**M.A. Thesis**

# Using lake sediment records to examine recent productivity in Lough Gur, Co. Limerick.

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## Authors Declaration

I declare that this thesis is my own work and has never been previously submitted by me or any other individual for the purpose of obtaining a qualification.

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## ABSTRACT

Lough Gur is a small, shallow lake located on limestone bedrock in County Limerick which has been classed as hypereutrophic in recent decades. The lake has no surface inflow and water level is maintained by groundwater and surface runoff. In the most recent EPA monitoring programme 2012-15 Lough Gur was classified with a 'poor' water quality rating (www.catchments.ie). Questions regarding the balance of the contribution of the inherent natural geographical conditions and the onset of anthropogenic human influences on the lake have prevailed for some time. Palaeolimnological techniques were used to infer historical water quality and identify periods of nutrient enrichment in the lake. Two short sediment cores were radiometrically dated however radionuclide concentrations were low. An approximate chronology with a basal date of 1650 at 50 cm and the cores were cross correlated using organic matter (%LOI) allowing for a multi proxy study with synchronous and asynchronous changes. A lack of intact diatoms and poor diatom preservation necessitated the identification of fossil algal pigments. Physical geochemical and biological responses suggests that the lake has been productive since the mid-1600s but a marked increase occurred in all proxies between 1950 and 2000. Concentrations of algal pigments vary throughout the sediment core and high concentrations of cyanobacteria may be indicative of enriched waters since the mid-1700s. Increases in both OM and algal pigments are consistent with geochemical measurements of TN and TP which show sustained increases from 1950-1990 followed by peaks into the 1990s and 2000s. This increase in lake productivity was likely driven by increasing amounts of nitrogen and phosphorus entering the lake from diffuse anthropogenic sources in the surrounding catchment. P loading from the intensification of agricultural activities and residential dwellings has previously been identified as contributing to the nutrient enrichment of the lake. Recent efforts to promote the heritage of the lake has additionally resulted in a large increase in visitor number which may also be contributing to further increases in nutrient loads. This intensification of nutrient loading puts pressure on the already limited natural buffering capabilities of Lough Gur. Future management measures should focus on reducing anthropogenic sources of nutrients to the lake and raise environmental awareness in the catchment.

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# CHAPTER 1 INTRODUCTION

Fresh water is an essential resource for human life and has no viable substitute (Carpenter *et al.,* 2011). Freshwater ecosystems are among the most extensively altered ecosystems on earth and in recent decades, cultural eutrophication due to agriculture has become the leading form of pollution of lakes worldwide (Yang *et al.,* 2008). Local nutrient enrichment of Irish lakes has resulted from diffuse and point sources of contaminants arising from domestic, agricultural and industrial catchment activities (Taylor *et al.,* 2006; Bunting *et al.,* 2007; Carson *et al.,* 2014). Typical responses include increased primary production which can result in harmful algal blooms that may produce toxins impairing water quality (IPCC, 2014).

Lough Gur is Limerick's largest lake. It is situated in an internationally important archaeological landscape and consequently is an important asset to the county historically, aesthetically and economically. This unique shallow lake is underlain by limestone geology and is fed by groundwater springs and surface runoff. Lough Gur has been described as a eutrophic and hypereutrophic lake with unsightly algal blooms present on the lake during summer months in a series of studies (Layden, 1993; King and O'Grady, 1994; Ball, 2004). More recently poor oxygenation conditions, elevated pH (>9) and excess total phosphorus (TP) and ammonia were reported (McGarrigle *et al.,* 2010) raising heightened concerns (LCC, 2009). In the most recent EPA monitoring programme 2012-15 Lough Gur was classified with 'poor' water quality classification and an 'at risk' lake waterbody classification (www.catchments.ie). Questions regarding the balance of the contribution of the inherent natural geographical conditions and the onset of anthropogenic human influences on the lake have prevailed for some time. Lough Gur therefore provides an opportunity to study the sediment record for the onset, rate and trajectory of cultural eutrophication. This information is required to help inform future efforts to improve the water quality of Lough Gur in order for it to achieve a good ecological status and meet the requirements of the Water Framework Directive (WFD) of the European Union. High ecological status shows no or minimal deviation from its reference condition, followed by good, moderate, poor and bad as the degree of deviation increases. Recent palaeolimnological research undertaken in Ireland has used lake sediments to confirm pre-impact conditions or reference status and has highlighted the complexity, locally specific and often long histories of enrichment (Leira *et al.*, 2006; Taylor *et al.*, 2006; Dalton *et al.*, 2009). It is essential that evidence and data are collected so a comprehensive history of water quality at Lough Gur can be reconstructed in order to assist in setting appropriate restoration targets. Palaeolimnological coring of the lake was suggested in the mid-1990s as a possible investigative method to track eutrophication in Lough Gur (King and O'Grady, 1994).

The research aims explore the historical water quality of Lough Gur through inferences of lake sediment proxy records. Two surface sediment cores were collected. Geochemical measurements were conducted by Virginie Viaene on one core in Trinity College Dublin in an MSc supervised by Dr Norman Allott. The other core focussed on biological fossil investigation in this MA project in Mary Immaculate College, Limerick.

## 1.1 Thesis structure

The thesis is structured in the following manner. Firstly, a literature review of contemporary and classic literature of lake characteristics, eutrophication, and the role of palaeolimnology in assessing eutrophication is outlined in Chapter 2. This is followed by an outline of the study site in Chapter 3. Chapter 4 describes the methods followed throughout the course of this project. Chapter 5 profiles the catchment and describes the sediment core reconstructions of lithographical and biological fossils. Chapter 6 contains a detailed discussion of the results which is followed by a conclusion in Chapter 7.

# CHAPTER 2 LITERATURE REVIEW

Lake basins are unique ecosystems characterised by a series of geomorphological and hydrological processes. Productivity of lakes varies between regions but most generally support a variety of flora and fauna. The evolutionary history of a lake in a landscape can be unlocked through sediment analysis. Palaeolimnological reconstructions of past lake environments are important in understanding reference or baseline conditions and subsequent influence by human activities. This chapter evaluates these key components of lake ecosystems as context for the current research.

## 2.1 Lakes and lake catchments

Lake catchments and lake water bodies are intrinsically linked as processes and activities occurring within drainage areas have a direct influence on physical, chemical and biological water quality. A catchment area is a natural physiographic unit that has definite characteristics such as shape, size, area, gradients, soils, geology, geomorphology, climate and land use (Dwarakish *et al.,* 2015). Natural geomorphic processes create stable yet dynamic catchments which are generally bounded by physical features most commonly a series of high topographic points that determines their area. Geological and pedological processes regulate water movement between saturated and unsaturated areas within the catchment and therefore affect the extent to which groundwater and surface water interact (Ferrier and Jenkins, 2009). Catchments exist at all spatial scales, however the number of catchments within a particular area varies. Regions that have undergone glaciation have been known to possess greater amounts of individual catchments (Slaymaker, 2009). The characteristics of a catchment influences the quality of water as it passes through the landscape from source to sea. Bedrock mineralogy (Kamenik *et al.,* 2001), pedology (Meybeck, 1995; Cohen, 2003), land use (Nielsen *et al.,* 2012), and ecology (Sayer *et al.,* 2010) all play a part in regulating water quality in a catchment. Increases in human population and the need for potable water supplies are rising in tandem, resulting in surface and groundwater's becoming increasingly impacted by anthropogenic forcing. Recently studies suggest that freshwater species have halved in the last 30 years (Ferrier and Jenkins, 2009) and the risk of extinction for freshwater species is consistently above that of their terrestrial counterparts (Collen *et al.*, 2014).

The earths hydrological cycle is composed of a series of processes (evaporation,precipitation, run off, infiltration) which are intrinsically linked together to allow for constant renewal or purification of water (Bengtsson *et al.*, 2014). These processes operate at both regional and local scales. The magnitude and intensity of precipitation events within a given catchment has been known to directly influence stream dynamics, lake water levels and groundwater recharge (Ferrier and Jenkins, 2009). As water travels through the catchment, minerals and nutrients are transported and can be deposited in water bodies such as lakes and rivers. This action can have positive or negative impacts on the water quality in the catchment depending on the amount of nutrients deposited. (Curtis and Morgenroth, 2013) reported that catchments with a high rainfall (>1500mm per annum) had better water quality and suggested that it may be due to increased dilution or flushing of water through the catchment.

### 2.1.1. Geomorphology and morphology

To gain a full comprehension of lake processes it is important to understand their evolution. Lakes form in topographical depressions on earth's surface that become filled with water (Cohen, 2003). The forces that formed the depression and subsequent lake basin have a close relationship to the type of lake existing in the landscape. Knowledge of a lakes evolution is therefore very beneficial when constructing a palaeolimnological record of a lake. Globally, lakes can be categorised into three main groups' glacial, tectonic or fluvial. Glaciation during the Pleistocene and Quaternary period has had significant impact on the distribution of lakes worldwide with some 48% of all lakes categorised as glacial lakes (Meybeck, 1995; Cohen, 2003). The spatial distribution of lakes worldwide is uneven as most are located at mid latitudes between 40-60°N and 40-50°S (Downing *et al.*, 2006). Countries that exist at these latitudes have high precipitation and low rates of evapotranspiration. Ireland is a prime example, located at 53.4129° N it has abundant glacial lakes evident throughout its landscape. Glacial lakes form in glacial scoured depressions and as a glacier retreats water can accumulate in depressions created by current or previous glaciations or within deposition features associated with glaciation. However, a depression alone is not sufficient enough for the formation of a lake, the balance between the amount of water entering the depression through surface and ground waters and water exiting the lake must be a positive one (Visconti *et al.,* 2006). An import factor in the supply of water to these lakes is the geology of the catchment. Impermeable rock types such as igneous and metamorphic restrict the movement of water underground resulting in increased surface runoff. In contrast, karstic geology can cause increased groundwater movement as permeable rocks such as limestone and dolomite allow for percolation to easily penetrate their porous materials (Ford *et al.,* 2007). Lakes and lake catchments underlain with karstic geology are far more likely to have significant ground water influences (Cohen, 2003). Coxon and Drew, (2000) carried out a case study in the Burren, Co. Clare which highlighted the significant interconnection of surface water and groundwater in karstic areas resulting in lakes in the region having a complex hydrology. Surface water inflows to lakes are easy to identify and can be characterised with relative ease, ground water on the other hand is not so obvious and can be difficult to locate (Shaw *et al.,* 2013).

Morphometric measurements are an important element of limnological studies and include characteristics such as catchment area, lake area, basin shape, volume, depth, and water residence. It is a characteristic feature of lakes that their morphology will change over time (Wetzel and Likens, 2013). These characteristics vary between lakes and can have significant influence on them. Early studies of lake morphology aimed to identify the effect it may have on primary productivity and eutrophication (Fee, 1979). Since then more investigations have noted morphological influences on lake water temperature (Becker and Daw, 2005), aquatic vegetation (Kolada, 2014) and water quality (Moses *et al.,* 2011). Size and depth have been identified as major factors in influencing water quality. Lakes with a small surface area and a low volume of water have been noted to reduce flushing of contaminants out of the lake, resulting in a build-up of nutrients in the lake (Moses *et al.,* 2011). Large deep lakes are less susceptible to nutrient loading as they have a greater carrying capacity for increases in nutrients.

### 2.1.2 Limnology

Limnology is the multidisciplinary scientific study of inland waterbodies. It can also include associated sub disciplines such as geology, ecology, pedology, chemistry, physics and biology (Cole, 2009). Depending on the research aim various approaches are taken by limnologists to gain a greater understanding of limnological processes.

Limnologists often engage in both field and laboratory research for both long and short term studies. Direct experiments, observational and comparative studies are some methods employed, along with theoretical studies. Limnology has advanced scientific understanding of various fields such as ecology and biogeography (Hortal *et al.,* 2014) and also evolution (Merilä, 2013). In addition limnological studies not only help in identifying current threats to lentic systems such as climate change, habitat conservation and invasive species but also include investigations into the past environment of waterbodies through the field of palaeolimnology (Boggero *et al.,* 2014). Most theoretical contemporary studies are focused on two topics; the first is in relation to catchment management and the anthropogenic effects of eutrophication, pollution and acidification and the second being direct studies of climate change influence on lake systems and distinguishing climate induced changes from that of a lakes natural cycle (Whitmore and Riedinger-Whitmore, 2014).

Ecology is the study of organisms and their relationship to their surrounding environment (Chapman and Reiss, 1999). All lakes have their own unique ecology of flora and fauna which can vary depending on the catchment characteristics and lake morphology. Productive lakes located in low land areas which receive ample amounts of nutrients tend to have more evolved and complex ecosystems in comparison with their high altitude counterparts (O'Sullivan and Reynolds, 2008). A lake's ecology consists of three different habitat zones, littoral, pelagic, and benthos. Most of the flora and fauna in lakes can be found in the littoral and pelagic photic zones as sunlight allows for photosynthesis in these areas. The littoral zone of a lake is important as it is the most productive zone and also forms the interface between the terrestrial landscape and the deeper open water pelagic zone. It's high level of productivity is due to the relatively shallow depth allowing sunlight to reach sediment enabling growth (Likens, 2010). Marcophytes are the dominant flora in this zone as optimum conditions are present for their growth. The pelagic zone occurs where macrophytes are no longer able to grow due to increase in water depth and lack of light penetration but sufficient sunlight allows for phytoplankton to carry out photosynthesis. Below this is the benthos or benthic zone. Depending on the depth of this zone it can be either oxic or anoxic. Shallow lakes often have oxic conditions at the benthos as mixing allows for oxygen to reach the sediment whereas deeper lakes often have anoxic conditions due to stratification (Scheffer, 2013).

Density differences in water occur due to varying amounts of dissolved substances and temperature levels which can in turn be indicative of thermal vertical stratification of the water column (Boehrer and Schultze, 2008). Seasonal stratification between winter and summer is typical in dimictic lakes situated in temperate climates, meaning that the water mixes from the surface to the bottom twice a year. The top layer of the water column is known as the epilimnion which is warmest in summer. The metalimnion has the thermocline which exhibits a temperature gradient while the hypolimnion generally warmer than the epilimnion in the winter. Lake geomorphology and morphology impact on thermal stratification. Shallower lakes that are sheltered from wind cover may not experience any stratification and have a uniform temperature profile.

Lake water residence time plays an important role in limnological processes. Water residence time is the time taken for water in a lake to be replaced and can be calculated by dividing lake out flow by lake volume. Evaluations of water residence can give an insight into chemical processes in a lake and estimations of lake nutrient budgets. The length of time water stays in a lake is directly linked to catchment hydrology and also to the geomorphology. Internal catchment form and structure play an important role in water residence time (McGuire *et al.,* 2005), for example, lakes with no inflow or outflow are drained by evaporation and ground water. It can be difficult to estimate water residency time in these lakes unless all ground water influences have been measured. Karstic limestone catchments have substantial ground water flows and it is assumed that this may cause them to have a very short water residence time (O'Sullivan and Reynolds, 2008). Flushing of lakes occurs when an influx of clean water enters the lake. Flushing can have benefits for lake health as excess phytoplankton populations can be flushed out of the lake (Scheffer, 2013). Romo *et al.,* (2013) investigated links between water residency time and cyanobacteria in a shallow lake and found that an increase in some species of cyanobacteria could be related to higher water residence time.

Lake water alkalinity can be a signal for lake water quality as it is a measure of the acid neutralising capacity of a water body (Pharino, 2007). Alkalinity is directly linked with lake morphology and also with the underlying geology of the catchment. Lakes situated in catchments with karst geology can be subject to increased levels of calcium bicarbonate ($CaCO_3$) as surface and ground water pass through the catchment they react with limestone releasing it into the lake water which can affect the $CaCO_3$ equilibrium

(Bhateria and Jain, 2016). Increased photosynthesis can cause a decrease in alkalinity as $CO_2$ is removed from the water, additionally calcium carbonate can also be precipitated out of the water in order to achieve an equilibrium. This process also removes large amounts of phosphorus associated with the carbonate complexes from the water which subsequently accumulate in lake sediments (Wetzel, 2001).

