peterseni Hustedt*
- *Encyonema neogracile Krammer*
- *Epithemia adnata (Kutzing) Brebisson*
- *Eunotia arcus Ehrenberg var. arcus*
- *Eunotia bilunaris (Ehr.) Mills var. bilunaris*
- *Eunotia bilunaris var. mucophila Lange-Bertalot Norpel & al. f. Teratogene*
- *Eunotia exigua (Brebisson ex Kützing) Rabenhorst*
- *Eunotia faba Grunow*

- *Eunotia fallax A.Cleve var. fallax*
- *Eunotia formica Ehrenberg*
- *Eunotia incisa Gregory var.incisa*
- *Eunotia paludosa Grunow in Van Heurck var. paludosa*
- *Eunotia pectinalis (Dyllwyn) Rabenhorst var.pectinalis*
- *Eunotia praerupta Ehrenberg var. praerupta*
- *Eunotia pyramidata Hustedt*
- *Eunotia rhomboidea Hustedt*
- *Eunotia rhynchocephala Hustedt var. rhynchocephala*
- *Eunotia serra Ehrenberg var.serra*
- *Fragilaria arcus (Ehrenberg) Cleve var. arcus*
- *Fragilaria bicapitata A.Mayer*
- *Fragilaria brevistriata Grunow (Pseudostaurosira)*
- *Fragilaria capucina Desm. var. perminuta (Grunow) Lange-Bertalot*
- *Fragilaria capucina Desm. var.gracilis(Oest.) Hustedt forme teratogene*
- *Fragilaria capucina Desmazieres var.distans(Grunow)Lange-Bertalot*
- *Fragilaria capucina Desmazieres var.vaucheriae(Kutzing)Lange-Bertalot*
- *Fragilaria construens (Ehr.) Grunow f.construens (Staurosira)*
- *Fragilaria construens (Ehr.) Grunow f.venter (Ehr.) Hustedt*
- *Fragilaria crotonensis Kitton*
- *Fragilaria exigua Grunow*
- *Fragilaria leptostauron(Ehr.)Hustedt var.dubia(Grunow)Hustedt*

- *Fragilaria parasitica (W.Sm.) Grun. var. parasitica*
- *Fragilaria parasitica (W.Sm.) Grun. var. subconstricta Grunow*
- *Fragilaria pinnata Ehrenberg var. pinnata (Staurosirella)*
- *Fragilaria pseudoconstruens Marciniak*
- *Fragilaria robusta (Fusey) Manguin*
- *Fragilaria tenera (W.Smith) Lange-Bertalot*
- *Fragilaria tenuistriata Oestrup*
- *Frustulia rhomboides(Ehr.)De Toni var.saxonica (Rabenhorst)De Toni*
- *Frustulia rhomboides(Ehr.)De Toni var.viridula (Brebisson) Cleve*
- *Gomphonema acuminatum Ehrenberg*
- *Gomphonema angustum Agardh*
- *Gomphonema clavatum Ehr.*
- *Gomphonema gracile Ehrenberg*
- *Gomphonema insigne Gregory*
- *Gomphonema parvulum (Kützing) Kützing var. parvulum f. Parvulum*
- *Gomphonema parvulum var.exilissimum Grunow*
- *Gomphonema truncatum Ehr.*
- *Navicula angusta Grunow*
- *Navicula arvensis Hustedt*
- *Navicula begerii Krasske*
- *Navicula bryophila Boye Petersen*
- *Navicula capitata Ehrenberg (=Hippodonta)*
- *Navicula cocconeiformis Gregory ex Greville*
- *Navicula disjuncta Hustedt*

- *Navicula elginensis (Gregory) Ralfs in Pritchard*
- *Navicula halophila (Grunow) Cleve*
- *Navicula jaernefeltii Hustedt*
- *Navicula leptostriata Jorgensen*
- *Navicula mediocris Krasske*
- *Navicula minuscula Grunow in Van Heurck 1880*
- *Navicula modica Hustedt*
- *Navicula muraliformis Hustedt ex Brendemuhl*
- *Navicula placentula (Ehr.) Kutzing*
- *Navicula pseudoscutiformis Hustedt*
- *Navicula pupula Kutzing*
- *Navicula radiosa Kützing*
- *Navicula rhynchocephala Kutzing*
- *Navicula salinarum Grunow in Cleve et Grunow var.salinarum*
- *Navicula schmassmanii Hustedt*
- *Navicula soehrensis Krasske*
- *Navicula soehrensis Krasske var.hassiaca (Krasske) Lange-Bertalot*
- *Navicula stroemii Hustedt*
- *Navicula veneta Kutzing*
- *Neidium ampliatum (Ehrenberg) Krammer*
- *Neidium binodeforme Krammer*
- *Neidium bisulcatum (Lagerstedt) Cleve*
- *Nitzschia angustata Grunow*
- *Nitzschia dissipata(Kutzing)Grunow var.media (Hantzsch.) Grunow*

- *Nitzschia fonticola Grunow in Cleve et Möller*
- *Nitzschia gracilis Hantzsch*
- *Nitzschia nana Grunow in Van Heurck*
- *Nitzschia palea (Kutzing) W.Smith*
- *Nitzschia parvula Lewis*
- *Nitzschia perminuta(Grunow) M.Peragallo*
- *Peronia fibula (Breb.ex Kutz.)Ross*
- *Pinnularia appendiculata (Agardh) Cleve var. appendiculata*
- *Pinnularia divergens W.M.Smith var. divergens*
- *Pinnularia gibba Ehrenberg*
- *Pinnularia gibba Ehrenberg var.linearis Hustedt*
- *Pinnularia intermedia (Lagerstedt) Cleve*
- *Pinnularia interrupta W.M.Smith*
- *Pinnularia microstauron (Ehr.) Cleve var. microstauron*
- *Pinnularia rupestris Hantzsch in Rabenhorst 1861*
- *Pinnularia semicruciata (A.Schmidt) A.Cleve*
- *Pinnularia subcapitata Gregory var. subcapitata*
- *Pinnularia viridis (Nitzsch) Ehrenberg var.viridis*
- *Rhoicosphenia abbreviata (C.Agardh) Lange-Bertalot*
- *Rhopalodia rupestris (W.Smith) Krammer*
- *Stauroneis anceps Ehrenberg*
- *Stauroneis kriegeri Patrick*
- *Stauroneis nana Hustedt*
- *Stauroneis phoenicenteron (Nitzsch) Ehrenberg*

- *Stephanodiscus niagarae Ehr.var. niagarae*
- *Surirella robusta Ehrenberg*
- *Tabellaria flocculosa(Roth)Kutzing*

Appendix C

Codes and names of diatoms used for ordination

Code	Taxon Name
AAMB	*Aulacoseira ambigua* (Grun.) Simonsen
ACNP	*Achnanthes pusilla* (Grunow)De Toni
ADMI	*Achnanthes minutissima* Kutzing *v.minutissima* Kutzing
ADMS	*Navicula minuscula Grunow in Van Heurck 1880*
AFOR	*Asterionella formosa Hassall*
AINA	*Amphora inariensis Krammer*
AMJA	*Achnanthes minutissima Kutzing var.jackii(Rabenhorst) Lange-Bertalot*
BBRE	*Anomoeoneis brachysira(Brebisson in Rabenhorst) Grunow in Cleve*
BSTY	*Anomoeoneis styriaca (Grunow) Hustedt*
BVIT	*Anomoeoneis vitrea (Grunow) Ross*
CBAC	*Caloneis bacillum (Grunow) Cleve*
CBOL	*Cyclotella bodanica Grunow var.lemanica (O.Muller ex Schroter) Bachman*
CCIS	*Cymbella cistula(Ehrenberg)Kirchner*
CCMS	*Cyclotella comensis Grunow in Van Heurck*
CCOC	*Navicula cocconeiformis Gregory ex Greville*
CHME	*Navicula mediocris Krasske*
CKRM	*Cyclotella krammeri HÅkansson*
CNDI	*Cocconeis neodiminuta Krammer*

CPST	*Cyclotella pseudostelligera Hustedt*
DITE	*Diatoma tenuis Agardh*
DMON	*Diatoma moniliformis Kutzing*
ECFA	*Cymbella falaisensis (Grunow) Krammer et Lange-Bertalot*
EFAB	*Eunotia faba Grunow*
EGAE	*Cymbella gaeumannii Meister*
EINC	*Eunotia incisa Gregory var.incisa*
ELSE	*Cymbella silesiaca Bleisch in Rabenhorst (Encyonema)*
ENMI	*Cymbella minuta Hilse ex Rabenhorst (Encyonema)*
ENNG	*Encyonema neogracile Krammer*
EPEC	*Eunotia pectinalis (Dyllwyn) Rabenhorst var.pectinalis*
EUPA	*Eunotia paludosa Grunow in Van Heurck var. paludosa*
FCVA	*Fragilaria capucina Desmazieres var.vaucheriae(Kutzing)Lange-Bertalot*
FERI	*Frustulia rhomboides(Ehr.)De Toni var.viridula (Brebisson) Cleve*
FGRT	Fragilaria capucina Desm. var.gracilis(Oest.) Hustedt
FSAX	*Frustulia rhomboides(Ehr.)De Toni var.saxonica (Rabenhorst)De Toni*
GANT	*Gomphonema angustum Agardh*
GGRA	*Gomphonema gracile Ehrenberg*
GPAR	*Gomphonema parvulum (Kützing) Kützing var. parvulum*
NAAN	*Navicula angusta Grunow*
NARV	*Navicula arvensis Hustedt*
NFON	*Nitzschia fonticola Grunow in Cleve et Möller*

NLST	*Navicula leptostriata Jorgensen*
NPAL	*Nitzschia palea (Kutzing) W.Smith*
PDIS	*Achnanthes distincta Messikommer*
PLVU	*Achnanthes lacus-vulcani Lange-Bertalot*
PPSW	*Achnanthes pseudoswazi Carter*
PRAD	*Cyclotella radiosa (Grunow) Lemmermann*
PSAT	*Achnanthes subatomoides (Hustedt) Lange-Bertalot et Archibald*
SCON	*Fragilaria construens (Ehr.) Grunow f.construens (Staurosira)*
SEXG	*Fragilaria exigua Grunow*
STAN	*Stauroneis anceps Ehrenberg*
TFLO	*Tabellaria flocculosa(Roth)Kutzing*

Appendix D

DI-TP and diatom relative abundance data used for RDA

a. Coring site one

- The DI-TP and diatom taxa comprising >5% relative abundance at any depth at Coring Site One. Linear interpolation was used to provide DI-TP values and diatom relative abundance values for the years between those shown here.