### 2.1.3 Shallow Lake Ecosystems

Shallow lakes are abundant in many regions and commonly out number their deeper counterparts. Shallow lakes are generally defined by depth but the consensus on an exact depth at which a lake becomes a 'deep' lake is unclear. Various depths ≤2m (Heinonen, 2003), <3m (Likens, 2010) and <4m (WFD, 2005) have all been suggested as transition depths. The boundary between lakes being non-stratified shallow lakes and temporarily or permanently stratified lakes has been described as approximately ≤3m (Søndergaard *et al.,* 2003). Shallow lakes are capable of greater recycling of nutrients and typically have large amounts of rooted, submerged and emergent aquatic macrophytes. Shallow lakes are often therefore more productive than deeper lakes (Likens, 2010). An intense sediment-water interaction and vegetation community exist in shallow lakes making them highly diverse in comparison to deeper lake systems (Scheffer, 2013). Shallow lakes ecosystems can also be vulnerable to change and have become one of the most threatened aquatic ecosystems on earth as they are extremely fragile (Davidson *et al.,* 2013). Anthropogenic forcing has led to major declines in biodiversity in these ecosystems as they are far more susceptible to eutrophication, altered hydrology, salinization acidification and altered sediment accumulation all of which reduce the biomass of shallow lake systems.

## 2.2 Water Quality

Water is of vital importance to aquatic ecosystems and also to the human population as it serves domestic, commercial and agricultural activities. Water is composed of physical, chemical, biological parameters that reflect its state in nature and natural or human induced changes affect its water quality and aesthetics (krantzberg *et al.,* 2010; Carpenter *et al.,* 2011). Water quality is generally highest in catchment headwaters, due to high amounts of precipitation and little human interference. As water travels downstream through a catchment the possibility of pollutants entering waterways increases along with human activities and land use variation. In recent times declining water quality has been associated with diffuse source pollution from the intensification of agricultural activities and the development of large urban areas (Lam *et al.*, 2012). Pollutants can vary from solid inorganic debris and sediment such as mud suspended in water to biological pollutants like bacteria and virus harmful to flora and fauna. Chemical pollutants such as nitrogen (N) and phosphorus (P) from agriculture or domestic activities can be hazardous by affecting water quality through chemical reactions that can be difficult to identify and remedy (Hoornbeek, 2012). Pollutants enter rivers and lakes through two sources; diffuse pollution or point source pollution. Diffuse pollution occurs when pollutants enter water due to rainfall, surface runoff and surface or ground water infiltration. Diffuse pollution occurs across broad geographical areas and is most commonly connected with improper fertiliser use, poor management of livestock waste and commercial or domestic drainage issues (Hranova, 2006). Eutrophication is a prime example of diffuse pollution as it can be hard to identify an exact source. Conversely, point source pollution occurs when pollutants enter the water through a clear identifiable point such as a pipeline and is most commonly in industrial or municipal locations. Lakes can be classed based on their trophic state or fertility which can be measured by concentrations of plant nutrients such as N or P or by its sediment organic matter content and also chlorophyll. Lakes can be classified into four trophic states; oligotrophic (Low productivity), mesotrophic (moderately productive), eutrophic (highly productive) and hypereutrophic (extremely or overly productive) (Likens, 2010). In 1982, the organisation for Co-operation and Development (OECD) set boundaries for the annual values for total P, chlorophyll and water transparency as a means assess eutrophication (Table 2.1). Organic matter can enter lakes either externally (allotrophy) or be produced internally (autotrophic). Organic matter can also be produced internally by the decay of macrophytes and phytoplankton.

Table 2.1:Trophic classification scheme for lake waters (Tierney, 2008)

| **Lake category** | **Total P (mg/m$^3$)** | **Chlorophyll (mg/m$^3$)** | | **Transparency (m)** | |
|---|---|---|---|---|---|
| | **Mean** | **Mean** | **max** | **Mean** | **Max** |
| Ultra- Oligotrophic | <4 | <1 | <2.5 | >12 | >6 |
| Oligotrophic | <10 | <2.5 | <8 | >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 |

### 2.2.1 Eutrophication

Cultural eutrophication, or over enrichment of nutrients has become the most prevalent form of fresh water pollution in surface waters including lakes due to recent anthropogenic activities (Yang *et al.,* 2008; Schindler, 2012). In Ireland, cultural eutrophication of many lakes has been identified and attributed to increases in domestic, industrial and agricultural pollutants (Jennings *et al.,* 2003; Taylor *et al.,* 2006; Bunting *et al.,* 2007; Chen *et al.,* 2007; Bennion *et al.,* 2012; Carson *et al.,* 2014). Eutrophication is characterised by a shift from benthic macrophyte to pelagic filamentous algal production and algal blooms (Davidson and Jeppesen, 2013), and an ordinarily an increase in cyanobacteria (Romo *et al.,* 2013). Human activities such as agriculture in lake catchments give rise to water bodies loaded with excess nutrients such as N and P. These normally limiting nutrients allow for increased plant growth in lake systems resulting in high internal loading and can eventually lead to harmful algal blooms (Smol, 2008). When these large algal blooms die and decay decomposition occurs expending large amounts of the waters dissolved oxygen needed to support other flora and fauna. They also impede sunlight from entering below the surface of the water resulting in reduced transparency and macrophyte productivity. Studies such as (Schindler, 2006a), (Dupuis and Hann, 2009) and (Qin *et al.,* 2012) have highlighted that shallow lakes in particular can be more susceptible to eutrophication processes due to increased nutrients loads and low water volume.

## 2.3 Lake sediments

Lake sediments are a mixture of both organic and inorganic materials with some atmospheric inputs to the sediments also occurring in trace quantities. Sediments are directly influenced by the lake and its surrounding catchment area and so contain an integration of material resulting from catchment and lake basin dynamics (Oldfield, 1977). Materials deposited in deeper waters in the basin are assumed to experience the least disturbance and, can, under favourable conditions adhere to the law of superposition. This infers that accumulating materials are systematically overlain by younger materials to form a stratigraphic sediment record (Glew *et al.,* 2001). Sediment accumulation rate (SAR) differs between lakes but generally deposition is greater than 1mm per year and this allows for high temporal resolution analysis of changes in lake dynamics (Battarbee, 1999). A lakes SAR can be affected by a range of factors including lake morphology, surface area, land use catchment size and material inputs (Gąsiorowski, 2008). Increases in SAR of many lakes has been observed over the last hundred years. Rose *et al.,* (2010) complied a database of sediment accumulation rates from 278 European lakes in which over 70% showed an increase in SAR between basal and surface sediment. Changes in SAR in low land areas around Europe were attributed to changes in land use, agricultural practices and eutrophication.

### 2.3.1 Palaeolimnology

Palaeolimnology is the study of past physical, chemical and biological information held within lake sediment deposits that can provide the basis for historical interpretation of past environmental conditions of the lake (Smol *et al.,* 2001a). Mounting evidence suggests lakes are one of the few ecosystems that can reveal a relatively pristine record of past environmental conditions through deposition of lake sediments. These sediments can then be investigated using appropriate methods to unlock the history of the lake (Davidson and Jeppesen, 2013). To successfully reconstruct a complete history and understanding of a lake from sediment records a range of measurements or proxy records can be established such as radiometrically estimated chronology, physical (textural) and geochemical (organic and inorganic) elements as well as preserved biological fossils (plant macrofossils, diatoms, algal pigments, cladocera remains, cysts, pollen and spores) (Battarbee, 1999; Battarbee *et al.,* 2001; Bradshaw *et al.*, 2005; Waters *et al.*, 2005; Dalton *et al.*, 2009; Hausmann and Pienitz, 2009; Davidson and Jeppesen, 2013). A proxy record (e.g. diatoms, organic matter content) is a natural recorder of lake system variation therefore changes within the proxy can signify changes in the environment. Once these sediment elements have been established links can be made between the chronology and the physio-geochemical and biological fossils to create a palaeolimnological reconstruction of a lake environment.

#### 2.3.1.2 Chronology

Establishing a chronological framework for lake sediments is vital in order to identify timing of changes to lakes and the length of periods that changes may have encompassed. As part of establishing a chronology an estimation of sedimentation rate is also calculated. Radiometric analysis of radiometric lead ($^{210}$Pb), caesium ($^{137}$Cs) and radium ($^{226}Ra$) can be used as independent time markers to establish a time frame for the past 150 years, which makes it the preferential dating method employed by researchers when investigating recent anthropogenic influences on lakes (Taylor *et al.,* 2006; Bunting *et al.,* 2007; Gąsiorowski, 2008; Rose *et al.,* 2010; Carson *et al.,* 2014). $^{210}Pb$ has become a widely accepted and recognised method for establishing a chorology of lake sediments (Kirchner, 2011). $^{210}Pb$ occurs naturally as a radionuclide in the $^{238}U$ decay series and originates from two separate sources; firstly through decay of $^{226}Ra$ in sediments and secondly from the decay of atmospheric $^{222}Rn$. Both $^{226}Ra$ and $^{222}Rn$ are part of the same decay series, but supported $^{210}Pb$ is from Rn seeping into catchment soils and lake sediments, while unsupported $^{210}Pb$ comes from Rn seeping into the atmosphere. After dry deposition or precipitation scavenging this radionuclide present in the water column can attach and absorb to suspended material and be deposited in lake sediments (Appleby, 2001; Kirchner, 2011). Fallout $^{210}Pb$ is assumed to have a constant flux depending on factors such as rainfall and geographical location, the fallout of $^{210}Pb$ in Great Britain is suggested to be in the range of 80-100 Bq/m$^2$/yr (Appleby, 1971). Artificial fallout radionuclides such as $^{137}Cs$ are the result of atmospheric nuclear weapons testing 1953-63 and the Chernobyl reactor incident in 1986. Fallout radionuclides are used to help validate the chronology derived from $^{210}Pb$ records.

#### 2.3.1.3 Sedimentary organic matter

Sedimentary organic matter is derived from both external and internal biotic inputs to aquatic ecosystems. Analysis of organic matter components from lake sediments can help interpret natural and human influenced alterations to lake systems along with changes in past climates and  environments (Meyers, 2003). The main source of organic matter in lakes are derived from plants which can be divided into two groups, autocthonous and allochthonous. Autochthonous materials come from the lake itself for example primary producers such as phytoplankton and zooplankton, while allochthonous materials such as plants and decomposing humic debris come from the surrounding catchment. Deposition of organic matter can be influenced by a variety of factors including lake morphology such as depth (Meyers and Ishiwatari, 1993), catchment topography, climatic conditions and abundance of aquatic and terrestrial organisms  (Meyers and Lallier-vergés, 1999). Sequential loss on ignition (%LOI) is commonly used method to determine organic and carbonate content of sediments (Dean, 1974; Heiri *et al.,* 2001a). Organic matter content (%LOI) can be used to infer past lake productivity with periods of increased deposition of organic matter possibly associated with nutrient enrichment (Cassina *et al.,* 2013). Taylor *et al.*, (2006) attributed increases in organic matter since the 1950s to nutrient enrichment from increase agricultural activities in five out of six Irish lakes studied. The organic matter content of three small shallow lake in Poland was used to infer nutrient enrichment increases from the 1950s onwards which was also attributed to increased agricultural activities (Gąsiorowski, 2008). However, measurements of %LOI do not directly link to cause and must be supported by other evidence such as biological fossils.

#### 2.3.1.4 Biological fossils

Interpreting past lake environments and their associated catchment areas requires comprehensive analysis of multiple proxy records, including biological fossil remains. Pollen, for example, can be used to identify changes in a lakes external environment including deforestation and re-afforestation (Cohen, 2003). Fossil remains of diatoms and algal pigments have been utilised to interpret internal historic changes in lake productivity and identify periods of nutrient enrichment. Algae can be classified into four main groups: planktonic which spend their life cycle suspended in the water column; meroplankton which spend some time resting on lake sediment; tychoplankton who belong to benthos community but can be found re-suspended in the water column and benthic species who live their entire life cycle near the bottom of the water column (Battarbee *et al.,* 2001). Algal assemblages tend to shift from benthic to pelagic production when increased nutrients are available for consumption. This shift in algal species makes it possible to identify lake eutrophication from fossil records of stored in lake sediments (Davidson and Jeppesen, 2013).

Diatoms (Bacillariophyta) are fossil remains of one group of algae and have historically dominated palaeolimnological studies as indicators of past environments. The presence, absence and diatom species type can give indications of water quality (Hall *et al.,* 1997; Smol *et al.,* 2001a; Clarke *et al.,* 2005; Taylor *et al.,* 2006; Bunting *et al.,* 2007; Birks and Smol, 2013; Dalton *et al.,* 2009). Diatoms are unicellular, eukaryotic organisms that have a siliceous cell wall and generally have a yellow-brown pigmentation. This tough siliceous cell wall allows diatoms to preserve intact in lake sediment, making them a valuable and popular proxy to infer past changes in water quality (Smol *et al.,* 2001b). Previous studies have utilised diatoms to infer past changes in nutrient or trophic state

(Bradshaw *et al.,* 2005; Chen *et al.,* 2007; Pędziszewska *et al.,* 2015) and climate (Massaferro *et al.*, 2013).

### 2.3.1.5 Fossil preservation

The transformational processes that organisms undergo after death and before being classified as a fossil is known as taphonomy (Flower and Ryves, 2009). Taphonomy is an important consideration in all sediment based studies including palaeolimnology as it can affect fossil preservation. Partial or complete dissolution of siliceous diatom frustules may occur in the water column or sediment, with a variety of physical, chemical and biological factors influencing the preservation. High energy environments may increase turbulent mixing of upper sediments from wind leading to breakage of diatom valves (Ryves *et al.,* 2006). Studies have also shown that salt concentration levels have an effect on diatom valve dissolution (Barker, 1992a; Flower and Ryves, 2009). The pH of lake water has also been associated with increasing dissolution rates. A study of East African rift lakes (Barker, 1992a) and laboratory studies (Barker *et al.,* 1994) found that diatom dissolution increased in alkaline waters (with high pH). However, another study of 26 high alkaline lakes in East Africa showed low levels of diatom dissolution in the lakes demonstrating a poor correlation between pH and silica (Hecky and Kilham, 1973). Intact diatoms were found well preserved in sediments of 21 lakes, some with pH levels of >10. Dissolved silica ($SiO_2$) content of water also plays a major role in both the taphonomy and ecology of planktonic diatoms as it is the core component of diatom frustule structure. Large spring blooms of planktonic diatoms are terminated by $SiO_2$ uptake and depletion in water column concentrations (Gibson *et al.,* 2000; Ryves *et al.*, 2013; Carson *et al.,* 2014). Bradshaw *et al.,* (2005) reported strong correlation between high levels of sedimentary biogenic silica concentrations and good diatom preservation in small shallow lake in Denmark. However, as all lakes are unique it is difficult to generalise which environmental factors stimulate dissolution in any particular lake. Ryves *et al.,* (2013) recently noted that there is a lack of studies on small, permanent, freshwater lakes to date as many are assumed to have little or no dissolution problems.

### 2.3.1.6 Algal Pigments

While some algae (e.g. diatoms) leave behind morphological fossils that can be found in sediment, many do not. These algal groups can be reconstructed using biogeochemical measurements of what are also termed fossil pigments (Smol, 2008). The introduction of High Performance Liquid Chromatographic (HPLC) has allowed for automated analysis of sedimentary pigments to distinguish and quantify algal groups (Hou et al., 2011). Photosynthetic algae have the benefit of possessing pigments such as chlorophylls, carotenoids and phycobiliproteins which are very useful as chemotaxonomic markers. Most bacteria, protozoa or detritus do not contain these pigments which allows phytoplankton to be distinguished from other taxa in the microbial community (Wright and Jeffrey, 2006). Preserved fossil pigments in lake sediments are a mainly derived from planktonic and benthic algal communities along with aquatic macrophytes. Leavitt and Hodgson, (2001) identified pigments commonly recovered from marine and lake sediments along with source, stability and taxonomic affinities. Broadly distributed pigments or more common pigments (β-carotene, chlorophyll *a*, pheophytin *a*) can give good insight into total algal abundance in an aquatic ecosystem. Pigments such as zeaxanthin, canthaxanthin and echinenone represent cyanobacteria while chlorophyll *b* and lutein are classed as chlorophytes. Fucoxanthin and diatoxanthin are both chrystophytes though diatoxanthin is representative of siliceous algae including diatoms.

Algal pigments have been used in many limnological studies and multi-proxy environmental reconstructions and have successfully tracked increases in algal production and changes in assemblages while also identifying the presence eutrophication events such as toxic algal blooms (McGowan *et al.*, 1999; Buchaca *et al.*, 2011; Davidson and Jeppesen, 2013). For example, Bunting *et al.*, (2007) carried out a multi proxy palaeolimnological investigation on Lough Neagh, a shallow, polymictic, hypertrophic lake in Northern Ireland using algal pigments as a proxy to identify periods of nutrient enrichment over the last 60 years. The main historical trends in algal abundance and gross community composition were successfully identified, resulting in a lake water characterisation of hypertrophic with nutrient maximums in the mid-1990s. Carson *et al.*, (2014) also used algal pigments track the eutrophication of Milltown Lake in Co. Monaghan, eutrophication was inferred from up core increases of algal pigments since the 1970s. Mc Gowan *et al.*, (2012) presented concentrations of algal pigments in Windermere Lake, U.K. since the 1800s, and attributed up core increases to intensification of domestic, industrial and agricultural activities in the catchment from the 1900s onwards. Changes in sedimentary pigments can therefore give a good indication of anthropogenic impacts such as eutrophication, acidification, land use changes and climate change on fresh water aquatic ecosystems (Leavitt and Hodgson, 2001).

## 2.4 Water Management

Management of water quality is developed and implemented by various governing bodies at both at local, national and international level. Declining water quality across Europe during the 1960s and 1970s resulted prompted the European Union to take action in the form of water quality policy such as EU directives (Aubin and Varone, 2004). A European Directive is a legislative act that outlines a target for all EU counties to achieve while individual countries have the power to draft their own laws in order to achieve the target goal. The first Environmental Action Programme was drafted by the European Commission in the 1970s. Since its implementation in excess of 30 directives concerning water quality have been set many aiming to limit discharge of pollutants into rivers and create quality standards. The most prominent is Directive 2000/60/EC or the EU Water Framework Directive (WFD) (Kallis and Butler, 2001). The WFD outlined the need for all waterbodies to achieve a "good ecological status" by 2015 – 2027 and also to identify "reference conditions" for restoration efforts to aim towards. Palaeolimnological reconstructions have proved useful in deriving reference conditions and verifying timing of degradation, and thus helping inform strategies for lake restoration (Dalton et al., 2009). Leira *et al.,* (2006) used a "top-bottom" study on 35 of 76 candidate reference lakes (CRL) using biological (diatom) and chemical proxies to identify changes in water quality. A "top-bottom" study is used in large studies and analyses only one surface sample and one bottom sample (Smol, 2008). The findings presented by Leira *et al.,* (2006) show that over two-thirds of the Irish lakes examined deviated from reference status and attributed the change to nutrient enrichment from anthropogenic activities. Taylor *et al.,* (2006) additionally demonstrated how degraded lakes in Ireland can have complex and locally specific trophic histories, and thus many may require a site specific management strategy to improve water quality.

In conclusion this chapter has outlined key topic areas and revealed research providing context for the research questions and informing the study site and research methodologies adopted which are now outlined in the following chapters.

# CHAPTER 3 <u>STUDY SITE</u>

The following chapter will outline the geographical characteristics of the study site along with a review of publications of relevant archaeological and palaeoenvironmental history.

## 3.1 Site description

Lough Gur is the largest lake in County Limerick and is located just 20km south of Limerick City in the Ballyhoura region (Figure 3.1). The lake is situated in small river subbasin Ballycullane River which flows into the larger Camouge river catchment and subsequently into the larger Maigue river catchment. The lake has a surface area of $0.78km^2$ and is shallow with a mean depth of 1.59m and 4.4m at its deepest point (Layden, 1993) which places it in the 'shallow lake' (≤4m) category of the EPA lake typology scheme. The lake and catchment are subject to a temperate climate with annual precipitation of 1000mm, double that of evapotranspiration at 500mm (Ahlberg *et al.*, 2001). The surrounding topography results in the lake being enclosed by a series of topographic high points including Grange Hill (145 OD) to the north west, Knockfennell (161 OD) to the north, Knockroe (OD 140) to the north east, Knockadoon Hill (130 OD) to the east and Knocksrahir (122 OD) to the south east (Figure 3.2). The lake is elevated in the landscape at 72m OD and forms the shape of a crescent as it pulls around the foot of Knockadoon. The lake and its environs serve the surrounding and wider community in a number of ways including farming, recreation, tourism and biodiversity.

### 3.1.1 Heritage

The lake has a rich archaeological history with evidence of human occupation dating back to 3000 BC. Over 130 archaeological sites are situated in the lands surrounding the lake (Hollis, 2001; LCC, 2009) including Neolithic and Bronze Age settlements, a late $8^{th}$ century settlement, Black Castle ($13^{th}$ century), Bourchiers Castle ($15^{th}$ century) and Lake View Farm ($18^{th}$ century). The development of Lough Gur as a heritage amenity was proposed in the 1960s and initial debates were between county planners who wanted to develop the lake to commercially and local historians who favoured some development while preserving its archaeological heritage (O'Shannon, 1967). The potential Lough Gur has as a tourist destination has not yet been fully exploited according to the 2008-2010 tourism strategy for the Shannon Region. Lough Gur was identified as a potential site for the development of an “outdoor archaeological and heritage park of international significance” (LCC, 2009). The Lough Gur Environmental Management study was prepared by the Lough Gur Environmental Management Steering Group in 2009. The study aimed to provide a framework for consideration of issues relating to nature, archaeology, water quality, tourism and community in the area and identify specific actions and projects.

### 3.1.2 Conservation

In 2007, a flora and fauna study of Lough Gur was carried out by Natura Environmental Consultants Ltd to gather valuable ecological information in order to help guide future decision making in relation to future conservation efforts (LCC, 2009). The study reported that the lake and areas around it were suitable to be proposed as Special Areas of Conservation. Currently Lough Gur has not been designated as a recognised SAC and its designation is under review by the Lough Gur Environmental Management Group. It also suggested that reduced water quality in the lake is having a negative effect on wintering wildfowl and the whooper swan is no longer using the lake consistently. Currently, Lough Gur is a designated proposed National Heritage Area (pNHA 437), and therefore considered of national importance. Limerick City and Co. Council hope that the lake can achieve World Heritage Status to further raise its profile (LCC, 2009).

### 3.1.3 Visitor centre

In 1981, a visitor centre, car park and public recreation facilities were opened on the north east shore of Lough Gur in an effort promote the historical heritage of the lake environs. Tourist numbers increased and in 2006 over 2800 people visited the site (LCC, 2009). In 2013, the visitor centre was upgraded in an effort to further promote Lough Gur as a tourist attraction. In 2016, the lake front recorded 135,000 visitors while the visitor centre recorded 45,000 (K Harold 2017, pers.comm.).

### 3.1.4 Biodiversity

Lough Gur is home to a diverse range of flora and fauna. The submerged macrophyte assemblage is composed primarily of rigid hornwort (Ceratophyllum demersum) and fennel pondweed (Potamogeton pectinatus) while the aquatic flora of the lake comprises a number of species including several species of pondweed (Potamogeton crispus, P. natans), whorled water-milfoil (Myriophyllum spp.), Canadian waterweed (Elodea canadensis) and common duckweed (Lemna trisulca) (LCC, 2009). Common club-rush (Schoenoplectus lacustris) dominate the shores of Lough Gur however bulrush (Typha latifolia), water horsetail (Equisetum fluviatile) and reed canary-grass (Phalaris arundinacea) are also present. Spring phytoplankton blooms of diatom Asterionella formosa are present and blue green algae Anabaena spp can be found in early summer along with others such as Cryptomonas ovata, Aphanizomenon spp and Stephanodiscus spp (Layden, 1993). King and O'Grady, (1994) indicated that the lake was heavily populated by relatively young rudd in the early 1990s with pike and eel also present in low numbers. Lough Gur is home to a variety of breeding birds including tufted duck, mallard, mute swan, grey heron, coot, moorhen, great crested grebe and little grebe (LCC, 2009). It is also home to wintering birds such as the whooper swan but in recent years numbers have been decreasing.

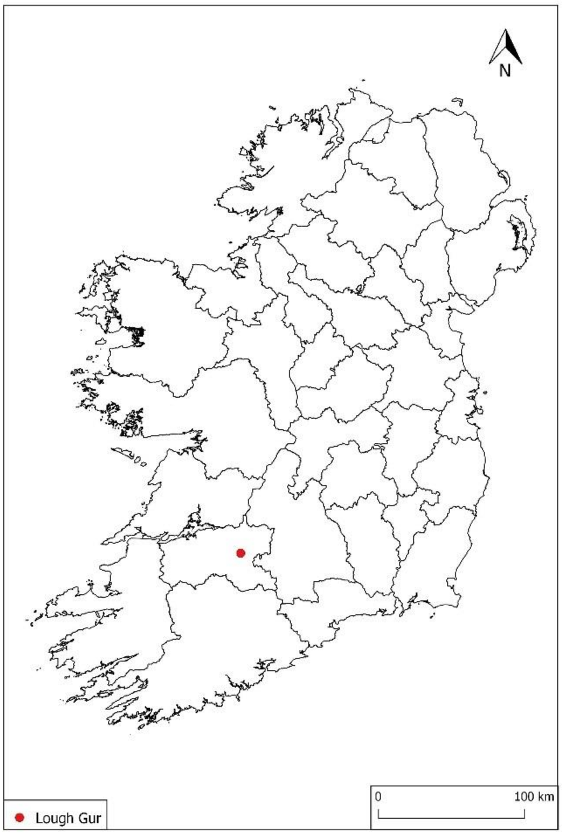



Figure 3:1: County boundaries and location of Lough Gur in west County Limerick, Ireland.

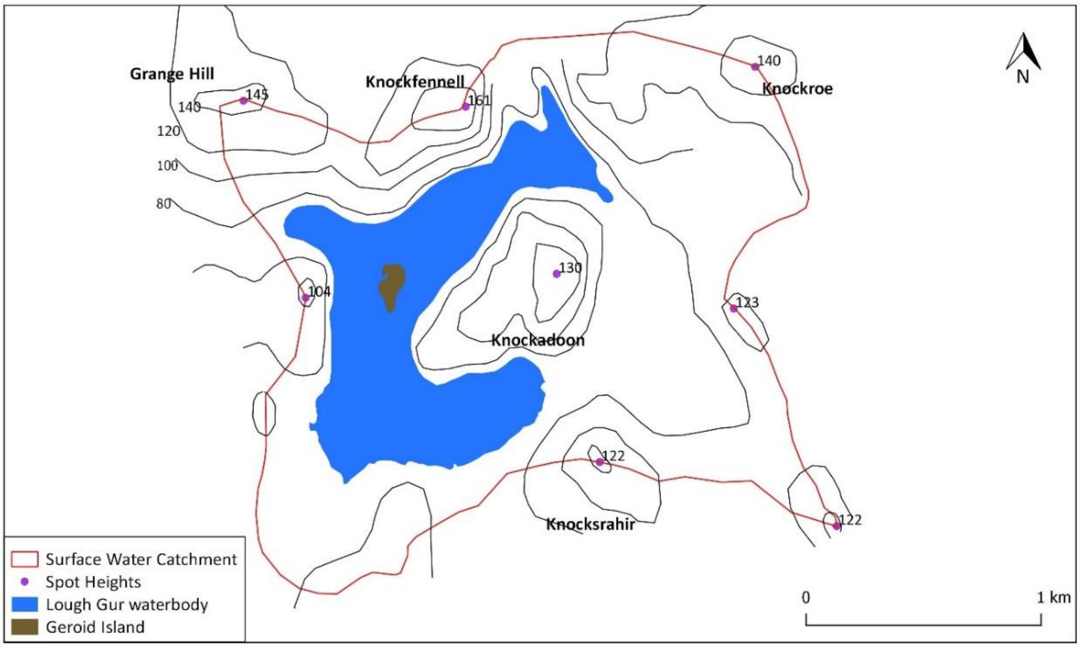



Figure 3:2: Topography of Lough Gur, with 20 m contour intervals along with delineation of the surface water catchment.

### 3.2 Hydrogeology

The underlying geology of Lough Gur is consists of a mix of limestone and volcanic rock types (Figure 3.3)(Ball, 2004). At the very top of the formation is the Hebertstown limestone below which lies a layer Knockroe basalt. The Knockroe volcanic rocks are fractured but the presence of multi-coloured clays prevents water flowing through. Below this is the Lough Gur limestone formation. This karstic rock can be dissolved by water and forms an important groundwater aquifer. Most of the Lough Gur surface catchment is underlain by Waulsortian limestone which is associated with shale limestones. To the south of the lake is the Ballynash and Ballysteen limestone which contain little or no shale leading to increased movement of ground water.

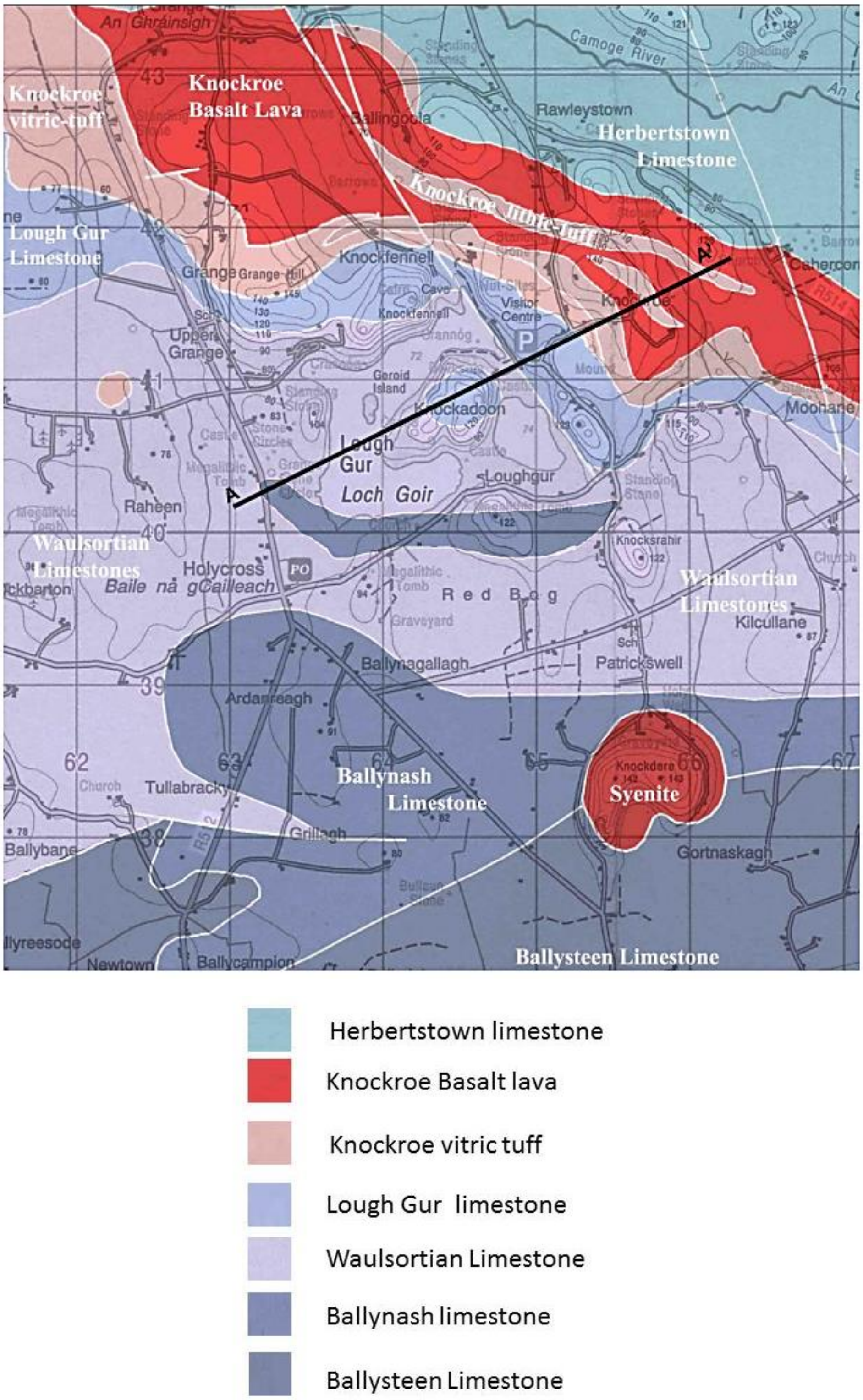



Figure 3:3: Geology of Lough Gur (Ball, 2004).