Depth	Year AD CRS Model	DI-TP	ADMI	BVIT	AFOR	CKRM	CCMS	CPST	PRAD	SEXG	TFLO
0.5	2006	15.77	13.78	3.04	10.10	13.14	11.70	12.66	1.28	2.08	5.45
1	1999	15.68	11.65	4.53	7.44	11.33	15.86	20.55	2.59	1.29	3.88
1.5	1995	11.52	16.92	2.85	4.82	12.96	15.34	4.90	5.06	2.53	6.80
2	1990	15.38	13.41	3.48	5.79	8.94	16.06	15.73	1.49	1.99	8.28
2.5	1987	11.78	17.98	4.61	4.85	12.09	20.05	5.73	0.64	2.39	4.77
3	1983	15.48	12.85	4.34	8.59	10.44	15.58	10.92	0.96	1.93	8.84
3.5	1980	11.54	12.41	3.55	5.72	23.21	9.19	5.80	3.06	3.38	5.16
4	1976	10.63	15.47	3.51	5.10	18.18	22.65	5.58	1.91	2.71	3.35
4.5	1968	7.57	10.78	5.39	0.65	36.11	11.93	0.82	2.78	3.27	3.59
5	1959	9.07	12.76	3.78	2.99	28.82	17.48	4.88	1.10	2.20	4.25
7	1936	8.38	13.79	5.42	1.32	19.05	33.46	3.87	0.15	2.01	2.01
9	1909	7.99	15.02	5.91	0.00	19.97	28.75	1.76	0.16	3.51	3.51
11	1878	7.80	13.90	8.67	0.00	17.50	28.45	2.13	0.00	3.43	2.29

- Linearly interpolated DI-TP and diatom taxa comprising >5% relative abundance at any depth at Coring Site One

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	SEXG %	TFLO %
0.5	**2006**	**15.8**	**13.8**	**3.0**	**10.1**	**13.1**	**11.7**	**12.7**	**1.3**	**2.1**	**5.4**
	2005	15.8	13.5	3.3	9.7	12.9	12.3	13.8	1.5	2.0	5.2
	2004	15.7	13.2	3.5	9.3	12.6	12.9	14.9	1.7	1.9	5.0
	2003	15.7	12.9	3.7	9.0	12.4	13.5	16.0	1.8	1.7	4.8
	2002	15.7	12.6	3.9	8.6	12.1	14.1	17.2	2.0	1.6	4.6
	2001	15.7	12.3	4.1	8.2	11.8	14.7	18.3	2.2	1.5	4.3
	2000	15.7	12.0	4.3	7.8	11.6	15.3	19.4	2.4	1.4	4.1
1	**1999**	**15.7**	**11.7**	**4.5**	**7.4**	**11.3**	**15.9**	**20.6**	**2.6**	**1.3**	**3.9**
	1998	14.6	13.0	4.1	6.8	11.7	15.7	16.6	3.2	1.6	4.6
	1997	13.6	14.3	3.7	6.1	12.1	15.6	12.7	3.8	1.9	5.3
	1996	12.6	15.6	3.3	5.5	12.6	15.5	8.8	4.4	2.2	6.1
1.5	**1995**	**11.5**	**16.9**	**2.8**	**4.8**	**13.0**	**15.3**	**4.9**	**5.1**	**2.5**	**6.8**
	1994	12.3	16.2	3.0	5.0	12.2	15.5	7.1	4.3	2.4	7.1
	1993	13.1	15.5	3.1	5.2	11.4	15.6	9.2	3.6	2.3	7.4
	1992	13.8	14.8	3.2	5.4	10.6	15.8	11.4	2.9	2.2	7.7
	1991	14.6	14.1	3.4	5.6	9.7	15.9	13.6	2.2	2.1	8.0
2	**1990**	**15.4**	**13.4**	**3.5**	**5.8**	**8.9**	**16.1**	**15.7**	**1.5**	**2.0**	**8.3**
	1989	14.2	14.9	3.9	5.5	10.0	17.4	12.4	1.2	2.1	7.1
	1988	13.0	16.5	4.2	5.2	11.0	18.7	9.1	0.9	2.3	5.9
2.5	**1987**	**11.8**	**18.0**	**4.6**	**4.9**	**12.1**	**20.0**	**5.7**	**0.6**	**2.4**	**4.8**
	1986	12.7	16.7	4.5	5.8	11.7	18.9	7.0	0.7	2.3	5.8
	1985	13.6	15.4	4.5	6.7	11.3	17.8	8.3	0.8	2.2	6.8
	1984	14.6	14.1	4.4	7.7	10.9	16.7	9.6	0.9	2.0	7.8
3	**1983**	**15.5**	**12.9**	**4.3**	**8.6**	**10.4**	**15.6**	**10.9**	**1.0**	**1.9**	**8.8**
	1982	14.2	12.7	4.1	7.6	14.7	13.5	9.2	1.7	2.4	7.6
	1981	12.9	12.6	3.8	6.7	19.0	11.3	7.5	2.4	2.9	6.4
3.5	**1980**	**11.5**	**12.4**	**3.5**	**5.7**	**23.2**	**9.2**	**5.8**	**3.1**	**3.4**	**5.2**
	1979	11.3	13.2	3.5	5.6	22.0	12.6	5.7	2.8	3.2	4.7
	1978	11.1	13.9	3.5	5.4	20.7	15.9	5.7	2.5	3.0	4.3
	1977	10.9	14.7	3.5	5.3	19.4	19.3	5.6	2.2	2.9	3.8
4	**1976**	**10.6**	**15.5**	**3.5**	**5.1**	**18.2**	**22.6**	**5.6**	**1.9**	**2.7**	**3.3**

Depth cm	Year AD	DI-TP $\mu g\ l^{-1}$	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	SEXG %	TFLO %
	1975	10.3	14.9	3.7	4.5	20.4	21.3	5.0	2.0	2.8	3.4
	1974	9.9	14.3	4.0	4.0	22.7	20.0	4.4	2.1	2.9	3.4
	1973	9.5	13.7	4.2	3.4	24.9	18.6	3.8	2.2	2.9	3.4
	1972	9.1	13.1	4.5	2.9	27.1	17.3	3.2	2.3	3.0	3.5
	1971	8.7	12.5	4.7	2.3	29.4	15.9	2.6	2.5	3.1	3.5
	1970	8.3	12.0	4.9	1.8	31.6	14.6	2.0	2.6	3.1	3.5
	1969	8.0	11.4	5.2	1.2	33.9	13.3	1.4	2.7	3.2	3.6
4.5	**1968**	**7.6**	**10.8**	**5.4**	**0.7**	**36.1**	**11.9**	**0.8**	**2.8**	**3.3**	**3.6**
	1967	7.7	11.0	5.2	0.9	35.3	12.5	1.3	2.6	3.1	3.7
	1966	7.9	11.2	5.0	1.2	34.5	13.2	1.7	2.4	3.0	3.7
	1965	8.1	11.4	4.9	1.4	33.7	13.8	2.2	2.2	2.9	3.8
	1964	8.2	11.7	4.7	1.7	32.9	14.4	2.6	2.0	2.8	3.9
	1963	8.4	11.9	4.5	2.0	32.1	15.0	3.1	1.8	2.7	4.0
	1962	8.6	12.1	4.3	2.2	31.2	15.6	3.5	1.7	2.6	4.0
	1961	8.7	12.3	4.1	2.5	30.4	16.2	4.0	1.5	2.4	4.1
	1960	8.9	12.5	4.0	2.7	29.6	16.9	4.4	1.3	2.3	4.2
5	**1959**	**9.1**	**12.8**	**3.8**	**3.0**	**28.8**	**17.5**	**4.9**	**1.1**	**2.2**	**4.3**
	1958	9.0	12.8	3.9	2.9	28.4	18.2	4.8	1.1	2.2	4.2
	1957	9.0	12.8	3.9	2.8	28.0	18.9	4.8	1.0	2.2	4.1
	1956	9.0	12.9	4.0	2.8	27.5	19.6	4.8	1.0	2.2	4.0
	1955	9.0	12.9	4.1	2.7	27.1	20.3	4.7	0.9	2.2	3.9
	1954	8.9	13.0	4.1	2.6	26.7	21.0	4.7	0.9	2.2	3.8
	1953	8.9	13.0	4.2	2.6	26.3	21.6	4.6	0.9	2.2	3.7
	1952	8.9	13.1	4.3	2.5	25.8	22.3	4.6	0.8	2.1	3.6
	1951	8.8	13.1	4.4	2.4	25.4	23.0	4.5	0.8	2.1	3.5
	1950	8.8	13.2	4.4	2.3	25.0	23.7	4.5	0.7	2.1	3.4
	1949	8.8	13.2	4.5	2.3	24.6	24.4	4.4	0.7	2.1	3.3
	1948	8.7	13.2	4.6	2.2	24.1	25.1	4.4	0.6	2.1	3.2
	1947	8.7	13.3	4.6	2.1	23.7	25.8	4.4	0.6	2.1	3.1
	1946	8.7	13.3	4.7	2.0	23.3	26.5	4.3	0.6	2.1	3.0
	1945	8.7	13.4	4.8	2.0	22.9	27.2	4.3	0.5	2.1	2.9
	1944	8.6	13.4	4.9	1.9	22.5	27.9	4.2	0.5	2.1	2.8

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	SEXG %	TFLO %
	1943	8.6	13.5	4.9	1.8	22.0	28.6	4.2	0.4	2.1	2.7
	1942	8.6	13.5	5.0	1.8	21.6	29.3	4.1	0.4	2.1	2.6
	1941	8.5	13.6	5.1	1.7	21.2	30.0	4.1	0.4	2.1	2.5
	1940	8.5	13.6	5.1	1.6	20.8	30.7	4.0	0.3	2.0	2.4
	1939	8.5	13.7	5.2	1.5	20.3	31.4	4.0	0.3	2.0	2.3
	1938	8.4	13.7	5.3	1.5	19.9	32.1	4.0	0.2	2.0	2.2
	1937	8.4	13.7	5.4	1.4	19.5	32.8	3.9	0.2	2.0	2.1
7	**1936**	**8.4**	**13.8**	**5.4**	**1.3**	**19.1**	**33.5**	**3.9**	**0.2**	**2.0**	**2.0**
	1935	8.4	13.8	5.4	1.3	19.1	33.3	3.8	0.2	2.1	2.1
	1934	8.4	13.9	5.5	1.2	19.1	33.1	3.7	0.2	2.1	2.1
	1933	8.3	13.9	5.5	1.2	19.2	32.9	3.6	0.2	2.2	2.2
	1932	8.3	14.0	5.5	1.1	19.2	32.8	3.6	0.2	2.2	2.2
	1931	8.3	14.0	5.5	1.1	19.2	32.6	3.5	0.2	2.3	2.3
	1930	8.3	14.1	5.5	1.0	19.3	32.4	3.4	0.2	2.3	2.3
	1929	8.3	14.1	5.5	1.0	19.3	32.2	3.3	0.2	2.4	2.4
	1928	8.3	14.2	5.6	0.9	19.3	32.1	3.2	0.2	2.5	2.5
	1927	8.2	14.2	5.6	0.9	19.4	31.9	3.2	0.2	2.5	2.5
	1926	8.2	14.2	5.6	0.8	19.4	31.7	3.1	0.2	2.6	2.6
	1925	8.2	14.3	5.6	0.8	19.4	31.5	3.0	0.2	2.6	2.6
	1924	8.2	14.3	5.6	0.7	19.5	31.4	2.9	0.2	2.7	2.7
	1923	8.2	14.4	5.7	0.7	19.5	31.2	2.9	0.2	2.7	2.7
	1922	8.2	14.4	5.7	0.6	19.5	31.0	2.8	0.2	2.8	2.8
	1921	8.2	14.5	5.7	0.6	19.6	30.8	2.7	0.2	2.8	2.8
	1920	8.1	14.5	5.7	0.5	19.6	30.7	2.6	0.2	2.9	2.9
	1919	8.1	14.6	5.7	0.5	19.6	30.5	2.5	0.2	3.0	3.0
	1918	8.1	14.6	5.7	0.4	19.7	30.3	2.5	0.2	3.0	3.0
	1917	8.1	14.7	5.8	0.4	19.7	30.1	2.4	0.2	3.1	3.1
	1916	8.1	14.7	5.8	0.3	19.7	30.0	2.3	0.2	3.1	3.1
	1915	8.1	14.7	5.8	0.3	19.8	29.8	2.2	0.2	3.2	3.2
	1914	8.1	14.8	5.8	0.2	19.8	29.6	2.1	0.2	3.2	3.2
	1913	8.0	14.8	5.8	0.2	19.8	29.5	2.1	0.2	3.3	3.3