Figure 3.4 shows the Geological Survey Ireland (GSI) classification of bedrock aquifers in the Lough Gur rock formation. The volcanic top layer and the Lough Gur Limestone formation are classified as locally important aquifers that are generally moderately productive the latter only in local zones. The Waulsortian formation is a regionally important aquifer that is karstified (Rk) while the Ballynash formation is a locally important aquifer which is moderately productive only in local zones.

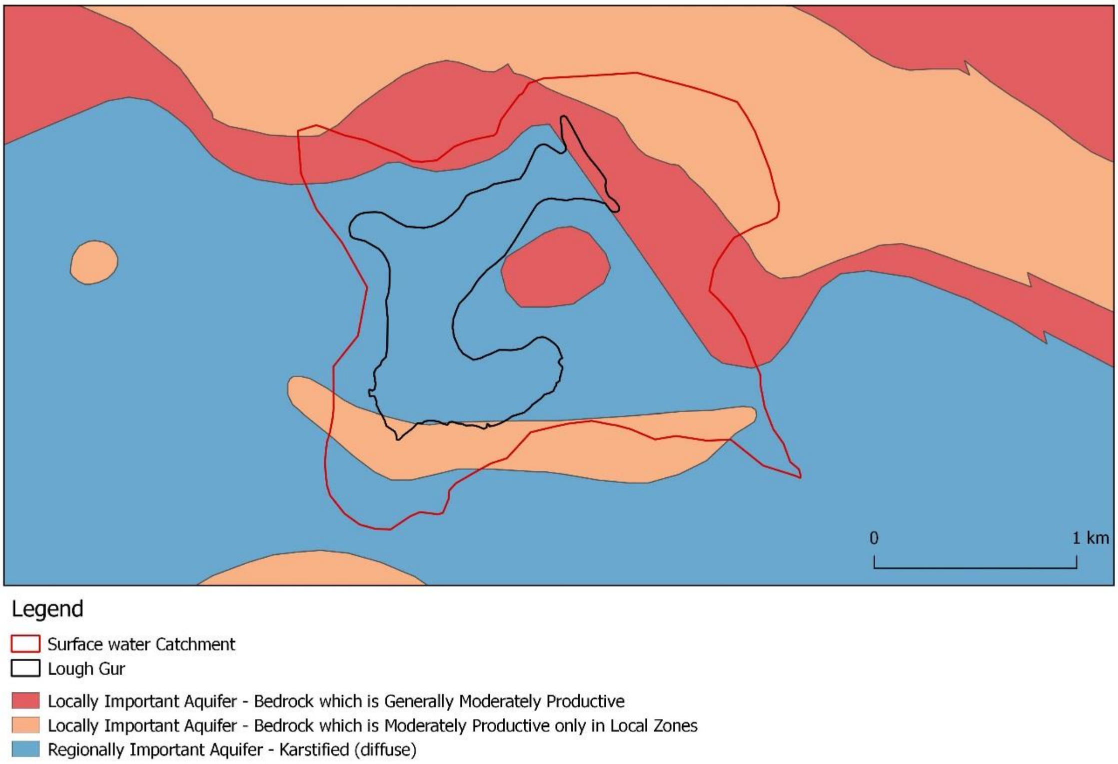



Figure 3:4: GSI classifications of bedrock aquifers around Lough Gur.

### 3.3 Soils

The main soil type found around Lough Gur is grey brown podzolic soil (70%) followed by gley soil (20%) and brown earths (10%) (Gardiner and Radford, 1980). These soils have good moisture hold capacity which supports excellent grassland making them suitable for farming activities (King and O'Grady, 1994). Figure 3.5 shows the GSI subsoil map for the area around the lake catchment revealing that the majority consists of bed rock outcrop, with smaller areas of alluvial material, fen peats and glacial till derived from limestone and igneous rock types.

Figure 3:5: GSI subsoil map (Langford and Gill, 2016).

### 3.4 Hydrology

Lough Gur's hydrology is unique and is a direct result of its geology and topography. In the past 23 years a range of calculations of Lough Gur's ground water and surface water catchment areas have been reported. An initial catchment area of 5.38km$^2$ was reported (King and O'Grady, 1994) which presumably includes surface and groundwater inputs. Ball, (2004) separately reported a surface drainage area of 3.7km$^2$ along with a ground water catchment area of 4.68km$^2$. The most recent delineation of a surface and groundwater catchment areas for Gur were calculated to be 3.68km$^2$ and 3.48km$^2$ respectively by (Langford and Gill, 2016). The lake sits elevated in the landscape higher than other water bodies and therefore has no lake inflow. Water levels are maintained from catchment runoff and also from groundwater springs located in Lake Bog to the south west of the lake. These springs enable water to flow into the lake (King and O'Grady, 1994). Ball, (2004) suggested that the lack of a major river inflow means there is no flushing of lake water to dilute or refresh nutrients. Water accumulated in the lake is discharged from the lake through two drainage outlets. The main drainage outlet is an artificial channel situated in the north west corner of the lake which discharges into the Ballycullane River and subsequently to the Camouge River (Ball, 2004; Layden, 1993). The second is a sinkhole (Pollavddra) in the North East corner of the lake (see Figure 4.1) which emerges at the Creamery spring 2km to the west and subsequently into Ballycullane River (Langford and Gill, 2016), however this is only functional when the water level is above 72m OD. In the 1830s, the first Ordnance Survey of Ireland was undertaken and the surface area of the lake was larger and enclosed Knockadoon Hill suggesting the lake water level was higher. In conjunction with a famine relief scheme (1845-1852), drainage works were carried out on the lake in order to gain access to peat fuels (O'Kelly and O'Kelly, 1978). This included the construction of an artificial outlet in the North West corner to lower water level. It is estimated that this action resulted in lowering average water level by approximately 2.1 metres (Ball, 2004).

## 3.5 Palaeoenvironmental History

The majority of studies on Lough Gur focus on the rich archaeological history associated with the lake and its environs, however some palaeoenvironmental studies have been undertaken. Mitchell, (1954) carried out an environmental reconstruction of Lough Gur using pollen to detail the evolution of the vegetated landscape in which he suggested that human settlements were first established around the lake during the Neolithic (c. 5000 BP). He also reported deforestation from 2000 BC onwards to allow for agriculture have influenced the woodland around the lake. Almgren, (1989) and Ahlberg *et al.*, (2001) also investigated the catchment for evidence of human occupation and suggested similar findings of deforestation and also reforestation as population fluctuated.

## 3.6 Land use

The land use around the lake is mainly agricultural and residential. The residential settlement pattern is largely dispersed and is heavily influenced by proximity of Limerick City (LCC, 2009). The main agricultural land use is pasture farming including cattle grazing on the hills surrounding the lake. The land surrounding the lake was not considered to be heavily fertilised in the 1990s (Layden, 1993; King and O'Grady, 1994). A total of 83 houses and seven farms were found to be in the 3.7km$^2$ surface water catchment (LCC, 2009).

### 3.7 Water Quality

(Praeger, 1900) described the water in Lough Gur as 'dirty pea-soup coloured waters' when noting the flora of Limerick. In the 1970s, Young, (1971) reported on areas of scientific interest around Co. Limerick in which he describes Lough Gur as "highly eutrophic". Heuff, (1984) carried out a detailed vegetation assessment of the lake in which he noted two species of *Chara* sp commonly associated with low to medium nutrient status waters, however these species were not present when the lake was later examined in 1988 suggesting a possible change in nutrient status (King and O'Grady, 1994). In 1988, Shannon Development commissioned the Central Fisheries Board to assess Lough Gur's viability for recreational fishing. The report was completed by King and O'Grady, (1994) in which it stated the lake had elevated levels of TP and had a unique eutrophic-macrophyte dominated status. The report also suggested sediment coring of the lake bed would be of value to establish rates of sedimentation and a timeline for the onset of eutrophication.

The first comprehensive water quality study was carried out by Layden, (1993) as part of a Master's degree measured various water quality parameters such as alkalinity, temperature, conductivity, $CO_2$, phosphorus, nitrogen, ammonia, and chlorophyll *a*. These measurements suggested that the lake was between eutrophic and hypereutrophic during summer months. Ball, (2004) carried out a hydrological assessment of the lake which suggested the lake periodically becomes nutrient enriched and undergoes eutrophication. In 2009, the EPA issued a report on 42 lakes in Ireland classifying Lough Gur as one of three hypereutrophic lakes based on OECD guidelines (McGarrigle *et al.,* 2010). The lake was found to have elevated pH levels (>9), failed to meet oxygenation conditions set out by WFD, and measurements of Total Phosphorus (TP) and ammonia levels were found to be high. The lake is classified as 'Poor' water quality and 'At Risk' in the latest EPA water quality assessment cycle (2010 – 2015). Figure 3.6 shows algal blooms present on the lake in recent years.

Figure 3:6: Image of algal blooms in Lough Gur (April 2014).

Limerick County Council has been collecting water samples from Lough Gur on behalf of the EPA since 2004. Samples were collected from two monitoring sites, site 1 is located at the amenity area close to the Lough Gur Visitor Centre, and site 2 is beside the Old Church (see Figure 4.1). Water samples are collected monthly however data for site 2 was only available up until 2012. Lake water was analysed for the following parameters pH, Conductivity, Biological Oxygen Demand (BOD), Nitrates ($NO_3$-N), Ammonia (NH3-N), Ammonium (NH4), Total Phosphorus (TP), Orthophosphate (PO4-P), Chlorophyll *a*, Alkalinity and Dissolved Oxygen. Table 3.1 shows a summary of these measurements pH levels averaged 8.5 and 8.6. Conductivity levels at both sites had an average value of c. 280 µS/cm while BOD had average value of 3.28mg/l. Average levels of Ammonia were 0.18 mg/l at site 1 and 0.14 mg/l at site 2. Total P levels averaged 0.04 mg/l and 0.02 mg/l while maximum TP of 0.290 mg/l and 0.09 mg/l were recorded. Average Chlorophyll A levels at site 1 were high 10.74 µg/l and reached a maximum of 121.35 µg/l. Average Alkalinity levels were similar at both sites 134.3 mg/l and 137mg/l. Dissolved Oxygen saturation was 108.5% at both sites. The average total P concentrations for site 1 is at the border line for eutrophic threshold of 0.04 mg/L set by the Organisation for Economic Co-operation and Development (OECD). The average Chlorophyll A concentrations exceed the OECD average eutrophic threshold level of 8 µg/L at both sites.

Table 3.1: Summary Water quality measurements from Limerick County Council at Lough Gur.

| | | Site 1 Jan 2004-Aug 2016 | | | Site 2 Jan 2004-Aug 2012 | | |
|---|---|---|---|---|---|---|---|
| **Parameter** | **Units** | **Min** | **Average** | **Max** | **Min** | **Average** | **Max** |
| pH | pH units | 7.50 | 8.49 | 10.30 | 7.10 | 8.60 | 9.90 |
| Conductivity @20 | µS/cm | 163.00 | 281.99 | 421.00 | 165.00 | 275.55 | 374.00 |
| BOD | mg/l | 2.00 | 3.27 | 7.38 | 2.00 | 2.98 | 5.75 |
| Nitrates (NO3-N) | mg/l | 0.01 | 0.85 | 8.32 | 0.03 | 0.62 | 4.42 |
| Ammonia (NH3-N) | mg/l | 0.02 | 0.18 | 0.80 | 0.03 | 0.14 | 0.65 |
| Ammonium (NH4) | mg/l | 0.05 | 0.17 | 0.46 | 0.05 | 0.14 | 0.36 |
| TP | mg/l | 0.00 | 0.04 | 0.29 | 0.00 | 0.02 | 0.09 |
| Ortho Phosphate (PO4-P) | mg/l | 0.00 | 0.01 | 0.15 | 0.00 | 0.01 | 0.07 |
| Chlorophyll *a* | µg/l | 0.47 | 10.74 | 121.35 | 0.52 | 11.13 | 58.22 |
| Alkalinity | mg/l | 34.4 | 134.30 | 331.00 | 65.30 | 137.02 | 400.00 |
| Dissolved Oxygen | Saturation | 45.0 | 108.51 | 199.00 | 73.00 | 108.74 | 193.00 |

Various sources have been attributed as being the cause of poor water quality in Lough Gur. Layden, (1993) suggested the lake was N and P limited and the main source of nutrients was from the lake itself as agricultural activities in the catchment were not intense at that time. Ball, (2004) reported that elevated nutrients potentially came from domestic sewage and agricultural activities such as application of fertilisers and land spreading of animal waste. He noted that the septic tank at the visitor centre is directly on bedrock and it would be very difficult to dispose of waste without direct percolation into the groundwater system feeding the lake. He also concluded that migratory birds are the main natural source of nutrient enrichment. A survey of domestic wastewater treatment systems was subsequently undertaken by Coris Environmental engineering on behalf of Limerick County Council (LCC, 2009). Results showed none of the 13 wastewater system inspected complied with S.R 1991 or more the recent EPA 2000 guidelines (National Standards Authority of Ireland, 1991). The vulnerability of ground water to contamination from surface activities in the catchment was classified as extreme. A survey of farms within the 4.68km$^2$ groundwater catchment was completed in 2007 and 17 farms were identified as potential contributors to nutrient enrichment in the lake. In 2015, Parkmore Environmental Service Ltd (PES) was retained by Lough Gur Group Water Scheme to investigate the sources and pathways of nutrients into the lake. The report concluded that there was no significant source of naturally occurring phosphorous (P), either from the limestone or volcanic bedrock locally. The report concluded that elevated P was from anthropogenic sources but suggested recycling of nutrients within the lake could also be an issue.

# CHAPTER 4 METHODOLOGY

This chapter focuses on the methods followed and materials utilised during the course of this research. Firstly this chapter outlines field work including sediment core collection and sensor deployment. Laboratory techniques employed will then be described, followed by steps undertaken in the cartography efforts. Finally palaeoenvironmental data analyses is outlined.

## 4.1 Field Methods

### 4.1.1 Sediment collection & sample extrusion

The maximum water depth of 4.1m was chosen for sediment core collection (Figure 4.1). A Renberg gravity corer was used to collect the lake sediments (Renberg and Hansson, 2008). This corer has a weight attached at the top to assist penetration of the lake bed when dropped from the boat. The corer was held at approximately two metres above the sediments and then released to ensure perpendicular sediment penetration and thus minimise the chance of mixing of strata. Two sediment cores measuring 40cm and 52cm were collected on the 9$^{th}$ of April 2015. The cores were then taken ashore and samples were processed using an extruding device and sampling tray. Samples were extruded at 1cm intervals, labelled and sealed in zip lock plastic bags. The 40cm core was taken to Mary Immaculate College and the 52cm core to Trinity College Dublin for storage at between 0 - 4°C and further analysis.