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	SEXG %	TFLO %
	1912	8.0	14.9	5.9	0.1	19.9	29.3	2.0	0.2	3.3	3.3
	1911	8.0	14.9	5.9	0.1	19.9	29.1	1.9	0.2	3.4	3.4
	1910	8.0	15.0	5.9	0.0	19.9	28.9	1.8	0.2	3.5	3.5
9	**1909**	**8.0**	**15.0**	**5.9**	**0.0**	**20.0**	**28.8**	**1.8**	**0.2**	**3.5**	**3.5**
	1908	8.0	15.0	6.0	0.0	19.9	28.7	1.8	0.2	3.5	3.5
	1907	8.0	14.9	6.1	0.0	19.8	28.7	1.8	0.1	3.5	3.4
	1906	8.0	14.9	6.2	0.0	19.7	28.7	1.8	0.1	3.5	3.4
	1905	8.0	14.9	6.3	0.0	19.6	28.7	1.8	0.1	3.5	3.4
	1904	8.0	14.8	6.4	0.0	19.6	28.7	1.8	0.1	3.5	3.3
	1903	8.0	14.8	6.4	0.0	19.5	28.7	1.8	0.1	3.5	3.3
	1902	7.9	14.8	6.5	0.0	19.4	28.7	1.8	0.1	3.5	3.2
	1901	7.9	14.7	6.6	0.0	19.3	28.7	1.9	0.1	3.5	3.2
	1900	7.9	14.7	6.7	0.0	19.3	28.7	1.9	0.1	3.5	3.2
	1899	7.9	14.7	6.8	0.0	19.2	28.7	1.9	0.1	3.5	3.1
	1898	7.9	14.6	6.9	0.0	19.1	28.6	1.9	0.1	3.5	3.1
	1897	7.9	14.6	7.0	0.0	19.0	28.6	1.9	0.1	3.5	3.0
	1896	7.9	14.5	7.1	0.0	18.9	28.6	1.9	0.1	3.5	3.0
	1895	7.9	14.5	7.2	0.0	18.9	28.6	1.9	0.1	3.5	3.0
	1894	7.9	14.5	7.2	0.0	18.8	28.6	1.9	0.1	3.5	2.9
	1893	7.9	14.4	7.3	0.0	18.7	28.6	1.9	0.1	3.5	2.9
	1892	7.9	14.4	7.4	0.0	18.6	28.6	2.0	0.1	3.5	2.8
	1891	7.9	14.4	7.5	0.0	18.5	28.6	2.0	0.1	3.5	2.8
	1890	7.9	14.3	7.6	0.0	18.5	28.6	2.0	0.1	3.5	2.8
	1889	7.9	14.3	7.7	0.0	18.4	28.6	2.0	0.1	3.5	2.7
	1888	7.9	14.3	7.8	0.0	18.3	28.6	2.0	0.1	3.5	2.7
	1887	7.9	14.2	7.9	0.0	18.2	28.5	2.0	0.0	3.5	2.6
	1886	7.8	14.2	8.0	0.0	18.1	28.5	2.0	0.0	3.5	2.6
	1885	7.8	14.2	8.0	0.0	18.1	28.5	2.0	0.0	3.5	2.6
	1884	7.8	14.1	8.1	0.0	18.0	28.5	2.1	0.0	3.4	2.5
	1883	7.8	14.1	8.2	0.0	17.9	28.5	2.1	0.0	3.4	2.5
	1882	7.8	14.0	8.3	0.0	17.8	28.5	2.1	0.0	3.4	2.4
	1881	7.8	14.0	8.4	0.0	17.7	28.5	2.1	0.0	3.4	2.4
	1880	7.8	14.0	8.5	0.0	17.7	28.5	2.1	0.0	3.4	2.4
	1879	7.8	13.9	8.6	0.0	17.6	28.5	2.1	0.0	3.4	2.3
11	**1878**	**7.8**	**13.9**	**8.7**	**0.0**	**17.5**	**28.5**	**2.1**	**0.0**	**3.4**	**2.3**

b. Coring Site Two

- The DI-TP and diatom taxa comprising >5% relative abundance at any depth at Coring Site Two. Linear interpolation was used to provide DI-TP values and diatom relative abundance values for the years between those shown here.

Depth	Year AD CRS Model	DI-TP	ADMI	BVIT	AFOR	CKRM	COCE	CPST	SEXG	TFLO
0.5	2006	16.82	12.80	3.49	7.32	6.65	14.46	14.63	2.33	4.66
1	1999	16.15	12.95	4.00	8.87	8.47	14.87	15.83	0.80	5.12
1.5	1995	15.31	13.64	3.73	8.28	11.53	15.42	13.31	1.30	3.41
2	1990	12.48	9.92	3.80	5.12	15.21	16.53	9.26	2.31	4.96
2.5	1987	11.54	11.30	3.17	4.14	18.54	23.81	6.93	2.26	2.26
3	1983	11.56	10.25	3.80	4.96	19.17	20.66	7.11	1.82	4.63
3.5	1980	10.61	11.48	3.23	3.96	15.52	27.00	7.60	1.62	3.07
4	1976	13.12	11.10	5.14	5.55	13.09	25.02	10.27	0.66	2.98
4.5	1968	8.20	12.89	5.00	1.21	17.89	34.97	3.38	1.61	2.90
5	1959	9.05	12.36	4.94	1.15	21.91	28.50	4.12	1.65	3.46
7	1922	7.51	14.30	5.09	0.16	18.41	31.72	3.29	3.12	1.48
9	1878	7.62	13.13	4.38	0.97	23.18	28.20	1.13	2.43	2.27

• Linearly interpolated DI-TP and diatom taxa comprising >5% relative abundance at any depth at Coring Site Two

Depth cm	Year AD	DI-TP $\mu g\ l^{-1}$	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	SEXG %	TFLO %
0.5	**2006**	**16.8**	**12.8**	**3.5**	**7.3**	**6.7**	**14.5**	**14.6**	**2.3**	**4.7**
	2005	16.7	12.8	3.6	7.5	6.9	14.5	14.8	2.1	4.7
	2004	16.6	12.8	3.6	7.8	7.2	14.6	15.0	1.9	4.8
	2003	16.5	12.9	3.7	8.0	7.4	14.6	15.1	1.7	4.9
	2002	16.4	12.9	3.8	8.2	7.7	14.7	15.3	1.5	4.9
	2001	16.3	12.9	3.9	8.4	8.0	14.8	15.5	1.2	5.0
	2000	16.2	12.9	3.9	8.7	8.2	14.8	15.7	1.0	5.1
1	**1999**	**16.2**	**12.9**	**4.0**	**8.9**	**8.5**	**14.9**	**15.8**	**0.8**	**5.1**
	1998	15.9	13.1	3.9	8.7	9.2	15.0	15.2	0.9	4.7
	1997	15.7	13.3	3.9	8.6	10.0	15.1	14.6	1.0	4.3
	1996	15.5	13.5	3.8	8.4	10.8	15.3	13.9	1.2	3.8
1.5	**1995**	**15.3**	**13.6**	**3.7**	**8.3**	**11.5**	**15.4**	**13.3**	**1.3**	**3.4**
	1994	14.7	12.9	3.7	7.6	12.3	15.6	12.5	1.5	3.7
	1993	14.2	12.1	3.8	7.0	13.0	15.9	11.7	1.7	4.0
	1992	13.6	11.4	3.8	6.4	13.7	16.1	10.9	1.9	4.3
	1991	13.0	10.7	3.8	5.8	14.5	16.3	10.1	2.1	4.6
2	**1990**	**12.5**	**9.9**	**3.8**	**5.1**	**15.2**	**16.5**	**9.3**	**2.3**	**5.0**
	1989	12.2	10.4	3.6	4.8	16.3	19.0	8.5	2.3	4.1
	1988	11.9	10.8	3.4	4.5	17.4	21.4	7.7	2.3	3.2
2.5	**1987**	**11.5**	**11.3**	**3.2**	**4.1**	**18.5**	**23.8**	**6.9**	**2.3**	**2.3**
	1986	11.5	11.0	3.3	4.3	18.7	23.0	7.0	2.2	2.9
	1985	11.6	10.8	3.5	4.6	18.9	22.2	7.0	2.0	3.4
	1984	11.6	10.5	3.6	4.8	19.0	21.4	7.1	1.9	4.0
3	**1983**	**11.6**	**10.2**	**3.8**	**5.0**	**19.2**	**20.7**	**7.1**	**1.8**	**4.6**
	1982	11.2	10.7	3.6	4.6	18.0	22.8	7.3	1.8	4.1
	1981	10.9	11.1	3.4	4.3	16.7	24.9	7.4	1.7	3.6
3.5	**1980**	**10.6**	**11.5**	**3.2**	**4.0**	**15.5**	**27.0**	**7.6**	**1.6**	**3.1**
	1979	11.2	11.4	3.7	4.4	14.9	26.5	8.3	1.4	3.0
	1978	11.9	11.3	4.2	4.8	14.3	26.0	8.9	1.1	3.0
	1977	12.5	11.2	4.7	5.2	13.7	25.5	9.6	0.9	3.0
4	**1976**	**13.1**	**11.1**	**5.1**	**5.6**	**13.1**	**25.0**	**10.3**	**0.7**	**3.0**