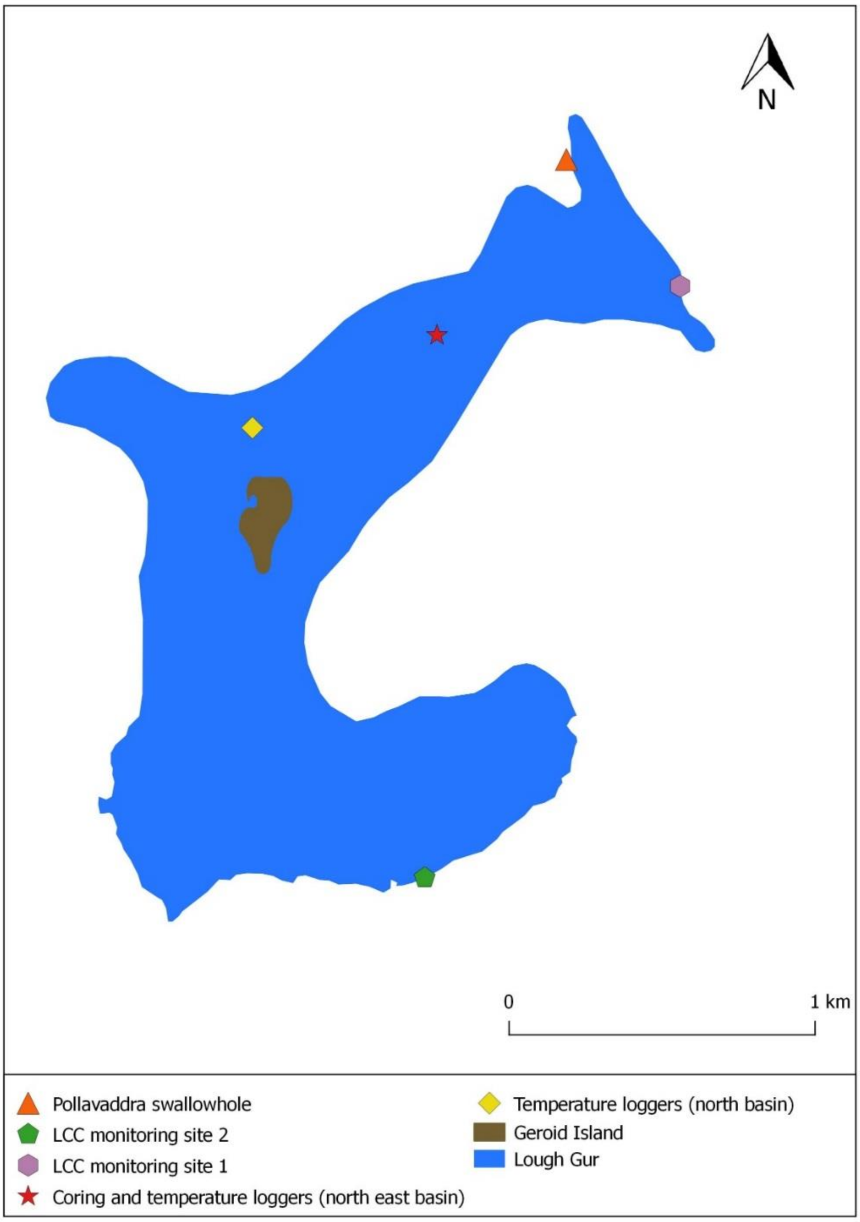



Figure 4:1: Sediment core and temperature logger sites and LCC WQ monitoring sites.

#### 4.1.1.2 Sensor deployment

Four tidbiT v2 water temperature data loggers were deployed in April 2016. These temperature loggers provide 12-bit resolution with ±0.2°C accuracy and record temperature every hour (Figure 4.2(a)). The loggers are designed for outdoor and underwater environments and are waterproof to 300m. The data loggers were deployed in two sets of two data loggers. The first set was placed in the deepest location at 4.1m in the north east basin while the second set was placed at a depth of 2.8m towards the north west of the lake. Sensors were deployed with one main anchor attached to a set of buoys using plastic cable ties (Figure 4.3). Sensors were deployed at two metre intervals at the 4.1m site and one metre intervals at 2.8m site. To download the data from the loggers a HOBOware water proof shuttle was used (Figure 4.2(b)). HOBOware Pro graphing and analysis software version 3 allowed for files to be exported to Microsoft Excel which was then used for analysis and display of the data recorded.

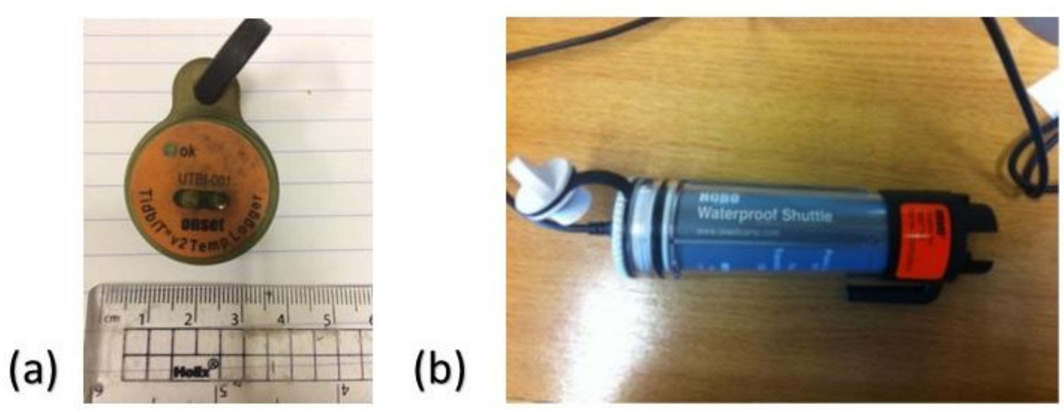



Figure 4:2: (a) tidbiT v2 water temperature data loggers, (b) HOBOware water proof shuttle.

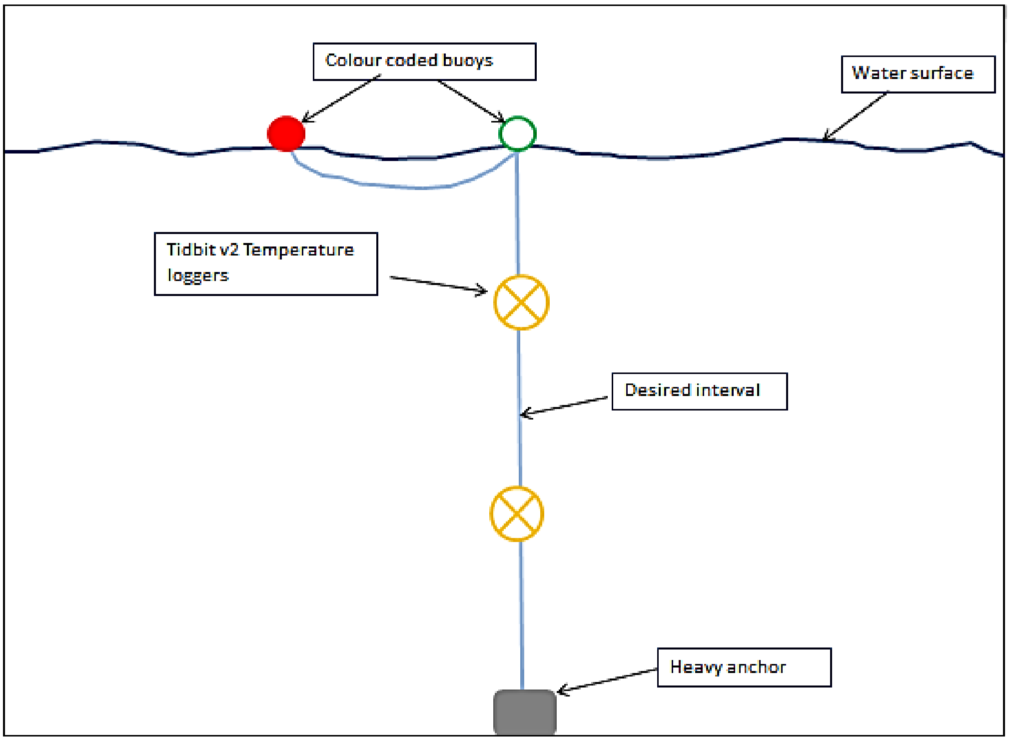



Figure 4:3: Deployment technique for Tidbit V2 temperature loggers.

## 4.2 Sediment Analysis

### 4.2.1 Lithostratigraphy

In order to identify variations in lithological composition (e.g. changes in colour, texture, particle size) a preliminary visual inspection was carried out. A series of lithological features (dry weight, organic matter and carbonate content) were subsequently determined to reflect changes in sediment composition. Laboratory work for lithostratigraphical analysis was undertaken at the Department of Geography at Mary Immaculate College on the 40cm core.

#### 4.2.1.1 Wet density

Wet density measurement can reflects changes in sediment composition. The process involved using a 2cm$^3$ capacity brass phial which was first cleaned and weighted to four decimal places. The top of the phial was then filled with wet sediment and air bubbles were removed by tapping the base of the phial on a firm surface. The phial was then re-weighed to and the result divided by 2 to determine the density.

#### 4.2.1.2 Dry Weight

Dry weight is a measurement used to establish sediment water content. Heat resistant crucibles were cleaned, numbered and weighed to four decimal. Approximately five grams from each one centimetre slice/interval of sediment was placed in the crucible. A spatula was used to scrape the sediment into the crucibles and then washed in tap water followed by distilled water between each sample to avoid contamination. The crucibles were placed in an oven at 105°C for 24 hours. The crucibles were then removed from the oven using a tongs and to ensure minimal moisture contact, the samples were placed in a desiccator to cool. Samples were then re-weighed again to retrieve dry weight. Percentage dry weights were calculated as follows:

$$\text{Dry Weight}(\%) = \left(\frac{\text{DW}_{105}}{\text{WW}}\right)\text{X}100$$

Where: WW is the wet weight and $\text{DW}_{105}$ is the weight after oven drying at 105°C.

### 4.2.1.3 Loss on Ignition

Sequential loss on ignition (LOI) is a common and widely used method to estimate the organic and carbonate content of sediments (Dean, 1974; Heiri *et al.*, 2001). Dry weight is first established as part of this method, then, in a second step, organic matter is oxidised at 500–550°C to carbon dioxide and ash. Sample crucibles were placed in a furnace at 550°C for 4 hrs and again removed and placed in the desiccator to cool. Samples were then weighed again to establish the organic content loss. The weight loss during the reaction represents the sediment organic matter.

$$LOI_{550} = \left\{\frac{(DW_{105} - DW_{550})}{DW_{105}}\right\} X100$$

Where: $DW_{105}$ and $DW_{550}$ is the weight after oven drying at 105°C and 550°C respectively.

In a third step, samples were placed in the furnace at 950°C for two hours and again left to cool in the desiccator (Heiri *et al.*, 2001). In this reaction, carbon dioxide is evolved from carbonate, leaving oxide. Samples were weighed to reveal the amount of $CO_2$ evolved from carbonate minerals.

$$LOI_{950} = \left\{\frac{(DW_{550} - DW_{950})}{DW_{105}}\right\} X100$$

Where: $DW_{950}$ is the weight after oven drying at 950°C.

### 4.2.2 Radiometric dating

Sediments (c. 1g DW) from the top 20cm and lithostratigraphy measurements were sent to the Environmental Radiometric facility at University College London to be measured for $^{210}Pb$, $^{226}Ra$, and $^{137}Cs$ and $^{241}Am$ by direct gamma assay under the supervision of Dr Handong Yang. Additional material was requested when it was discovered that there was insufficient material for radiometric analysis. The samples were analysed using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors. This enables sediment chronologies of up to 150 years to be established from estimated sediment accumulation rates based on activities of $^{210}Pb$, $^{226}Ra$, and $^{137}Cs$ analyses. Lead-210 was determined via its gamma emissions at 46.5keV, and 226Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope 214Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. Cesium-137 and 241Am were measured by their emissions at 662keV and 59.5keV (Appleby *et al.,* 1986). Sedimentation rate was calculated using unsupported $^{210}Pb$ activities and expressed as g $cm^{-1}$ $yr^{-1}$. Chronologies were calculated using the CRS (constant rate of 210Pb supply) dating model (Appleby and Oldfield, 1978; Appleby, 2001).

### 4.2.3 Biological fossils

#### 4.2.3.1 Diatoms

The preparation of diatom microscope slides from sediment core samples followed the methodology proposed by Battarbee *et al.,* (2001). Core 1 (MIC) measured 40cm in length and samples from every second centimetre were prepared. Approximately 1-2g of wet sediment was placed in glass beakers to which 5 ml of $H_2O_2$ (30% v/v) was added. Digestion of samples was achieved on a hotplate until oxidation was complete. This step removes any organic matter present in the sediment while leaving the diatoms intact. The volume of the suspension and temperature was regularly controlled to avoid desiccation. After digestion 1-2 drops of 10% (v/v) HCl were added to eliminate any remaining $H_2O_2$ and any carbonates. Samples were then placed in 12ml plastic centrifuge test tubes and topped up with deionised water. Thereafter, samples were placed in a centrifuge for 4 minutes at 1200 rpm to separate the diatoms using centrifugal force. The supernatant liquid was decanted and the washing procedure was repeated four times. Samples were stored in glass vials and a few drops of $NH_3$ were added to prevent frustule clumping. Samples 0-1cm, 15-16cm, 39-40cm were prepared for diatom slide analyses. A small amount of sample solution was diluted with deionised water and using a micropipette 100 µL of 6.23 x 106 microspheres $mL^{-1}$ suspension was added to the samples to enable calculation of concentration of diatom frustule concentrations. The samples were then transferred onto microscope slide cover slips. Samples were left to dry at room temperature for 1-2 days. A drop of mounting medium (Naphrax) was applied to a glass slide and placed on a hotplate at c. 80°C. The inverted cover slip with the sample was subsequently placed over the slide. The slide was then heated on the hotplate for approximately 60 seconds to evaporate the toluene in the Naphrax, after which it was left to cool. Afterwards, the slides were individually examined under a Lecia DM750 M light microscope and Lecia Application Suite (version 2.8.1) software was used to capture photographic images.

Examination of the fixed slides suggested that diatoms were not well preserved and quantities were not sufficient to warrant diatom counts. In the top sample evidence of sporadic intact frustules were present, however, very few diatoms were present. This was in contrast to the relatively numerous microspheres. At deeper depths only broken fragments were present. At 15-16cm some evidence of dissolved frustules were scattered across the sample and also individual diatoms showed evidence of poor preservation (Figure 4.4). This trend continued to the deepest sample 39-40cm where again poor preservation was evident in the sample and only individual diatom fragments were evident (Figure 4.5). Mud slurry samples were also examined. This involved placing a small amount of sediment on a slide and dropping 2ml of distilled water on the sediment. A cover slip was placed over sediment at a 45° angle to reduce air pockets in the sample. Examination of a range of mud slurry samples revealed poor diatom concentrations throughout the sediment core and often showed no diatoms present (Figure 4.6).

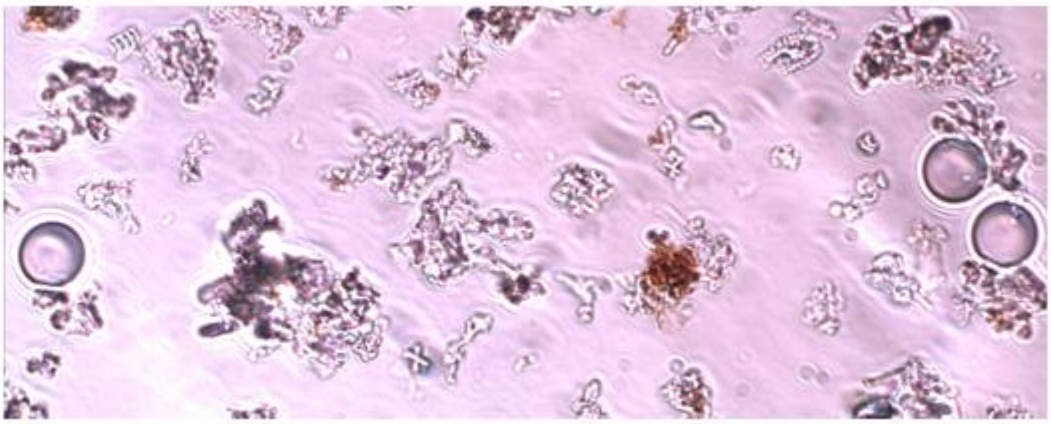


Figure 4:4: Image of sample 15-16cm x400 magnification.