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	SEXG %	TFLO %
	1975	12.5	11.3	5.1	5.0	13.7	26.3	9.4	0.8	3.0
	1974	11.9	11.5	5.1	4.5	14.3	27.5	8.6	0.9	3.0
	1973	11.3	11.8	5.1	3.9	14.9	28.8	7.7	1.0	3.0
	1972	10.7	12.0	5.1	3.4	15.5	30.0	6.8	1.1	2.9
	1971	10.0	12.2	5.0	2.8	16.1	31.2	6.0	1.3	2.9
	1970	9.4	12.4	5.0	2.3	16.7	32.5	5.1	1.4	2.9
	1969	8.8	12.7	5.0	1.8	17.3	33.7	4.2	1.5	2.9
4.5	**1968**	**8.2**	**12.9**	**5.0**	**1.2**	**17.9**	**35.0**	**3.4**	**1.6**	**2.9**
	1967	8.3	12.8	5.0	1.2	18.3	34.3	3.5	1.6	3.0
	1966	8.4	12.8	5.0	1.2	18.8	33.5	3.5	1.6	3.0
	1965	8.5	12.7	5.0	1.2	19.2	32.8	3.6	1.6	3.1
	1964	8.6	12.7	5.0	1.2	19.7	32.1	3.7	1.6	3.1
	1963	8.7	12.6	5.0	1.2	20.1	31.4	3.8	1.6	3.2
	1962	8.8	12.5	5.0	1.2	20.6	30.7	3.9	1.6	3.3
	1961	8.9	12.5	5.0	1.2	21.0	29.9	4.0	1.6	3.3
	1960	9.0	12.4	4.9	1.2	21.5	29.2	4.0	1.6	3.4
5	**1959**	**9.1**	**12.4**	**4.9**	**1.2**	**21.9**	**28.5**	**4.1**	**1.6**	**3.5**
	1958	9.0	12.4	4.9	1.1	21.8	28.6	4.1	1.7	3.4
	1957	9.0	12.5	5.0	1.1	21.7	28.7	4.1	1.7	3.4
	1956	8.9	12.5	5.0	1.1	21.6	28.8	4.1	1.8	3.3
	1955	8.9	12.6	5.0	1.0	21.5	28.8	4.0	1.8	3.2
	1954	8.8	12.6	5.0	1.0	21.4	28.9	4.0	1.8	3.2
	1953	8.8	12.7	5.0	1.0	21.3	29.0	4.0	1.9	3.1
	1952	8.8	12.7	5.0	1.0	21.2	29.1	4.0	1.9	3.1
	1951	8.7	12.8	5.0	0.9	21.2	29.2	3.9	2.0	3.0
	1950	8.7	12.8	5.0	0.9	21.1	29.3	3.9	2.0	3.0
	1949	8.6	12.9	5.0	0.9	21.0	29.4	3.9	2.0	2.9
	1948	8.6	12.9	5.0	0.9	20.9	29.5	3.9	2.1	2.9
	1947	8.6	13.0	5.0	0.8	20.8	29.5	3.8	2.1	2.8
	1946	8.5	13.0	5.0	0.8	20.7	29.6	3.8	2.2	2.8
	1945	8.5	13.1	5.0	0.8	20.6	29.7	3.8	2.2	2.7
	1944	8.4	13.1	5.0	0.8	20.5	29.8	3.8	2.2	2.7

Depth cm	Year AD	DI-TP $\mu g\ l^{-1}$	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	SEXG %	TFLO %
	1943	8.4	13.2	5.0	0.7	20.4	29.9	3.8	2.3	2.6
	1942	8.3	13.2	5.0	0.7	20.3	30.0	3.7	2.3	2.5
	1941	8.3	13.3	5.0	0.7	20.2	30.1	3.7	2.4	2.5
	1940	8.3	13.4	5.0	0.6	20.1	30.2	3.7	2.4	2.4
	1939	8.2	13.4	5.0	0.6	20.0	30.2	3.7	2.4	2.4
	1938	8.2	13.5	5.0	0.6	19.9	30.3	3.6	2.5	2.3
	1937	8.1	13.5	5.0	0.6	19.8	30.4	3.6	2.5	2.3
	1936	8.1	13.6	5.0	0.5	19.7	30.5	3.6	2.6	2.2
	1935	8.1	13.6	5.0	0.5	19.6	30.6	3.6	2.6	2.2
	1934	8.0	13.7	5.0	0.5	19.5	30.7	3.6	2.6	2.1
	1933	8.0	13.7	5.0	0.5	19.4	30.8	3.5	2.7	2.1
	1932	7.9	13.8	5.1	0.4	19.4	30.8	3.5	2.7	2.0
	1931	7.9	13.8	5.1	0.4	19.3	30.9	3.5	2.8	2.0
	1930	7.8	13.9	5.1	0.4	19.2	31.0	3.5	2.8	1.9
	1929	7.8	13.9	5.1	0.4	19.1	31.1	3.4	2.8	1.9
	1928	7.8	14.0	5.1	0.3	19.0	31.2	3.4	2.9	1.8
	1927	7.7	14.0	5.1	0.3	18.9	31.3	3.4	2.9	1.7
	1926	7.7	14.1	5.1	0.3	18.8	31.4	3.4	3.0	1.7
	1925	7.6	14.1	5.1	0.2	18.7	31.5	3.4	3.0	1.6
	1924	7.6	14.2	5.1	0.2	18.6	31.5	3.3	3.0	1.6
	1923	7.6	14.2	5.1	0.2	18.5	31.6	3.3	3.1	1.5
7	**1922**	**7.5**	**14.3**	**5.1**	**0.2**	**18.4**	**31.7**	**3.3**	**3.1**	**1.5**
	1921	7.5	14.3	5.1	0.2	18.5	31.6	3.2	3.1	1.5
	1920	7.5	14.2	5.1	0.2	18.6	31.6	3.2	3.1	1.5
	1919	7.5	14.2	5.0	0.2	18.7	31.5	3.1	3.1	1.5
	1918	7.5	14.2	5.0	0.2	18.8	31.4	3.1	3.1	1.6
	1917	7.5	14.2	5.0	0.3	18.9	31.3	3.0	3.0	1.6
	1916	7.5	14.1	5.0	0.3	19.1	31.2	3.0	3.0	1.6
	1915	7.5	14.1	5.0	0.3	19.2	31.2	2.9	3.0	1.6
	1914	7.5	14.1	5.0	0.3	19.3	31.1	2.9	3.0	1.6
	1913	7.5	14.1	4.9	0.3	19.4	31.0	2.8	3.0	1.6

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	SEXG %	TFLO %
	1912	7.5	14.0	4.9	0.3	19.5	30.9	2.8	3.0	1.7
	1911	7.5	14.0	4.9	0.4	19.6	30.8	2.7	2.9	1.7
	1910	7.5	14.0	4.9	0.4	19.7	30.8	2.7	2.9	1.7
	1909	7.5	14.0	4.9	0.4	19.8	30.7	2.7	2.9	1.7
	1908	7.5	13.9	4.9	0.4	19.9	30.6	2.6	2.9	1.7
	1907	7.5	13.9	4.8	0.4	20.0	30.5	2.6	2.9	1.7
	1906	7.5	13.9	4.8	0.5	20.1	30.4	2.5	2.9	1.8
	1905	7.6	13.8	4.8	0.5	20.2	30.4	2.5	2.9	1.8
	1904	7.6	13.8	4.8	0.5	20.4	30.3	2.4	2.8	1.8
	1903	7.6	13.8	4.8	0.5	20.5	30.2	2.4	2.8	1.8
	1902	7.6	13.8	4.8	0.5	20.6	30.1	2.3	2.8	1.8
	1901	7.6	13.7	4.8	0.6	20.7	30.0	2.3	2.8	1.9
	1900	7.6	13.7	4.7	0.6	20.8	30.0	2.2	2.8	1.9
	1899	7.6	13.7	4.7	0.6	20.9	29.9	2.2	2.8	1.9
	1898	7.6	13.7	4.7	0.6	21.0	29.8	2.1	2.7	1.9
	1897	7.6	13.6	4.7	0.6	21.1	29.7	2.1	2.7	1.9
	1896	7.6	13.6	4.7	0.6	21.2	29.6	2.0	2.7	1.9
	1895	7.6	13.6	4.7	0.7	21.3	29.6	2.0	2.7	2.0
	1894	7.6	13.6	4.6	0.7	21.4	29.5	1.9	2.7	2.0
	1893	7.6	13.5	4.6	0.7	21.6	29.4	1.9	2.7	2.0
	1892	7.6	13.5	4.6	0.7	21.7	29.3	1.8	2.7	2.0
	1891	7.6	13.5	4.6	0.7	21.8	29.2	1.8	2.6	2.0
	1890	7.6	13.4	4.6	0.8	21.9	29.2	1.7	2.6	2.1
	1889	7.6	13.4	4.6	0.8	22.0	29.1	1.7	2.6	2.1
	1888	7.6	13.4	4.5	0.8	22.1	29.0	1.6	2.6	2.1
	1887	7.6	13.4	4.5	0.8	22.2	28.9	1.6	2.6	2.1
	1886	7.6	13.3	4.5	0.8	22.3	28.8	1.5	2.6	2.1
	1885	7.6	13.3	4.5	0.8	22.4	28.8	1.5	2.5	2.1
	1884	7.6	13.3	4.5	0.9	22.5	28.7	1.4	2.5	2.2
	1883	7.6	13.3	4.5	0.9	22.6	28.6	1.4	2.5	2.2
	1882	7.6	13.2	4.4	0.9	22.7	28.5	1.3	2.5	2.2
	1881	7.6	13.2	4.4	0.9	22.9	28.4	1.3	2.5	2.2
	1880	7.6	13.2	4.4	0.9	23.0	28.4	1.2	2.5	2.2
	1879	7.6	13.2	4.4	1.0	23.1	28.3	1.2	2.4	2.3
9	**1878**	**7.6**	**13.1**	**4.4**	**1.0**	**23.2**	**28.2**	**1.1**	**2.4**	**2.3**

c. Coring Site Three

- The DI-TP and diatom taxa comprising >5% relative abundance at any depth at Coring Site Three. Linear interpolation was used to provide DI-TP values and diatom relative abundance values for the years between those shown here.

Depth	Year AD CRS Model	DI-TP	ADMI	BVIT	AFOR	CKRM	COCE	CPST	PRAD	ENNG	EINC	EUPA	FGRT	SEXG	TFLO
0.5	2006	17.24	16.28	3.78	5.76	4.11	8.72	14.14	0.49	2.14	0.49	0.99	4.44	1.32	6.91
1	1999	19.96	15.65	3.55	4.68	3.39	9.84	12.90	0.32	0.81	0.32	0.32	5.65	1.94	6.13
1.5	1995	16.00	14.87	3.27	2.78	7.19	14.54	15.03	0.65	0.98	0.65	0.49	4.25	2.12	3.43
2	1990	13.65	15.21	5.23	3.52	5.89	25.02	8.67	0.16	1.31	1.31	0.16	3.92	2.45	2.94
2.5	1987	11.75	13.59	4.53	1.78	11.00	23.95	8.58	0.32	1.13	1.13	0.97	2.10	2.27	3.07
3	1983	8.81	12.65	6.08	0.41	16.43	27.28	6.57	0.00	1.15	1.48	0.82	0.82	2.14	1.81
3.5	1980	7.47	8.01	3.60	0.08	31.56	14.23	1.96	1.64	1.14	0.98	0.98	0.65	7.52	1.96
4	1976	7.83	9.12	4.32	0.48	27.36	17.76	2.56	1.44	1.12	2.40	1.44	0.32	5.76	2.88
4.5	1968	7.08	7.53	1.97	0.41	27.35	13.10	1.80	2.46	2.29	2.62	3.44	0.66	10.81	2.62
5	1959	6.91	4.32	1.60	0.08	34.43	8.01	0.48	3.04	1.60	5.12	3.04	0.64	10.25	3.20
7	1948	6.85	4.28	2.14	0.16	27.47	8.22	0.49	7.57	1.15	5.76	4.77	0.99	7.57	3.78
9	1909	6.18	3.44	4.09	0.00	23.57	12.27	0.00	6.55	2.13	5.56	5.56	0.00	12.11	4.58
11	1878	6.61	3.96	2.64	0.00	23.27	11.55	0.17	6.44	1.98	5.94	4.29	0.00	10.89	3.80

- Linearly interpolated DI-TP and diatom taxa comprising >5% relative abundance at any depth at Coring Site Three

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	ENNG %	EINC %	EUPA %	FGRT %	SEXG %	TFLO %
0.5	2006	17.2	16.3	3.8	5.8	4.1	8.7	14.1	0.5	2.1	0.5	1.0	4.4	1.3	6.9
	2005	17.6	16.2	3.7	5.6	4.0	8.9	14.0	0.5	1.9	0.5	0.9	4.6	1.4	6.8
	2004	18.0	16.1	3.7	5.4	3.9	9.0	13.8	0.4	1.8	0.4	0.8	4.8	1.5	6.7
	2003	18.4	16.0	3.7	5.3	3.8	9.2	13.6	0.4	1.6	0.4	0.7	5.0	1.6	6.6
	2002	18.8	15.9	3.6	5.1	3.7	9.4	13.4	0.4	1.4	0.4	0.6	5.1	1.7	6.5
	2001	19.2	15.8	3.6	5.0	3.6	9.5	13.3	0.4	1.2	0.4	0.5	5.3	1.8	6.4
	2000	19.6	15.7	3.6	4.8	3.5	9.7	13.1	0.3	1.0	0.3	0.4	5.5	1.8	6.2
1	1999	20.0	15.6	3.5	4.7	3.4	9.8	12.9	0.3	0.8	0.3	0.3	5.6	1.9	6.1
	1998	19.0	15.5	3.5	4.2	4.3	11.0	13.4	0.4	0.8	0.4	0.4	5.3	2.0	5.5
	1997	18.0	15.3	3.4	3.7	5.3	12.2	14.0	0.5	0.9	0.5	0.4	4.9	2.0	4.8
	1996	17.0	15.1	3.3	3.3	6.2	13.4	14.5	0.6	0.9	0.6	0.4	4.6	2.1	4.1
1.5	1995	16.0	14.9	3.3	2.8	7.2	14.5	15.0	0.7	1.0	0.7	0.5	4.2	2.1	3.4
	1994	15.5	14.9	3.7	2.9	6.9	16.6	13.8	0.6	1.0	0.8	0.4	4.2	2.2	3.3
	1993	15.1	15.0	4.1	3.1	6.7	18.7	12.5	0.5	1.1	0.9	0.4	4.1	2.3	3.2
	1992	14.6	15.1	4.4	3.2	6.4	20.8	11.2	0.4	1.2	1.0	0.3	4.1	2.3	3.1
	1991	14.1	15.1	4.8	3.4	6.1	22.9	9.9	0.3	1.2	1.2	0.2	4.0	2.4	3.0
2	1990	13.6	15.2	5.2	3.5	5.9	25.0	8.7	0.2	1.3	1.3	0.2	3.9	2.5	2.9
	1989	13.0	14.7	5.0	2.9	7.6	24.7	8.6	0.2	1.2	1.2	0.4	3.3	2.4	3.0
	1988	12.4	14.1	4.8	2.4	9.3	24.3	8.6	0.3	1.2	1.2	0.7	2.7	2.3	3.0
2.5	1987	11.8	13.6	4.5	1.8	11.0	23.9	8.6	0.3	1.1	1.1	1.0	2.1	2.3	3.1
	1986	11.0	13.4	4.9	1.4	12.4	24.8	8.1	0.2	1.1	1.2	0.9	1.8	2.2	2.8
	1985	10.3	13.1	5.3	1.1	13.7	25.6	7.6	0.2	1.1	1.3	0.9	1.5	2.2	2.4
	1984	9.5	12.9	5.7	0.8	15.1	26.4	7.1	0.1	1.1	1.4	0.9	1.1	2.2	2.1
3	1983	8.8	12.7	6.1	0.4	16.4	27.3	6.6	0.0	1.2	1.5	0.8	0.8	2.1	1.8
	1982	8.4	11.1	5.3	0.3	21.5	22.9	5.0	0.5	1.1	1.3	0.9	0.8	3.9	1.9
	1981	7.9	9.6	4.4	0.2	26.5	18.6	3.5	1.1	1.1	1.1	0.9	0.7	5.7	1.9
3.5	1980	7.5	8.0	3.6	0.1	31.6	14.2	2.0	1.6	1.1	1.0	1.0	0.7	7.5	2.0
	1979	7.6	8.3	3.8	0.2	30.5	15.1	2.1	1.6	1.1	1.3	1.1	0.6	7.1	2.2
	1978	7.7	8.6	4.0	0.3	29.5	16.0	2.3	1.5	1.1	1.7	1.2	0.5	6.6	2.4
	1977	7.7	8.8	4.1	0.4	28.4	16.9	2.4	1.5	1.1	2.0	1.3	0.4	6.2	2.7
4	1976	7.8	9.1	4.3	0.5	27.4	17.8	2.6	1.4	1.1	2.4	1.4	0.3	5.8	2.9

Depth cm	Year AD	DI-TP $\mu g\ l^{-1}$	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	ENNG %	EINC %	EUPA %	FGRT %	SEXG %	TFLO %
	1975	7.7	8.9	4.0	0.5	27.4	17.2	2.5	1.6	1.3	2.4	1.7	0.4	6.4	2.8
	1974	7.6	8.7	3.7	0.5	27.4	16.6	2.4	1.7	1.4	2.5	1.9	0.4	7.0	2.8
	1973	7.5	8.5	3.4	0.5	27.4	16.0	2.3	1.8	1.6	2.5	2.2	0.4	7.7	2.8
	1972	7.5	8.3	3.1	0.4	27.4	15.4	2.2	1.9	1.7	2.5	2.4	0.5	8.3	2.8
	1971	7.4	8.1	2.8	0.4	27.4	14.9	2.1	2.1	1.9	2.5	2.7	0.5	8.9	2.7
	1970	7.3	7.9	2.6	0.4	27.4	14.3	2.0	2.2	2.0	2.6	2.9	0.6	9.5	2.7
	1969	7.2	7.7	2.3	0.4	27.4	13.7	1.9	2.3	2.1	2.6	3.2	0.6	10.2	2.7
4.5	**1968**	**7.1**	**7.5**	**2.0**	**0.4**	**27.4**	**13.1**	**1.8**	**2.5**	**2.3**	**2.6**	**3.4**	**0.7**	**10.8**	**2.6**
	1967	7.1	7.2	1.9	0.4	28.1	12.5	1.7	2.5	2.2	2.9	3.4	0.7	10.7	2.7
	1966	7.0	6.8	1.9	0.3	28.9	12.0	1.5	2.6	2.1	3.2	3.4	0.7	10.7	2.8
	1965	7.0	6.5	1.8	0.3	29.7	11.4	1.4	2.7	2.1	3.5	3.3	0.7	10.6	2.8
	1964	7.0	6.1	1.8	0.3	30.5	10.8	1.2	2.7	2.0	3.7	3.3	0.6	10.6	2.9
	1963	7.0	5.8	1.8	0.2	31.3	10.3	1.1	2.8	1.9	4.0	3.2	0.6	10.5	2.9
	1962	7.0	5.4	1.7	0.2	32.1	9.7	0.9	2.8	1.8	4.3	3.2	0.6	10.4	3.0
	1961	6.9	5.0	1.7	0.2	32.9	9.1	0.8	2.9	1.8	4.6	3.1	0.6	10.4	3.1
	1960	6.9	4.7	1.6	0.1	33.6	8.6	0.6	3.0	1.7	4.8	3.1	0.6	10.3	3.1
5	**1959**	**6.9**	**4.3**	**1.6**	**0.1**	**34.4**	**8.0**	**0.5**	**3.0**	**1.6**	**5.1**	**3.0**	**0.6**	**10.2**	**3.2**
	1958	6.9	4.3	1.7	0.1	33.8	8.0	0.5	3.5	1.6	5.2	3.2	0.7	10.0	3.3
	1957	6.9	4.3	1.7	0.1	33.2	8.0	0.5	3.9	1.5	5.2	3.4	0.7	9.8	3.3
	1956	6.9	4.3	1.7	0.1	32.5	8.1	0.5	4.3	1.5	5.3	3.5	0.7	9.5	3.4
	1955	6.9	4.3	1.8	0.1	31.9	8.1	0.5	4.7	1.4	5.4	3.7	0.8	9.3	3.4
	1954	6.9	4.3	1.8	0.1	31.3	8.1	0.5	5.1	1.4	5.4	3.8	0.8	9.0	3.5
	1953	6.9	4.3	1.9	0.1	30.6	8.1	0.5	5.5	1.4	5.5	4.0	0.8	8.8	3.5
	1952	6.9	4.3	1.9	0.1	30.0	8.1	0.5	5.9	1.3	5.5	4.1	0.9	8.5	3.6
	1951	6.9	4.3	2.0	0.1	29.4	8.2	0.5	6.3	1.3	5.6	4.3	0.9	8.3	3.6
	1950	6.9	4.3	2.0	0.1	28.7	8.2	0.5	6.7	1.2	5.6	4.5	0.9	8.1	3.7
	1949	6.9	4.3	2.1	0.2	28.1	8.2	0.5	7.2	1.2	5.7	4.6	1.0	7.8	3.7
7	**1948**	**6.9**	**4.3**	**2.1**	**0.2**	**27.5**	**8.2**	**0.5**	**7.6**	**1.2**	**5.8**	**4.8**	**1.0**	**7.6**	**3.8**
	1947	6.8	4.3	2.2	0.2	27.4	8.3	0.5	7.5	1.2	5.8	4.8	1.0	7.7	3.8
	1946	6.8	4.2	2.2	0.2	27.3	8.4	0.5	7.5	1.2	5.7	4.8	0.9	7.8	3.8
	1945	6.8	4.2	2.3	0.2	27.2	8.5	0.5	7.5	1.2	5.7	4.8	0.9	7.9	3.8
	1944	6.8	4.2	2.3	0.1	27.1	8.6	0.4	7.5	1.3	5.7	4.9	0.9	8.0	3.9