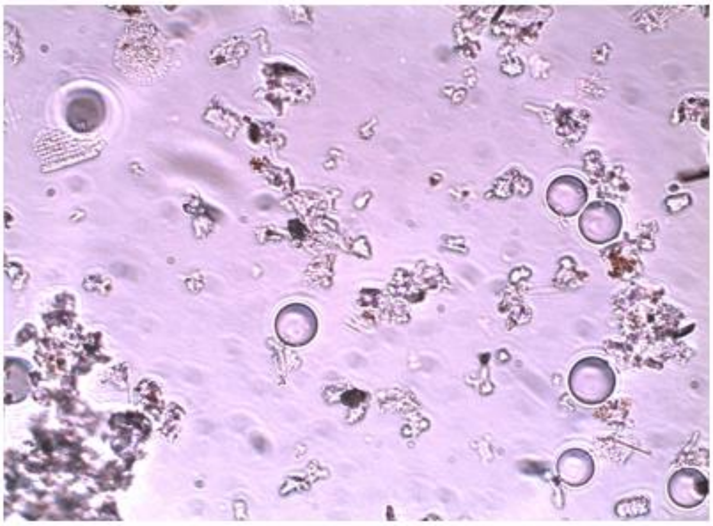


Figure 4:5: Image of sample 39-40cm showing poor diatom preservation at x400 magnification.

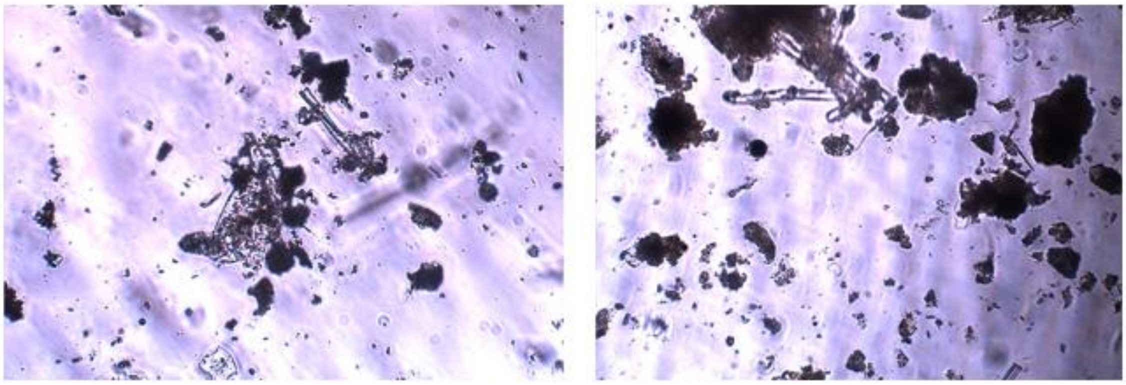


Figure 4:6: Images of mud slurry 9-10cm showing no presence of diatoms at x400 magnification.

### 4.2.3.2 Algal Pigments

As a result of the low concentrations and poor diatom preservation of diatoms in the Lough Gur sediments an alternative biological proxy, algal pigments, was examined.

***HPLC method***

A total of 30 samples (every slice down to 20cm and every second slice down to 40cm) were tested for algal pigment concentrations in the laboratories of the School of Geography, University of Nottingham using a reversed-phase High Pressure Liquid Chromatography (HPLC) under the supervision of laboratory technician Teresa Needham and Dr Heather Moorhouse. HPLC is an analytical technique that allows for rapid isolation and separation of biochemical markers such as sedimentary pigments. Samples of sediment were first freeze dried for approximately 1 hour. Then 0.2g of freeze dried sediment from each sample was weighed and transferred into labelled glass vials before undergoing extraction which involved adding 5ml solution of acetone, methanol and HPLC grade de-ionised water (80 : 15 : 5). The extract was then stored at -10°C overnight. After 12 hours samples were taken out of the freezer and the solvent extract was decanted into a clean 50ml beaker to form the pigment solution. Careful precaution was taken to minimise the transfer of the sediment or filter paper residue. Pigment solution was then drawn up a 10ml disposable syringe with a 0.45µm lock on filter placed on the top. Holding the syringe at 45° angle the pigment solution was gently pushed through the filter into a clean labelled vial. Using a wash bottle filled with HPLC grade acetone, the residue in the extraction vial was rinsed with approximately 5ml of acetone. Decanting and filtering procedures were repeated. Rinsing was also repeated again up to 3 times until the residue was not pigmented. Before proceeding with another sample the 50ml beaker was rinsed with acetone along with the syringe and filter tips. Contamination of samples was minimised by replacing filter tips every 5 samples. After each sample was rinsed they were evaporated under a stream of $N_2$ gas. Once dry samples were removed from $N_2$ gas, capped and placed in the freezer. When HPLC analysis was ready each sample was taken from the freezer and the measured quantity of inject solvent (70:25:5 = Acetone:IPR stock solution (1.875 g tetra butyl ammonium acetate, 19.25 g ammonium acetate, 250 ml de-ionised water: Methanol) was added to the dried sample using a 500µL pipette (Chen *et al.*, 2001; Leavitt and Hodgson, 2001). The volume of injection solution used was recorded and varied depending on the concentration of the sample. This was conducted by visual inspection. The dissolved extract was then transferred to auto sampler vials using a glass Pasteur pipette. Screw caps were then placed on the vials and glass pipettes were disposed of. The auto sampler tray was then placed in the HPLC unit.

***Separation and analyses of pigments in HPLC***

Pigments polarities differ therefore allowing them to be separated by reverse phase HPLC which uses two phases, non-polar and mobile. Pigments are initially forced under high pressure through a column of packing material which consists of small particles (5µm) coated in non-polar monomer or polymer, by a polar solvent stream (mobile phase) (Leavitt and Hodgson, 2001). Different pigments have greater affinity to either phase therefore they can be identified by their retention time or time they elute the column (Figure 4.10). The HPLC system used comprised of an Agilent 1200 series quaternary pump, auto sampler and photodiode array detector (PDA). Each 52 minute cycle started and ended with a “green” standard (pigment extract of grass containing known Chlorophylls and carotenoid pigments) which was used to identify drift in retention times. The separation method used followed an adaption of Chen *et al.,* (2001) as it is best suited to identifying chlorophyll and carotenoids from lake sediments. Resulting chromatographs from the HPLC run were used to identify pigments via comparison with known retention times and absorbance spectra of pigment standards (Moorhouse, 2016). After being eluted from the HPLC, a photodiode array (PDA) spectrophotometer scans the pigment at multiple UV and visible wavelengths (300-750nm) to produce an absorbance spectrum. Identification of the pigment was performed by comparison of position and retention time on the chromatogram, the shape of the spectrum and wave length of maximum absorbance with known commercial pigment standards (DHI Denmark) that have been analysed using the same separation conditions.

Concentrations of pigments were expressed as nano-moles (nmole) to account for different pigment molecular weights and calculated relative to OM (as estimated by $\%LOI_{550}$) to correct for dilution by allochthonous minerogenic material and pigment degradation a linear regression of pigment peak area against pigment mass (as volume x concentration) was then undertaken to give the calibration constant (slope) (Moorhouse, 2016).

Concentration of pigment (nmole pigment $g^{-1}$ organic weight sediment) = ((pigment peak area/calibration constant)*(TV*IV)) / ((EM)*(%LOI550/100))

Where: TV = Total solution and pigment volume (µl); IV = Injection solution volume (µl); EM = Extraction weight of sediment (g); %LOI550 = Organic matter content (as a % of dry mass).

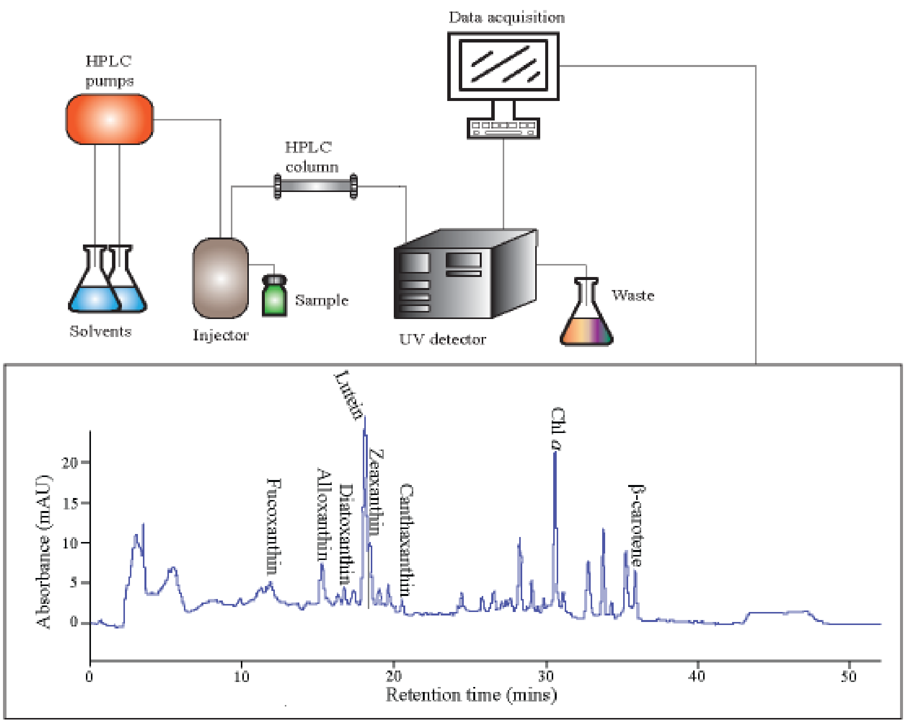



Figure 4:7:Schematic of HPLC instrumental system and chromatogram output used for pigment analysis at University of Nottingham (Moorhouse, 2016).

### 4.3 Cartography

Cartographic investigation and representation of Lough Gur and its environs was carried out using the open source software Quantum GIS (QGIS) (desktop version 2.16.3). QGIS allows for users to create, visualise, input and output data while interpreting spatial relationships, patterns and trends. WFD catchment boundaries, CORINE land use and GSI soils data was publicly available for download from the EPA website (http://gis.epa.ie/). Data files were download as shapefiles and then imported into QGIS. Geoprocessing tools were then used to clip CORINE land use data for the catchment. A plugin (MMQGIS) was then used to export the attribute data to Microsoft excel for further analyses.

### 4.4 Data Analysis

#### 4.4.1 Statistical analysis

##### 4.4.1.1 Pearson Product Moment Correlation

Pearson product moment correlation test is useful in determining the strength of a linear association between two variables and is denoted by r. The Pearson correlation coefficient, r, can take a range of values from +1 to -1. A value of 0 indicates there is no linear association between the two variables, a value greater than 0 indicates a positive association and a value less than 0 indicates a negative association. The statistical software package R commander was used to generate correlation matrix between variables for lithostratigraphical, biological and geochemical datasets.

#### 4.4.1.2 Ordination

Ordination methods have been used by ecologists since the 1950s as a means to investigate species turnovers in ecological communities (Lepš and Šmilauer, 2003). Principal Components Analysis (PCA) is a method which reduces multiple dimensional datasets (e.g. fossil assemblages) to two dimensions explaining maximum variability in the first axis followed by subsequent axes. PCA uses axes scores to summarise species variation in a dataset. Species and sample scores therefore reflect their influence (negative or positive values) on the dataset and community (Moorhouse, 2016). Prior to the PCA a detrended correspondence analysis (DCA) was first carried out to determine whether the dataset was linear or unimodal. Data included in ordinations were log transformed (x+1) in order to reduce the square distance of each data point to the axis line from the centroid. The DCA was then preformed in R using the decorana () function in the R package 'vegan', using the log transformed data (Borcard *et al.,* 2011). The datasets returned gradient lengths of <2 for axis 1 therefore allowing for the unconstrained ordination method of PCA to be used. PCA was carried out on the log (x+1) transformed data in the environmental statistical programme $C^2$ (Juggins, 2003). Stratigraphic plots were created for lithological, biological and geochemical proxies using $C^2$ software (Version 1.3)(Juggins, 2003). Zones were applied to algal pigment concentrations based on qualitative visual inspection of the stratigraphic plots.

# CHAPTER 5 RESULTS

This chapter firstly profiles the catchment, subcatchment and geographical characteristics of Lough Gur in a series of maps produced for the project. This followed by physical, chemical (including chronological) and biological details of the lake sediment cores collected from the lake. Two parallel sediment cores were collected from the deepest point in Lough Gur to facilitate this project and also a sister project being carried out in TCD. Separate chronologies were established for each core while historic changes in organic matter were identified in both. Core 1 (MIC) was examined for fossil diatoms and algal pigments while a geochemical approach was taken on core 2 (TCD). Lastly, lake water temperature data was examined.

## 5.1 Cartography

### 5.1.1 Catchment and Subcatchment

The delineation of catchment and subcatchment boundaries associated with Lough Gur was altered in 2016. Catchment boundaries pre-2016 were created in conjunction with the first cycle of the WFD (2009-2015). Nationally this included 152 Water Management Units (WMU), 372 River Basin Districts and 539 subdivisions or subcatchments of River Basin Districts. A reconfiguration of the catchment boundaries in the second cycle of the WFD catchments (2015-2021) saw a reduction to 46 National catchments, an increase to 583 sub catchments and 3194 river sub basins. This realignment was instigated to represent monitoring data more effectively. Lough Gur is located in the Maigue WMU (1122.53km$^2$) and in the Shannon Estuary South Catchment (2037.74km$^2$) (Figure 5.1). This catchment is made up of 18 sub catchments. Pre-2016 sub catchment delineation included 4 sub catchments of the Shannon Estuary South catchment with Lough Gur included in the largest Maigue/Deel catchment with an area of 1493.94km$^2$. The Maigue River catchment is now subdivided into 5 subcatchments and Lough Gur is situated in subcatchment Maigue SC_050 which has an area of 141.42km$^2$. The lake is further situated in a river subbasin of the Maigue SC_050 named BALLYCULLANE24_010 which has an area of 16.41km$^2$.

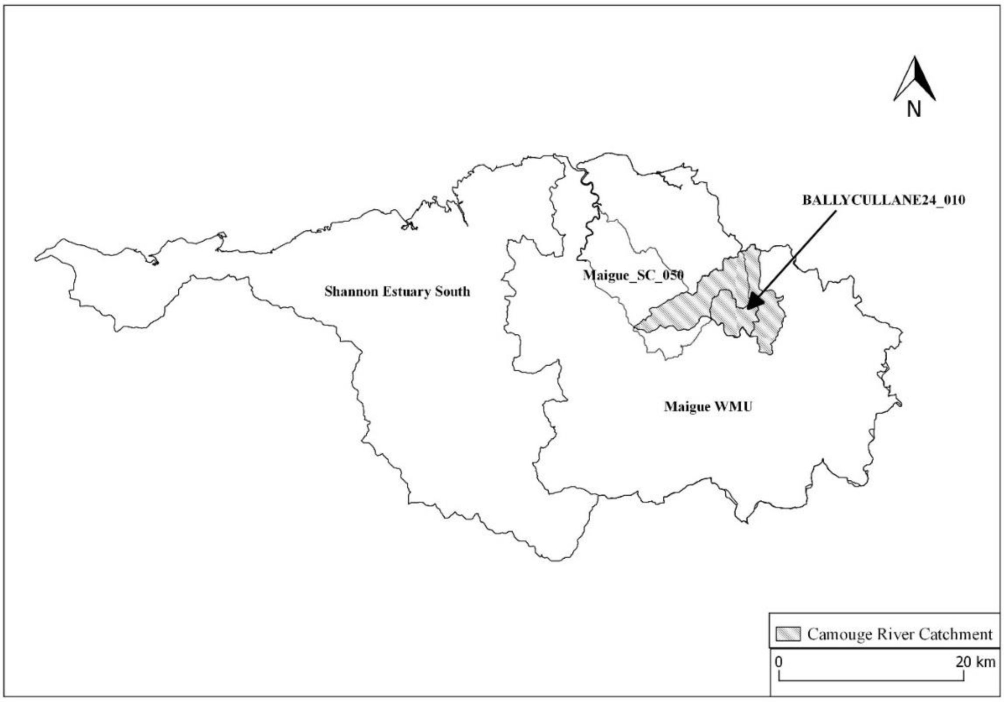


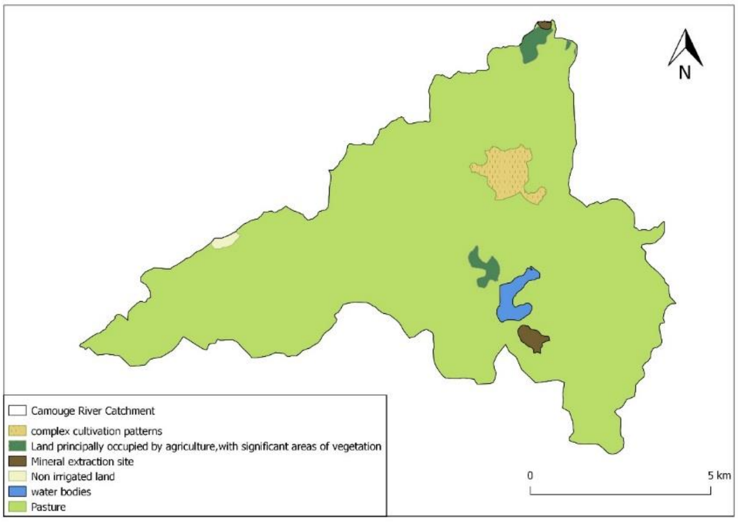

Figure 5:1: Catchments associated with Lough Gur (WFD 2016-2021) and the Camouge River Catchment.

### 5.1.2 Corine Land Use

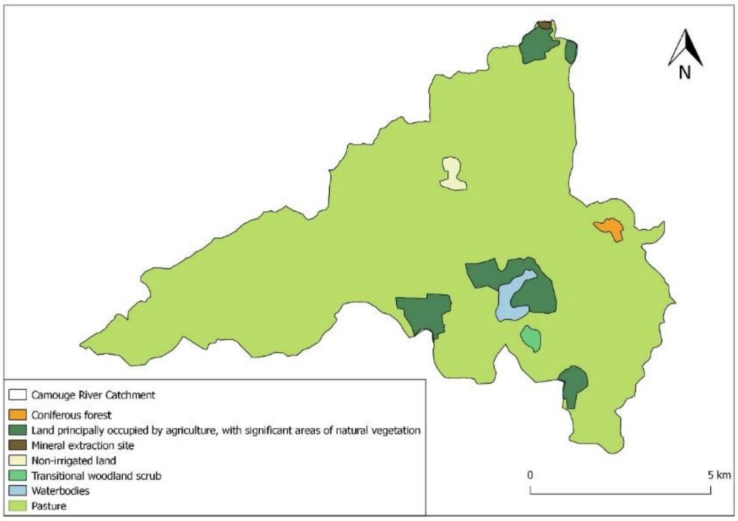
Corine land use in the Camouge river catchment (80.75km$^2$) was examined. This catchment has direct links to the lake in that the lake is situated in river subbasin BALLYCULLANE24_010 which discharges into the Camouge River. Three Corine datasets (2000, 2006 and 2012) were examined to explore land use and change over time in the catchment. In total eight land use types were identified in the catchment, including four agricultural land types, two forest and semi natural areas, one artificial surface and one waterbody.

Pasture was the main land use in 2000 accounting for 94.6% of total land use in 2000 (Figure 5.1(a); Table 5.1). Complex cultivation patterns were the next closest to it at 2.2% to the north of the lake. Land principally occupied by agriculture, with significant areas of vegetation accounted for 1.7% while waterbodies and mineral extraction site were that lowest at 1% and 0.4 % respectively. Pasture was also the dominant land use in the catchment in 2006 at 92.1% despite declining slightly. Land principally occupied by agriculture, with significant areas of vegetation increased to 5.7% with most of the increase situated around the lake (Figure 5.2(b)). Three new land types were identified in the catchment in 2006, non-irrigated arable land was the highest at 0.5% while coniferous forest and transitional woodland shrub accounted for 0.3%. Waterbodies remained similar at 0.9% but mineral extraction was reduced to 0.1% and was only to be found to the very north of the catchment. Pasture again remained the dominant land use in the catchment in 2012 and rose by 0.3% to 91.4%. Land principally occupied by agriculture, with significant areas of vegetation remained at 5.7%. Non-irrigated arable land grew to 1.2% with the addition of a new area in the west of the catchment (Figure 5.4). Water bodies, coniferous forest and transitional woodland shrub showed no change from 2006.

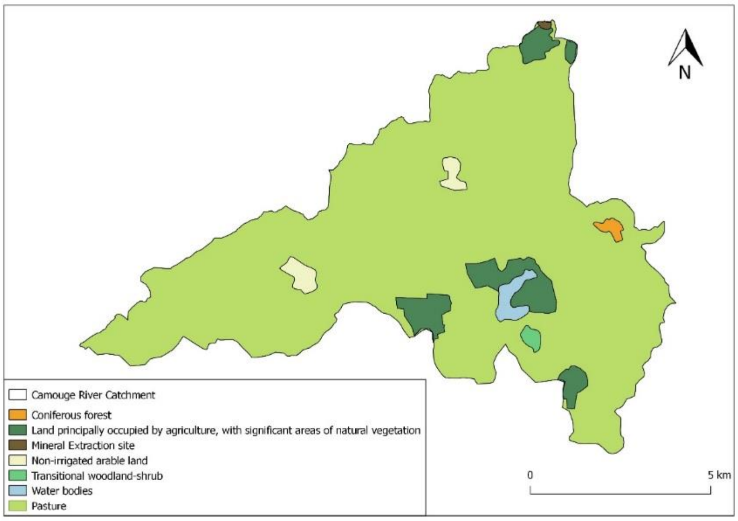
GIS analysis was constrained in a number of ways. First, the dataset for CORINE land use in 1990 was not downloadable (multiple error messages were received) therefore restricting analyses of land use change to between 2000, 2006 and 2012. Between 2000 and 2006 three new land use types were introduced to the Camouge catchment yet little change in land use is evident due to the small areas they occupied (1.1%). Some additional uncertainties can be seen in the GIS data, for example in 2000 there is a mineral extraction site to the south east of Lough Gur, however, aerial photography shows bogland at that location moreover there is no mention of a mineral extraction site in any literature. Secondly issues arose when trying to delineate Lough Gur's groundwater catchment. Hydrological connectivity and transmissivity in karstic catchments is complex, thus limiting GIS catchment delineation in this Masters project to the surface topographic catchment only.




(a)




(b)




(c)

Figure 5:2: Corine land use data for 2000 (a), 2006 (b) and 2012 (c) in the Camouge River Catchment.

Table 5.1: Corine land use in the Camouge river catchment (2000, 2006, and 2012).

| **Corine land use** | **2000** | | **2006** | | **2012** | |
|---|---|---|---|---|---|---|
| | **Km** | **%** | **Km** | **%** | **Km** | **%** |
| Mineral Extraction site | 0.36 | 0.4 | 0.07 | 0.1 | 0.07 | 0.1 |
| Non-irrigated arable land | 0.00 | 0.0 | 0.41 | 0.5 | 0.99 | 1.2 |
| Land principally occupied by agriculture, with significant areas of natural vegetation | 1.40 | 1.7 | 4.59 | 5.7 | 4.59 | 5.7 |
| Coniferous forest | 0.00 | 0.0 | 0.28 | 0.3 | 0.28 | 0.3 |
| Transitional woodland-shrub | 0.00 | 0.0 | 0.26 | 0.3 | 0.26 | 0.3 |
| complex cultivation patterns | 1.74 | 2.2 | 0.00 | 0.0 | 0.00 | 0.0 |
| Water bodies | 0.83 | 1.0 | 0.74 | 0.9 | 0.74 | 0.9 |
| Pastures | 76.42 | 94.6 | 74.40 | 92.1 | 73.82 | 91.4 |
| Total | 80.75 | 100 | 80.75 | 100 | 80.75 | 100 |

## 5.2 Water Temperature

Temperature loggers were placed in the north east (R 64238 41178) and north (R 63873 40966) basins of the lake. Temperature was recorded at depths of 1, 2 and 3 metres below the surface. Only one set of loggers was retrieved in the north east basin. The second set came off its anchor and was lost. At a depth of 1 metre the lowest average monthly temperatures recorded were 2.85°C in both November and December while the highest temperature of 23.38°C occurred in July (Figure 5.3). June had the warmest waters with an average temperature of 19.61°C closely followed by July with 19°C (Table 5.2). At 3 metres below the surface 2.9°C was the minimum water temperature recorded which occurred in November. This was 0.5°C warmer than the surface water. June recorded the warmest average water temperature of 18.42°C and also the maximum water temperature of 20.58°C for 3 metre depth. These levels were 1.19°C and 3.77°C colder than the surface waters. Figure 5.13 shows a graph of the average monthly water temperature of the two loggers. From May to August it is clear that the water temperature at 1 metre records a slightly higher average temperature. From August to January both depths record similar temperatures. Temperatures recorded by both loggers were highly correlated (r=0.99) illustrating little variation at different water depths.

Table 5.2: Summary of water temperature (°C) results from Lough Gur.

| **Depth** | **1 metre** | | | **3 metre** | | |
|---|---|---|---|---|---|---|
| **Temperature (°C)** | **Min** | **Average** | **Max** | **Min** | **Average** | **Max** |
| April | 10.66 | 11.86 | 13.02 | 10.49 | 11.77 | 13.02 |
| May | 11.54 | 15.96 | 11.54 | 11.54 | 15.39 | 11.54 |
| June | 16.82 | 19.61 | 20.58 | 16.92 | 18.42 | 20.58 |
| July | 16.32 | 19.00 | 23.28 | 16.39 | 17.78 | 19.58 |
| August | 16.96 | 18.37 | 20.17 | 16.92 | 18.02 | 19.72 |
| September | 13.88 | 16.33 | 19.70 | 13.81 | 16.29 | 19.65 |
| October | 9.61 | 11.88 | 14.70 | 9.68 | 11.89 | 14.65 |
| November | 2.85 | 6.82 | 11.66 | 2.90 | 6.98 | 11.69 |
| December | 2.85 | 6.03 | 8.49 | 3.17 | 6.09 | 8.52 |
| January | 3.99 | 5.48 | 7.24 | 4.19 | 5.55 | 7.27 |

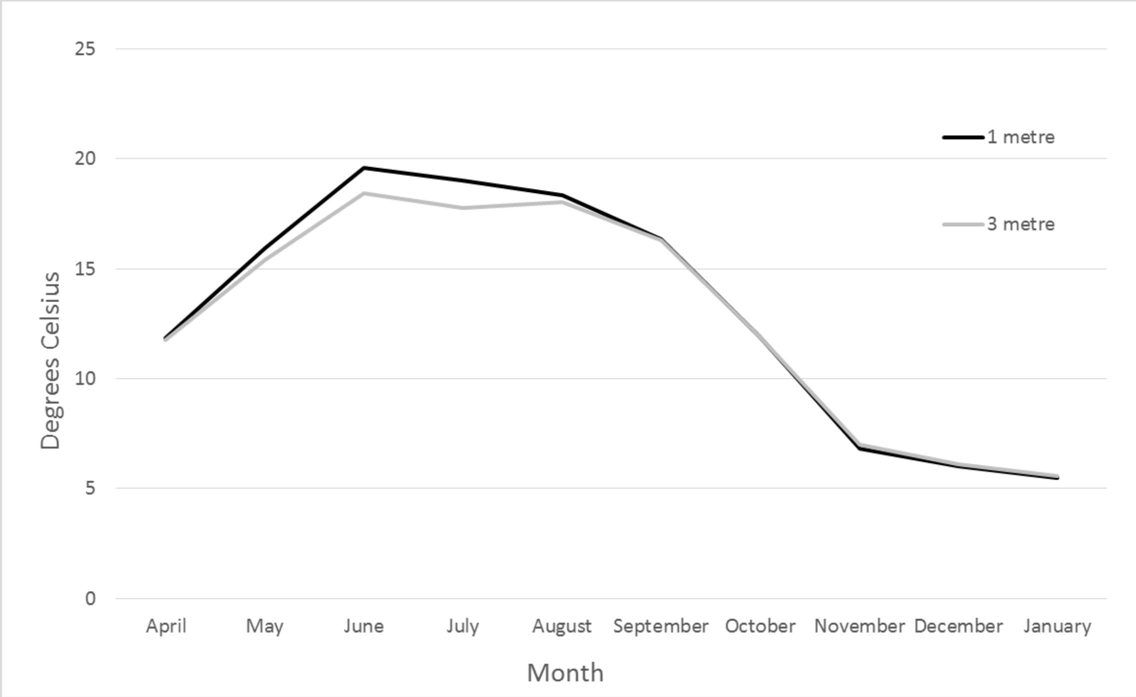



Figure 5:3: Average water temperature in Lough Gur April 2016 – January 2017

### 5.3 Sediment cores

Core 1 (MIC) was retrieved at R 64244 41178 in 4.1 m water depth and measured 40 cm in length (Figure 3.2). Sediment lithology for this core was carried out in Mary Immaculate College. Core 2 (TCD) was retrieved c. 1.5 m distance from the first core at R 64243, 41179 and measured 50cm in length. This core was analysed in Trinity College Dublin.

#### 5.3.1 Sediment lithology

Both core profiles contained homogenous dark brown organic sediments throughout. Sediment moisture content is illustrated in Figure 5.4 and shows a steady increase up core. The base of the core at 40cm has moisture levels of 78% followed by a clear increase to 96% at 9 cm. From 9cm to the core surface moisture content remains high (>95%). Organic matter (OM) content (%LOI) shows a steady increase from 19% at 40cm to 32% at 15cm. OM then rapidly increases to 50% at 8cm after which the core sustains >50 %LOI to the core surface peaking at 54% at 5cm. Carbonate content results show a decreasing trend. From 40 to 15cm a decrease is evident (30 - 20%$CaCO_3$).

Between 15cm and 7cm a steep decline can be seen from 20 to 12%, after which concentrations level off. Sediment lithology results measured on Core 2 are also illustrated in Figure 5.5 and show a similar pattern to Core 1 with high correlations between cores for % moisture (r=0.97), % organic matter (r=0.96) and % carbonate content (r=0.94).

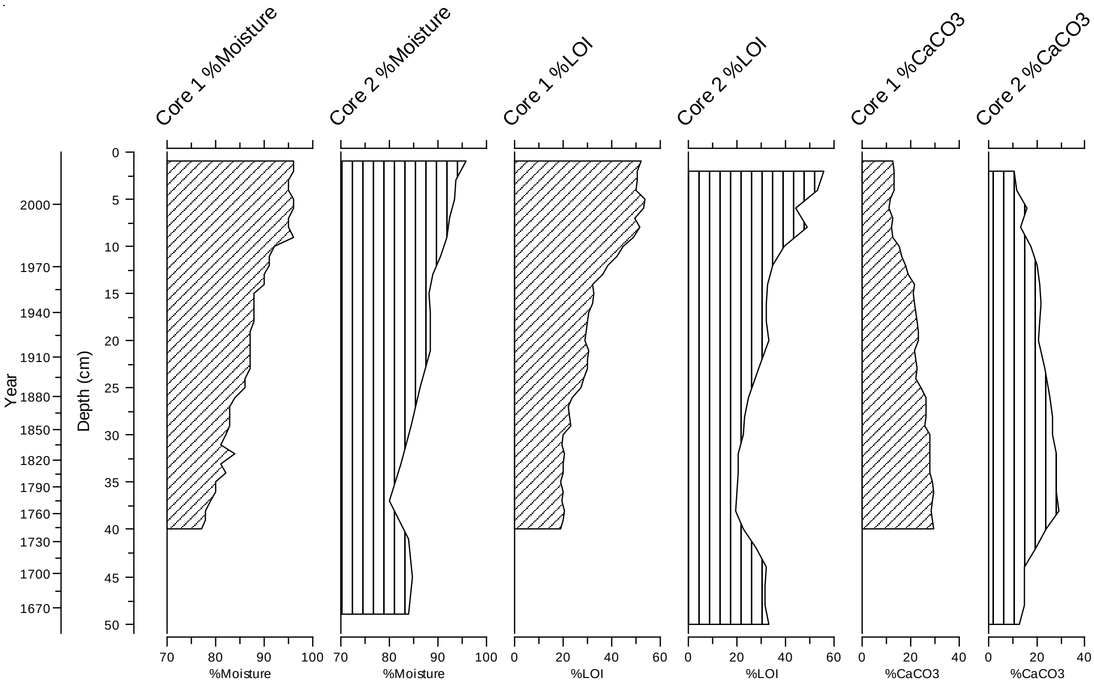



Figure 5:4: Sediment lithology (% moisture, % LOI and % $CaCO_3$) of Core 1 (MIC) and Core 2 (TCD).