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	ENNG %	EINC %	EUPA %	FGRT %	SEXG %	TFLO %
	1943	6.8	4.2	2.4	0.1	27.0	8.7	0.4	7.4	1.3	5.7	4.9	0.9	8.1	3.9
	1942	6.7	4.1	2.4	0.1	26.9	8.8	0.4	7.4	1.3	5.7	4.9	0.8	8.3	3.9
	1941	6.7	4.1	2.5	0.1	26.8	9.0	0.4	7.4	1.3	5.7	4.9	0.8	8.4	3.9
	1940	6.7	4.1	2.5	0.1	26.7	9.1	0.4	7.4	1.4	5.7	4.9	0.8	8.5	3.9
	1939	6.7	4.1	2.6	0.1	26.6	9.2	0.4	7.3	1.4	5.7	5.0	0.8	8.6	4.0
	1938	6.7	4.1	2.6	0.1	26.5	9.3	0.4	7.3	1.4	5.7	5.0	0.7	8.7	4.0
	1937	6.7	4.0	2.7	0.1	26.4	9.4	0.4	7.3	1.4	5.7	5.0	0.7	8.8	4.0
	1936	6.6	4.0	2.7	0.1	26.3	9.5	0.3	7.3	1.5	5.7	5.0	0.7	9.0	4.0
	1935	6.6	4.0	2.8	0.1	26.2	9.6	0.3	7.2	1.5	5.7	5.0	0.7	9.1	4.0
	1934	6.6	4.0	2.8	0.1	26.1	9.7	0.3	7.2	1.5	5.7	5.1	0.6	9.2	4.1
	1933	6.6	4.0	2.9	0.1	26.0	9.8	0.3	7.2	1.5	5.7	5.1	0.6	9.3	4.1
	1932	6.6	3.9	2.9	0.1	25.9	9.9	0.3	7.1	1.6	5.7	5.1	0.6	9.4	4.1
	1931	6.6	3.9	3.0	0.1	25.8	10.0	0.3	7.1	1.6	5.7	5.1	0.6	9.5	4.1
	1930	6.5	3.9	3.0	0.1	25.7	10.1	0.3	7.1	1.6	5.7	5.1	0.5	9.7	4.2
	1929	6.5	3.9	3.1	0.1	25.6	10.2	0.3	7.1	1.6	5.7	5.2	0.5	9.8	4.2
	1928	6.5	3.8	3.1	0.1	25.5	10.3	0.2	7.0	1.7	5.7	5.2	0.5	9.9	4.2
	1927	6.5	3.8	3.2	0.1	25.4	10.4	0.2	7.0	1.7	5.7	5.2	0.5	10.0	4.2
	1926	6.5	3.8	3.2	0.1	25.3	10.5	0.2	7.0	1.7	5.6	5.2	0.4	10.1	4.2
	1925	6.5	3.8	3.3	0.1	25.2	10.6	0.2	7.0	1.7	5.6	5.2	0.4	10.2	4.3
	1924	6.4	3.8	3.3	0.1	25.1	10.7	0.2	6.9	1.8	5.6	5.3	0.4	10.4	4.3
	1923	6.4	3.7	3.4	0.1	25.0	10.8	0.2	6.9	1.8	5.6	5.3	0.4	10.5	4.3
	1922	6.4	3.7	3.4	0.1	24.9	10.9	0.2	6.9	1.8	5.6	5.3	0.3	10.6	4.3
	1921	6.4	3.7	3.5	0.1	24.8	11.0	0.2	6.9	1.8	5.6	5.3	0.3	10.7	4.3
	1920	6.4	3.7	3.5	0.0	24.7	11.1	0.1	6.8	1.9	5.6	5.3	0.3	10.8	4.4
	1919	6.4	3.7	3.6	0.0	24.6	11.2	0.1	6.8	1.9	5.6	5.4	0.3	10.9	4.4
	1918	6.3	3.6	3.6	0.0	24.5	11.3	0.1	6.8	1.9	5.6	5.4	0.2	11.1	4.4
	1917	6.3	3.6	3.7	0.0	24.4	11.4	0.1	6.8	1.9	5.6	5.4	0.2	11.2	4.4
	1916	6.3	3.6	3.7	0.0	24.3	11.5	0.1	6.7	2.0	5.6	5.4	0.2	11.3	4.4
	1915	6.3	3.6	3.8	0.0	24.2	11.7	0.1	6.7	2.0	5.6	5.4	0.2	11.4	4.5
	1914	6.3	3.5	3.8	0.0	24.1	11.8	0.1	6.7	2.0	5.6	5.5	0.1	11.5	4.5
	1913	6.2	3.5	3.9	0.0	24.0	11.9	0.1	6.7	2.0	5.6	5.5	0.1	11.6	4.5

Depth cm	Year AD	DI-TP µg l⁻¹	ADMI %	BVIT %	AFOR %	CKRM %	CCMS %	CPST %	PRAD %	ENNG %	EINC %	EUPA %	FGRT %	SEXG %	TFLO %
	1912	6.2	3.5	3.9	0.0	23.9	12.0	0.0	6.6	2.1	5.6	5.5	0.1	11.8	4.5
	1911	6.2	3.5	4.0	0.0	23.8	12.1	0.0	6.6	2.1	5.6	5.5	0.1	11.9	4.5
	1910	6.2	3.5	4.0	0.0	23.7	12.2	0.0	6.6	2.1	5.6	5.5	0.0	12.0	4.6
9	**1909**	**6.2**	**3.4**	**4.1**	**0.0**	**23.6**	**12.3**	**0.0**	**6.5**	**2.1**	**5.6**	**5.6**	**0.0**	**12.1**	**4.6**
	1908	6.2	3.5	4.0	0.0	23.6	12.3	0.0	6.5	2.1	5.6	5.5	0.0	12.1	4.6
	1907	6.2	3.5	4.0	0.0	23.5	12.2	0.0	6.5	2.1	5.6	5.5	0.0	12.0	4.5
	1906	6.2	3.5	4.0	0.0	23.5	12.2	0.0	6.5	2.1	5.6	5.4	0.0	12.0	4.5
	1905	6.2	3.5	3.9	0.0	23.5	12.2	0.0	6.5	2.1	5.6	5.4	0.0	12.0	4.5
	1904	6.2	3.5	3.9	0.0	23.5	12.2	0.0	6.5	2.1	5.6	5.4	0.0	11.9	4.5
	1903	6.3	3.5	3.8	0.0	23.5	12.1	0.0	6.5	2.1	5.6	5.3	0.0	11.9	4.4
	1902	6.3	3.6	3.8	0.0	23.5	12.1	0.0	6.5	2.1	5.6	5.3	0.0	11.8	4.4
	1901	6.3	3.6	3.7	0.0	23.5	12.1	0.0	6.5	2.1	5.7	5.2	0.0	11.8	4.4
	1900	6.3	3.6	3.7	0.0	23.5	12.1	0.0	6.5	2.1	5.7	5.2	0.0	11.8	4.4
	1899	6.3	3.6	3.6	0.0	23.5	12.0	0.1	6.5	2.1	5.7	5.2	0.0	11.7	4.3
	1898	6.3	3.6	3.6	0.0	23.5	12.0	0.1	6.5	2.1	5.7	5.1	0.0	11.7	4.3
	1897	6.3	3.6	3.5	0.0	23.5	12.0	0.1	6.5	2.1	5.7	5.1	0.0	11.6	4.3
	1896	6.4	3.7	3.5	0.0	23.4	12.0	0.1	6.5	2.1	5.7	5.0	0.0	11.6	4.3
	1895	6.4	3.7	3.4	0.0	23.4	11.9	0.1	6.5	2.1	5.7	5.0	0.0	11.6	4.2
	1894	6.4	3.7	3.4	0.0	23.4	11.9	0.1	6.5	2.1	5.7	4.9	0.0	11.5	4.2
	1893	6.4	3.7	3.3	0.0	23.4	11.9	0.1	6.5	2.1	5.8	4.9	0.0	11.5	4.2
	1892	6.4	3.7	3.3	0.0	23.4	11.9	0.1	6.5	2.0	5.8	4.9	0.0	11.4	4.2
	1891	6.4	3.7	3.2	0.0	23.4	11.9	0.1	6.5	2.0	5.8	4.8	0.0	11.4	4.1
	1890	6.4	3.8	3.2	0.0	23.4	11.8	0.1	6.5	2.0	5.8	4.8	0.0	11.4	4.1
	1889	6.5	3.8	3.2	0.0	23.4	11.8	0.1	6.5	2.0	5.8	4.7	0.0	11.3	4.1
	1888	6.5	3.8	3.1	0.0	23.4	11.8	0.1	6.5	2.0	5.8	4.7	0.0	11.3	4.0
	1887	6.5	3.8	3.1	0.0	23.4	11.8	0.1	6.5	2.0	5.8	4.7	0.0	11.2	4.0
	1886	6.5	3.8	3.0	0.0	23.3	11.7	0.1	6.5	2.0	5.8	4.6	0.0	11.2	4.0
	1885	6.5	3.8	3.0	0.0	23.3	11.7	0.1	6.5	2.0	5.9	4.6	0.0	11.2	4.0
	1884	6.5	3.9	2.9	0.0	23.3	11.7	0.1	6.5	2.0	5.9	4.5	0.0	11.1	3.9
	1883	6.5	3.9	2.9	0.0	23.3	11.7	0.1	6.5	2.0	5.9	4.5	0.0	11.1	3.9
	1882	6.6	3.9	2.8	0.0	23.3	11.6	0.1	6.4	2.0	5.9	4.5	0.0	11.0	3.9
	1881	6.6	3.9	2.8	0.0	23.3	11.6	0.1	6.4	2.0	5.9	4.4	0.0	11.0	3.9
	1880	6.6	3.9	2.7	0.0	23.3	11.6	0.2	6.4	2.0	5.9	4.4	0.0	11.0	3.8
	1879	6.6	3.9	2.7	0.0	23.3	11.6	0.2	6.4	2.0	5.9	4.3	0.0	10.9	3.8
11	**1878**	**6.6**	**4.0**	**2.6**	**0.0**	**23.3**	**11.6**	**0.2**	**6.4**	**2.0**	**5.9**	**4.3**	**0.0**	**10.9**	**3.8**

Appendix E

Historical Records used as environmental variables for RDA of Diatom and DI-TP data

- The historical records used as environmental variables for the RDA of DI-TP and diatom data. Linear interpolation was used to provide yearly data on population, housing and livestock density for the years between those shown here. Climate data were recorded on a yearly basis

Population and housing			Livestock		
Year	People ha^{-1}	Houses ha^{-1}	Year	Number of sheep ha^{-1}	Number of cattle ha^{-1}
2006	0.07	0.03	**2000**	3.20	0.78
2002	0.07	0.02			
1996	0.07	0.02			
1991	0.08	0.02	**1991**	3.90	0.85
1986	0.08	0.02			
1981	0.09	0.03	**1980**	1.91	1.04
1979	0.09	0.00	**1975**	1.81	0.99
1971	0.10	0.00	**1970**	1.47	0.93
1966	0.11	0.00	**1965**	1.39	0.88
1961	0.12	0.00	**1960**	1.37	0.86
1956	0.13	0.00	**1955**	1.39	0.91
1951	0.14	0.00	**1954**	1.50	0.98
1946	0.15	0.00			
1936	0.14	0.00	**1933**	1.10	1.16
1926	0.19	0.00	**1926**	0.78	0.96
1911	0.23	0.04	**1911**	0.61	1.13
1901	0.24	0.04	**1901**	0.76	1.15
1891	0.24	0.04	**1891**	0.61	1.01
1881	0.27	0.04	**1881**	0.49	0.92
1871	0.26	0.04			
1861	0.26	0.04			
1851	0.25	0.04			
1841	0.32	0.05			

- Linearly interpolated values for the historical records used as environmental variables for the RDA of DI-TP and diatom data. Climate data were recorded on a yearly basis

Year AD	Population People ha^{-1}	Houses Houses ha^{-1}	Sheep Sheep ha^{-1}	Cattle Cattle ha^{-1}	Temperature °C	Precipitation mm
2006	0.07	0.03	2.73	0.73	11.5	1772.1
2005	0.07	0.03	2.81	0.74	11.3	1502.9
2004	0.07	0.03	2.89	0.75	11.1	1399.5
2003	0.07	0.03	2.97	0.76	11.2	1507.2
2002	0.07	0.02	3.04	0.76	11.0	1922.9
2001	0.07	0.02	3.12	0.77	10.7	1235.3
2000	0.07	0.02	3.20	0.78	10.7	1786.2
1999	0.07	0.02	3.28	0.79	11.2	1768.5
1998	0.07	0.02	3.36	0.80	11.3	1775.3
1997	0.07	0.02	3.43	0.80	11.5	1406.2
1996	0.07	0.02	3.51	0.81	10.4	1567.7
1995	0.07	0.02	3.59	0.82	11.3	1540.3
1994	0.07	0.02	3.67	0.83	10.9	1804.1
1993	0.08	0.02	3.74	0.83	10.7	1469.4
1992	0.08	0.02	3.82	0.84	10.7	1420.9
1991	0.08	0.02	3.90	0.85	10.8	1379.2
1990	0.08	0.02	3.72	0.87	11.2	1338.1
1989	0.08	0.02	3.54	0.88	11.2	1374.0
1988	0.08	0.02	3.36	0.90	10.7	1582.3
1987	0.08	0.02	3.18	0.92	10.5	1347.3
1986	0.08	0.02	3.00	0.94	9.7	1571.3
1985	0.08	0.02	2.81	0.95	10.3	1616.7
1984	0.08	0.02	2.63	0.97	10.5	1507.2
1983	0.08	0.02	2.45	0.99	11.0	1427.2
1982	0.08	0.03	2.27	1.01	10.8	1785.4
1981	0.09	0.03	2.09	1.02	10.6	1405.9
1980	0.09	0.03	1.91	1.04	10.4	1775.5
1979	0.09	0.03	1.89	1.03	9.8	1574.1
1978	0.09	0.03	1.87	1.02	10.4	1509.7
1977	0.09	0.03	1.85	1.01	10.4	1541.8
1976	0.09	0.03	1.83	1.00	10.7	1446.6
1975	0.10	0.03	1.81	0.99	10.9	1200.2
1974	0.10	0.03	1.74	0.98	10.3	1591.1
1973	0.10	0.03	1.67	0.97	10.8	1229.9
1972	0.10	0.03	1.61	0.95	10.0	1509.8
1971	0.10	0.03	1.54	0.94	10.9	989.6
1970	0.11	0.03	1.47	0.93	10.4	1389.4
1969	0.11	0.03	1.45	0.92	10.1	1131.6
1968	0.11	0.03	1.44	0.91	10.5	1457.7
1967	0.11	0.03	1.42	0.90	10.2	1347.5
1966	0.11	0.03	1.41	0.89	10.7	1407.2
1965	0.11	0.03	1.39	0.88	10.2	1358.0
1964	0.12	0.03	1.39	0.88	10.9	1487.2
1963	0.12	0.03	1.38	0.87	9.8	1395.9
1962	0.12	0.03	1.38	0.87	10.1	1232.3
1961	0.12	0.03	1.37	0.86	10.8	1375.6
1960	0.12	0.03	1.37	0.86	10.6	1690.5

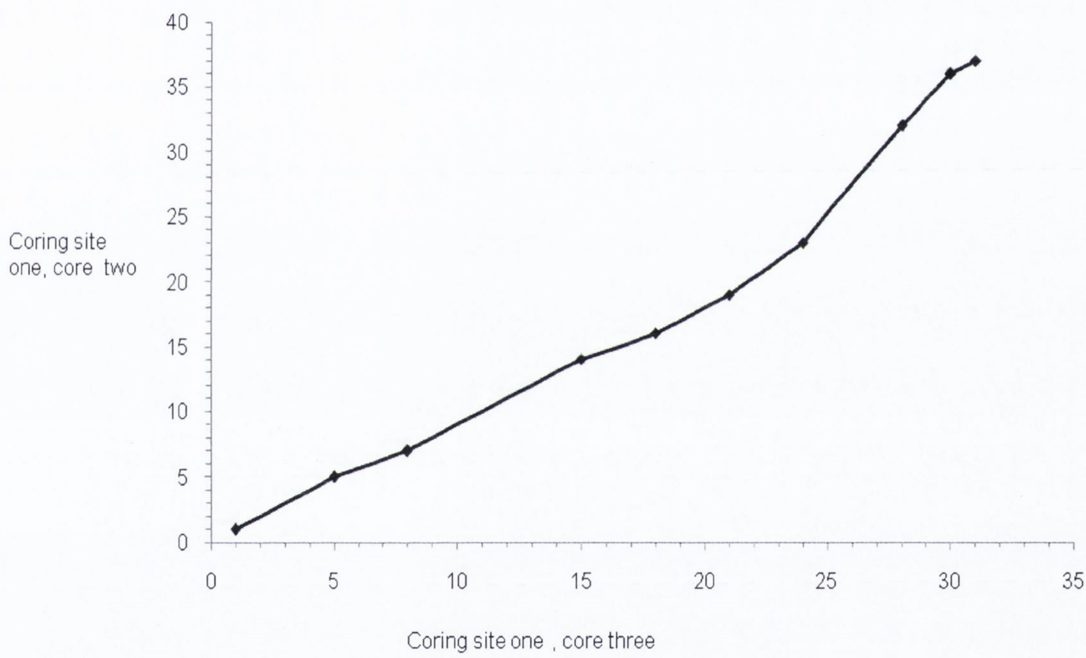
Year AD	Population People ha^{-1}	Houses Houses ha^{-1}	Sheep Sheep ha^{-1}	Cattle Cattle ha^{-1}	Temperature °C	Precipitation mm
1959	0.12	0.03	1.37	0.87	11.3	1472.8
1958	0.13	0.03	1.38	0.88	10.7	1582.7
1957	0.13	0.03	1.38	0.89	11.1	1439.6
1956	0.13	0.03	1.39	0.90	10.4	1240.3
1955	0.13	0.03	1.39	0.91	10.8	1122.1
1954	0.13	0.03	1.50	0.98	10.5	1548.7
1953	0.14	0.03	1.48	0.99	10.9	1279.5
1952	0.14	0.03	1.46	1.00	10.6	1064.4
1951	0.14	0.03	1.44	1.01	10.3	1596.3
1950	0.14	0.03	1.42	1.01	10.6	1633.6
1949	0.14	0.03	1.40	1.02	11.6	1314.8
1948	0.15	0.03	1.39	1.03	11.2	1481.2
1947	0.15	0.03	1.37	1.04	10.6	1506.6
1946	0.15	0.03	1.35	1.05	10.7	1544.6
1945	0.15	0.03	1.33	1.06	11.6	1448.7
1944	0.15	0.03	1.31	1.07	11.0	1261.6
1943	0.15	0.03	1.29	1.07	11.1	1408.1
1942	0.15	0.03	1.27	1.08	10.7	1249.9
1941	0.15	0.03	1.25	1.09	10.5	1276.7
1940	0.15	0.03	1.23	1.10	11.0	1327.2
1939	0.15	0.03	1.21	1.11	10.8	1309.9
1938	0.15	0.03	1.20	1.12	10.9	1557.4
1937	0.14	0.03	1.18	1.13	10.4	1624.4
1936	0.14	0.03	1.16	1.13	10.8	1252.9
1935	0.15	0.03	1.14	1.14	10.6	1304.0
1934	0.15	0.03	1.12	1.15	10.8	1575.6
1933	0.16	0.03	1.10	1.16	10.9	1147.3
1932	0.16	0.03	1.05	1.13	10.8	1244.6
1931	0.17	0.03	1.01	1.10	10.7	1423.7
1930	0.17	0.03	0.96	1.07	10.2	1661.7
1929	0.18	0.03	0.92	1.05	10.7	1531.4
1928	0.18	0.04	0.87	1.02	10.8	1781.2
1927	0.19	0.04	0.83	0.99	10.5	1345.1
1926	0.19	0.04	0.78	0.96	11.0	1300.0
1925	0.19	0.04	0.77	0.97	10.2	1331.3
1924	0.20	0.04	0.76	0.98	10.4	1580.2
1923	0.20	0.04	0.75	0.99	10.2	1520.9
1922	0.20	0.04	0.73	1.01	10.1	1359.7
1921	0.20	0.04	0.72	1.02	11.5	1173.2
1920	0.21	0.04	0.71	1.03	10.4	1667.8
1919	0.21	0.04	0.70	1.04	9.8	1169.1
1918	0.21	0.04	0.69	1.05	10.6	1568.2
1917	0.21	0.04	0.68	1.06	9.7	1222.8
1916	0.22	0.04	0.67	1.07	10.3	1358.9
1915	0.22	0.04	0.66	1.08	10.4	1595.1

Year AD	Population People ha^{-1}	Houses Houses ha^{-1}	Sheep Sheep ha^{-1}	Cattle Cattle ha^{-1}	Temperature °C	Precipitation mm
1914	0.22	0.04	0.64	1.10	10.5	1755.7
1913	0.22	0.04	0.63	1.11	10.3	1602.8
1912	0.23	0.04	0.62	1.12	10.3	1443.3
1911	0.23	0.04	0.61	1.13	10.6	1412.3
1910	0.23	0.04	0.63	1.13	10.3	1341.4
1909	0.23	0.04	0.64	1.13	10.0	1146.3
1908	0.23	0.04	0.66	1.14	10.9	1281.2
1907	0.23	0.04	0.67	1.14	10.2	1289.8
1906	0.24	0.04	0.69	1.14	10.5	1289.4
1905	0.24	0.04	0.70	1.14	10.3	1325.4
1904	0.24	0.04	0.72	1.14	10.2	1642.1
1903	0.24	0.04	0.73	1.15	10.3	1713.2
1902	0.24	0.04	0.75	1.15	10.5	1279.6
1901	0.24	0.04	0.76	1.15	10.1	1325.3
1900	0.24	0.04	0.75	1.14	10.4	1587.8
1899	0.24	0.04	0.73	1.12	11.2	1549.4
1898	0.24	0.04	0.72	1.11	11.2	1315.2
1897	0.24	0.04	0.70	1.09	10.7	1575.6
1896	0.24	0.04	0.69	1.08	10.5	1229.9
1895	0.24	0.04	0.67	1.07	9.9	1228.9
1894	0.24	0.04	0.66	1.05	10.7	1430.0
1893	0.24	0.04	0.64	1.04	11.2	1101.1
1892	0.24	0.04	0.63	1.02	9.9	1260.2
1891	0.24	0.04	0.61	1.01	10.2	1481.9
1890	0.24	0.04	0.60	1.00	10.4	1459.0
1889	0.25	0.04	0.59	0.99	10.5	1420.5
1888	0.25	0.04	0.57	0.98	10.2	1178.9
1887	0.25	0.04	0.56	0.97	10.4	1091.4
1886	0.25	0.04	0.55	0.97	10.3	1560.6
1885	0.26	0.04	0.54	0.96	10.1	1389.0
1884	0.26	0.04	0.53	0.95	10.7	1629.7
1883	0.26	0.04	0.51	0.94	10.3	1547.6
1882	0.27	0.04	0.50	0.93	10.6	1569.3
1881	0.27	0.04	0.49	0.92	10.3	1455.7
1880	0.27	0.04	0.48	0.91	10.9	1377.7
1879	0.27	0.04	0.47	0.90	9.5	1334.8
1878	0.27	0.04	0.45	0.89	10.8	1320.7

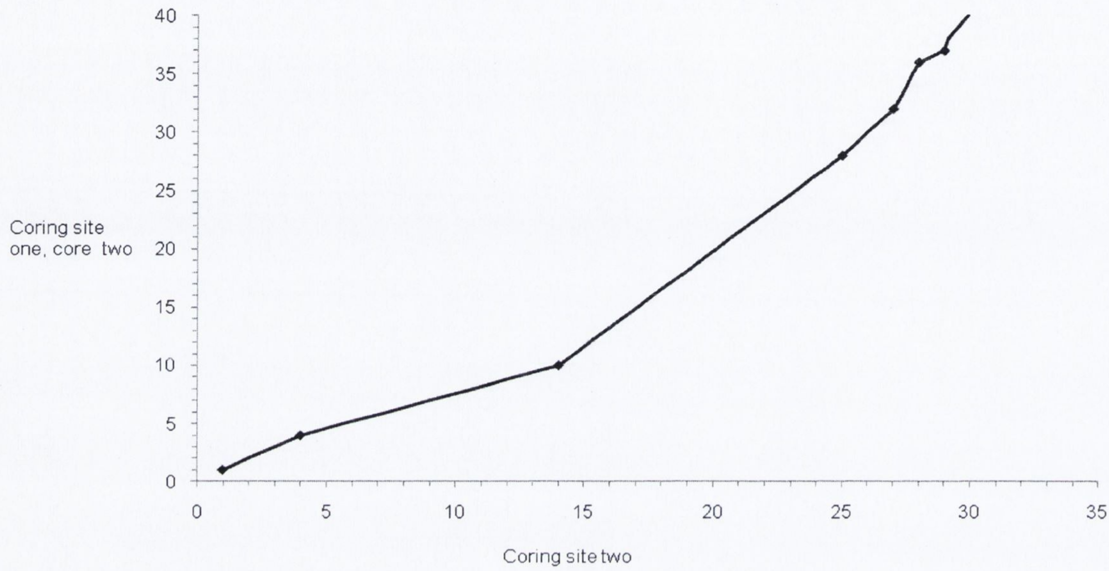
Appendix F

Plots used for inter-core correlation between Coring Site 1, Core 1 and the remaining plots used for analysis in Lough Currane

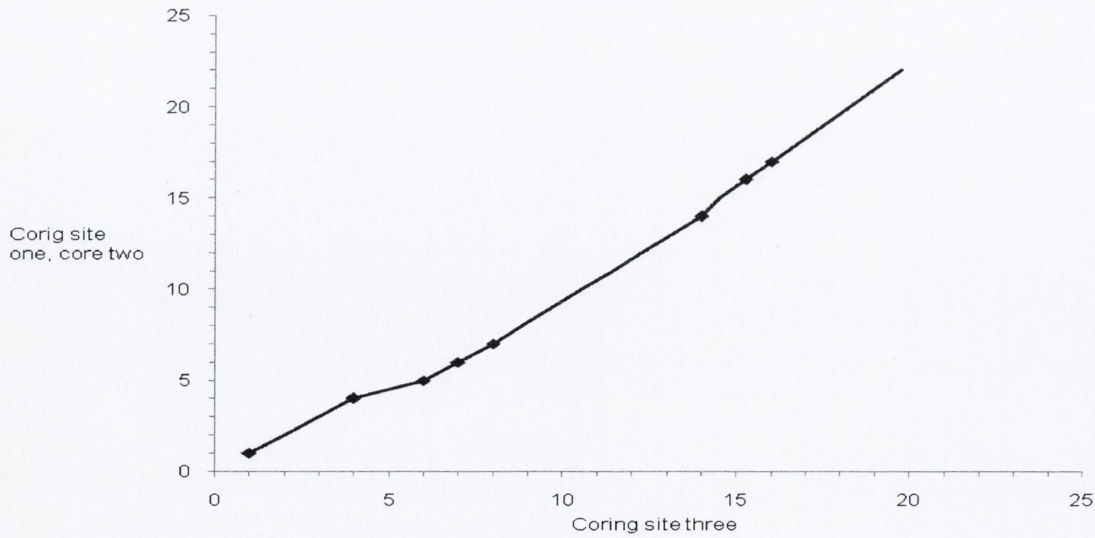
- Plot used for inter-core correlation between Coring Ste 1, Core 1 and Coring Site 1, Core 2



- Plot used for inter-core correlation between Coring Site 1, Core 1 and Coring Site 2



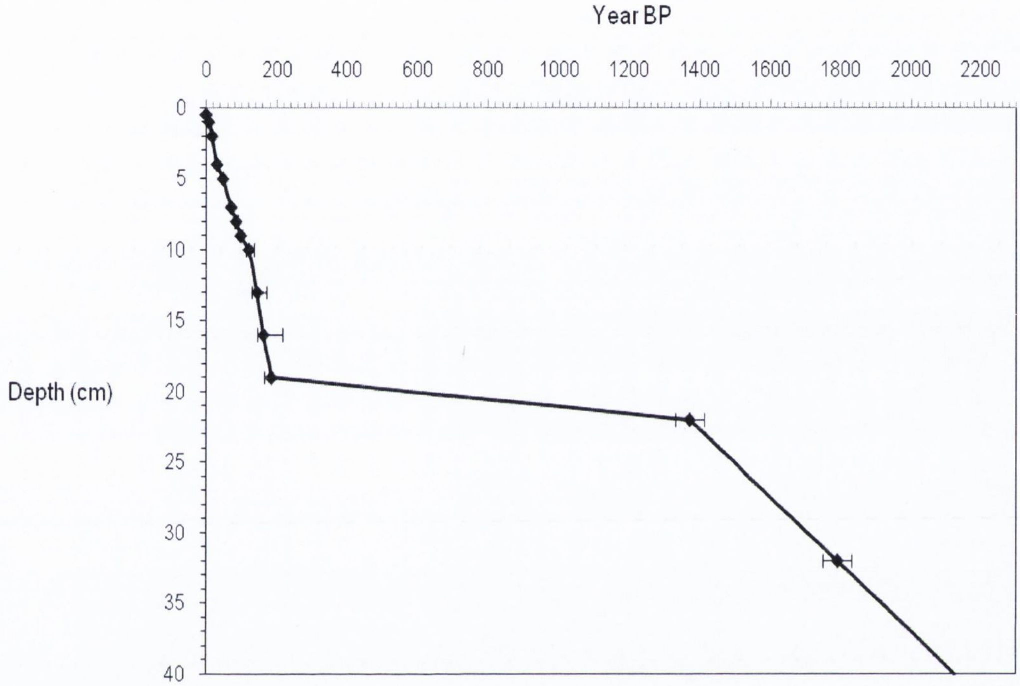
- Plot used for inter-core correlation between Coring Site 1, Core 1 and Coring Site 3



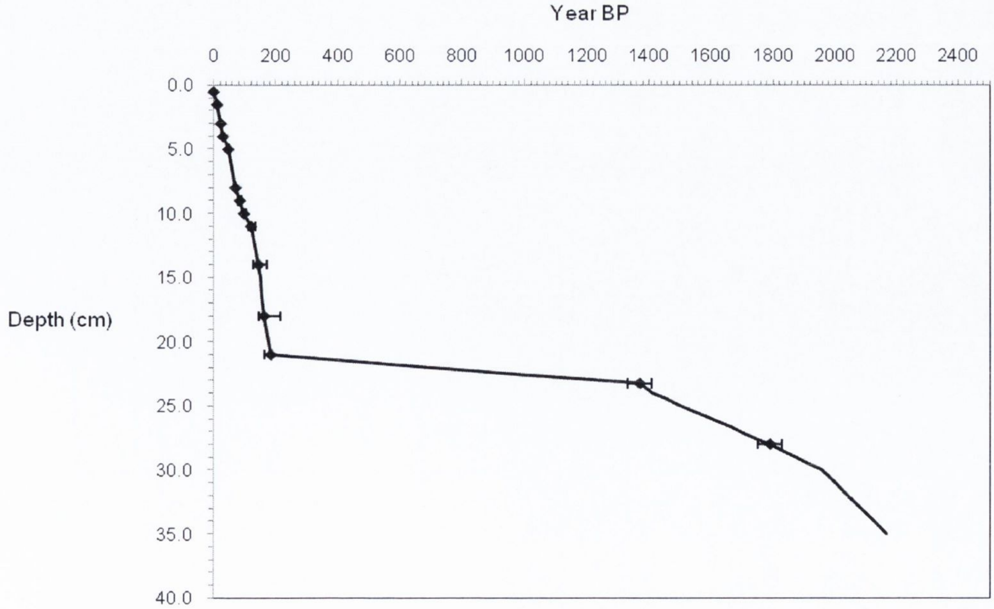
Appendix G

Depth-age plots for the sediment cores used for analysis at Lough Currane

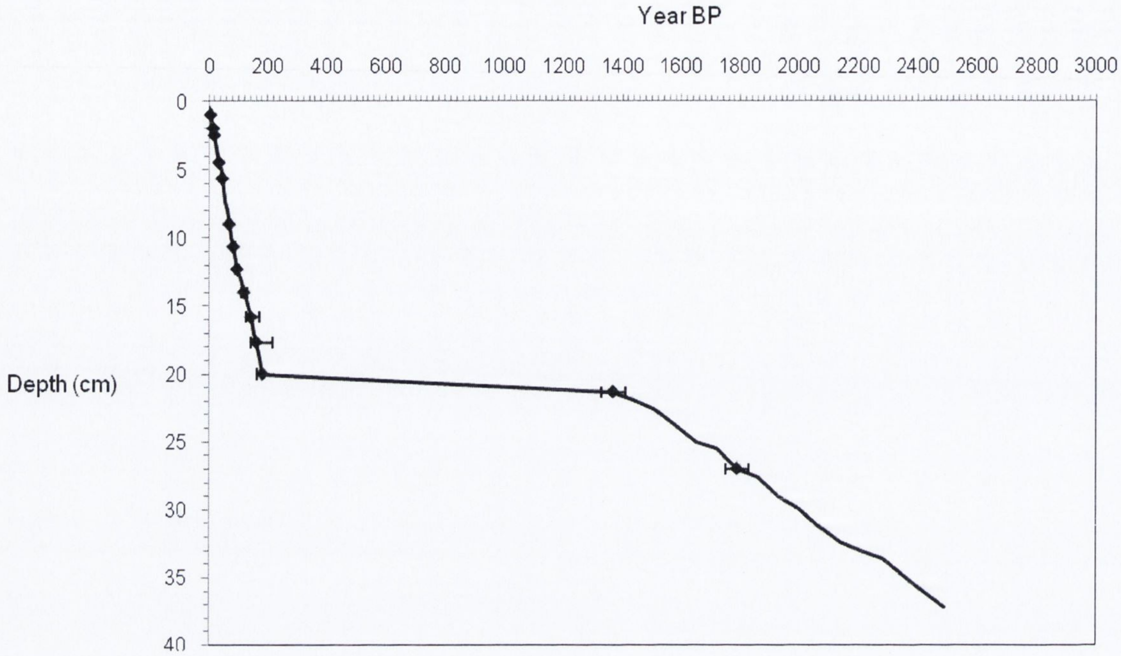
- Coring Site 1, Core 1



- Coring Site 1, Core 2



- Coring Site 2



- Coring Site 3