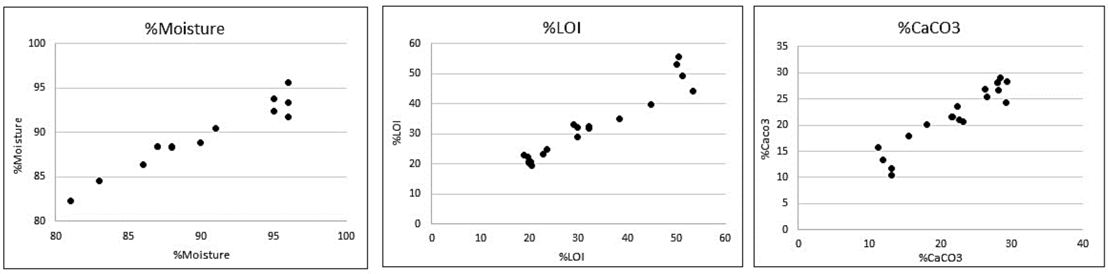



Figure 5:5: Scatter plots showing correlations between lithology measurements.

## 5.4 Sediment Chronology

A chronology was first established for Core 2 (Viaene, 2015). Sediments from Core 2 were analysed for $^{210}Pb$, $^{226}Ra$, and $^{137}Cs$ by direct gamma assay in the Liverpool University Environmental Radioactivity Laboratory. Results were received in August 2015 and suggested two potential chronologies. In order to test the potential chronologies, sediments from Core 1 (MIC) were radiometrically dated in the Environmental Radiometric Facility at University College London. Results were received in July 2016. In Core 2 (TCD) the $Pb^{210}$ inventory was 1142 Bq/m$^2$ and corresponded to a mean $Pb^{210}$ supply rate of 36 Bq/m$^2$/yr. Total $^{210}$Pb concentrations reached equilibrium with the supporting $^{226}$Ra at a depth of around 25cm while artificial fallout radionuclide $^{137}$Cs had its highest activity at c. 4.5cm after which it declines steeply until c. 15cm (Viaene, 2015) (Appendix 1). This indicated that the 1986 fallout from Chernobyl may have merged with the 1963 record. $^{210}$Pb dates calculated using the CRS and CIC dating models show a uniform sedimentation rate of 0.020 ± 0.03 g cm$^{-2}$ y$^{-1}$ (0.20 cm y$^{-1}$) for the last 100 years (Appleby *et al.*, 1978). The results however place 1986 at 8.5cm, significantly below the depth suggested by the $^{137}$Cs record, and 1963 at a depth of 12.5cm. Two hypothesis were suggested in order to explain the discrepancy between $^{210}$Pb and $^{137}$Cs: (i) loss of sediment from the top of the core amounting to 16 years and (ii) distortion of the $^{137}$Cs record by post- depositional inputs or migration.

Equilibrium of total $^{210}$Pb activity with supported $^{210}$Pb was reached at a higher depth of 15.5cm in Core 1 (MIC) (Figure 5.6) (Appendix 2). $Pb^{210}$ inventory was 609 Bq/m$^2$ and corresponded to a mean $Pb^{210}$ supply rate of 19 Bq/m$^2$/yr. Little net decline in $^{210}$Pb in the top 7cm suggests increased sedimentation in recent years, while unsupported $^{210}$Pb activities declined with depth from 8cm to 15cm signifying relatively uniform sedimentation up to 8cm (Figure 5.7). The $^{137}$Cs activity versus depth shows a peak between 7 and 9cm. The UCL CRS model also placed 1986 at around 8.5cm thus suggesting that the $^{137}$Cs peak between 7cm and 9cm may also be indicative of the 1986 Chernobyl fallout. The $^{210}$Pb chronology and CRS model returned a mean SAR of 0.010 g cm$^{-2}$ yr$^{-1}$ (0.12cm y$^{-1}$) for 132 years and only half of what was estimated for Core 2.

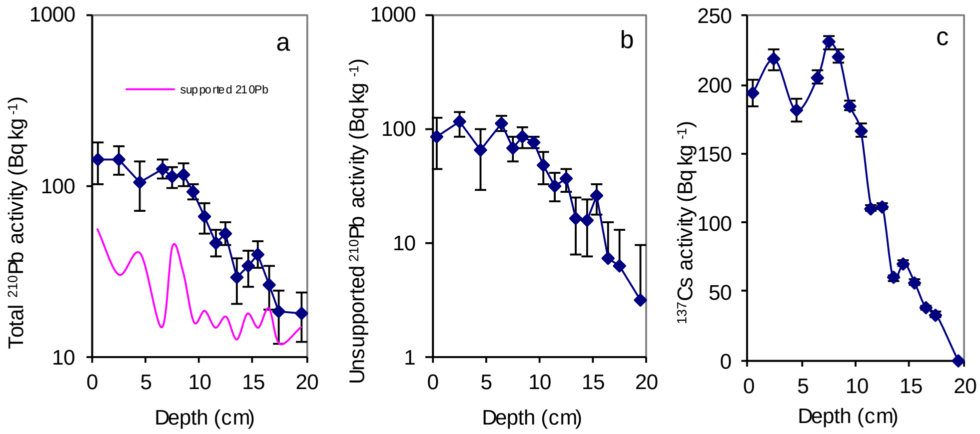



Figure 5:6: Radionuclide concentrations in Lough Gur Core 1 showing (a) total $^{210}$Pb, (b) unsupported $^{210}$Pb, and (c) $^{137}$Cs concentrations versus depth.

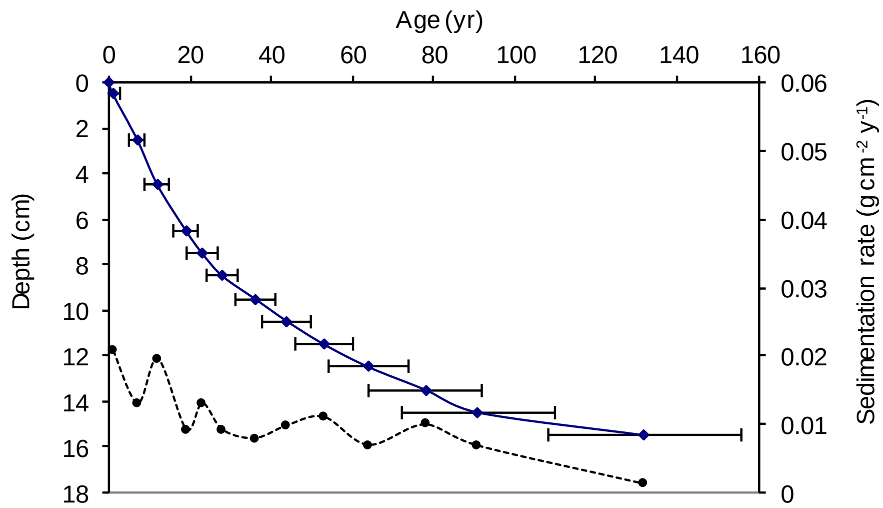



Figure 5:7: Age-depth plot of Lough Gur Core 1, showing the UCL CRS model $^{210}$Pb dates and sedimentation rates. The solid line shows age while the dashed line indicates sedimentation rate.

Three chronological scenarios for the Lough Gur sediments are therefore provided by two radiometric laboratories (Table 5.3). The first scenario suggests a surface sediment loss equivalent to 16 years, while the other two scenarios support intact surface sediments. The first chronology from Liverpool assumes surface sediment loss and encompasses 100 years of sedimentation spanning from c. 1999 at core surface to c. 1899 at 20.5cm. The second chronology also from Liverpool assumes no sediment loss and thus encompasses sediment from 2015 to 1915. The third chronology, from UCL suggests a total of 132 years and a date of c. 1883 at 15.5cm. The second chronology (Liverpool) and third chronology (UCL) show almost identical results for the top 9cm, however, the chronologies diverge after this point with chronology 3 exhibiting an older time frame (Figure 5.8). Linear extrapolations suggest a basal core date of 1651 AD for Core 2at 50cm and 1350 AD for Core 1 at 40cm. Subsequent stratigraphic plots will present the sediment core data utilising the Liverpool chronology with an intact surface and basal core date in the mid-1600s.

Table 5.3: Chronological scenarios for Core 1 (MIC) and Core 2 (TCD). Double lines indicate depth equilibrium of total $^{210}Pb$ activity with supported $^{210}Pb$ activity was reached and figures below are linear extrapolations.

| Depth (cm) | Core 2 (TCD) (Sediment Loss) | Core 2(TCD) | Core 1 (MIC) |
|---|---|---|---|
| 0 | 1999 | 2015 | 2015 |
| 0.5 | 1998 | 2014 | 2014 |
| 2.5 | 1993 | 2008 | 2008 |
| 4.5 | 1986 | 2002 | 2003 |
| 6.5 | 1978 | 1994 | 1996 |
| 8.5 | 1970 | 1986 | 1987 |
| 10.5 | 1960 | 1976 | 1971 |
| 12.5 | 1949 | 1965 | 1951 |
| 14.5 | 1937 | 1952 | 1924 |
| 15.5 | 1931 | 1945 | 1883 |
| 16.5 | 1924 | 1940 | 1842 |
| 18.5 | 1912 | 1927 | 1801 |
| 20.5 | 1899 | 1915 | 1760 |
| 22.5 | 1885 | 1901 | 1719 |
| 24.5 | 1871 | 1887 | 1678 |
| 26.5 | 1857 | 1871 | 1637 |
| 28.5 | 1843 | 1854 | 1596 |
| 30.5 | 1829 | 1836 | 1555 |
| 32.5 | 1815 | 1817 | 1514 |
| 34.5 | 1801 | 1795 | 1473 |
| 36.5 | 1787 | 1773 | 1432 |
| 38.5 | 1773 | 1753 | 1391 |
| 40.5 | 1759 | 1732 | 1350 |
| 42.5 | 1745 | 1714 | |
| 44.5 | 1731 | 1697 | |
| 46.5 | 1717 | 1679 | |
| 48.5 | 1703 | 1665 | |
| 50.5 | 1689 | 1651 | |

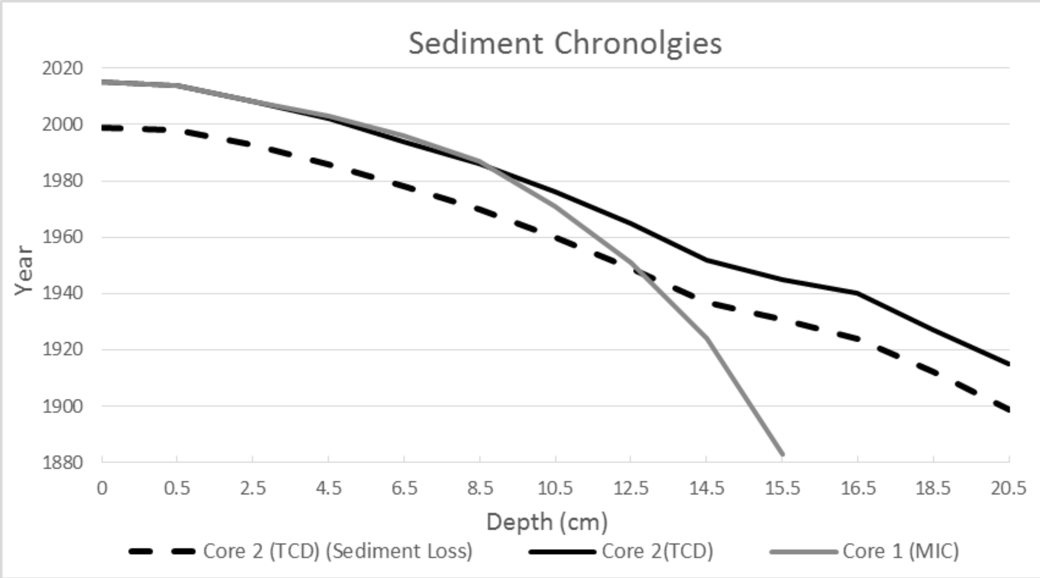



Figure 5:8: Sediment chronologies for Core 1 (MIC) and Core 2 (TCD).

### 5.5 Biological Fossils

Core 1 (MIC) was examined for diatom microfossils. Upon examination poor preservation of diatom frustules was evident, with few diatoms present throughout the core. The paucity of fossil diatoms meant that an alternative biological proxy needed targeting. Algal pigment concentrations were subsequently extracted in the University of Nottingham.

#### 5.5.1 Algal pigments

A total of 13 sedimentary pigments were identified from core 1 (MIC), with varying levels of preservation evident throughout the core (Figure 5.9). The 13 pigments are ordered according to the eight algal groups they represent, cyanobacteria, chlorophytes, total algae, cryptophtyes, chrystophytes, chl *b* derivative, siliceous and grazing senescent diatoms. Phaeophorbide *a*, lutein and zeaxanthin showed the best preservation while chlorophyll *b* had poor preservation and was only identified at the end of the 1800s or 25cm upwards in the sediment core. Analysis of one sample (38-39cm) returned incomplete results therefore pigment concentrations before the 1750s were unable to be identified.

*Cyanobacteria*

Zeaxanthin shows high concentrations from the base of the core with peak concentrations of 316.8 nmol $g^{-1}$ OM around the 1840s or 29cm, followed by a sustained decrease to 161 nmol $g^{-1}$ OM at the beginning of the 1900s or 21cm. Another peak of 211 nmol $g^{-1}$ OM in the 1950s at 16cm after which concentrations decrease into the 21$^{st}$ century with 60.4 nmol $g^{-1}$ OM at core surface. Highest concentrations of canthaxanthin, 25 nmol $g^{-1}$ OM, occur around the 1900s at 22cm. After the peak, concentrations steadily decrease through the 1900s and 2000s falling to 6.7 nmol $g^{-1}$ OM at core surface. Concentrations of cyanobacteria echinenone remain low until the 1920s with 10 nmol $g^{-1}$ OM at 16cm after which a gradual increase can be seen to 16 nmol $g^{-1}$ OM just before the 1990s or 8cm. A peak in concentrations of 26.1 nmol $g^{-1}$ OM occurs around 2000 or 4cm which is followed by a decrease. Concentrations then increase in the 2000s with 19 nmol $g^{-1}$ OM at the core surface.

*Chlorophytes*

Chl *b* concentrations are identified from the 1890s or 25cm onwards reaching 6.8 nmol $g^{-1}$ OM in the 1920s or 20cm. This is followed by fluctuations in concentration with levels reaching a peak of 9 nmol $g^{-1}$ OM in the 1990s or 5cm followed by declines at the core surface into the 21$^{st}$ century. Concentrations of lutein remain steady from the bottom of the core upwards with a maximum of 139.2 nmol $g^{-1}$ OM in the late 1940s or 15cm. Lutein then decreases into the end of the 20$^{th}$ and beginning of the 21$^{st}$ century.

*Total Algae*

β-carotene concentrations are identified throughout the core. Levels remain stable in the 1800s however they begin to rise from the early 1900s or 23cm onwards and concentrations increase summiting to 37.5 nmol $g^{-1}$ OM in the 1960s or 13cm. Levels then fluctuate again with an overall decreasing trend evident into the late 1980s or 6cm. A spike of c. 26 nmol $g^{-1}$ OM is evident in the 1990s or 4cm. Concentrations show an increasing trend into the 2000s. Chlorophyll *a* concentrations are generally low < 20 nmol $g^{-1}$ OM in the 1800s. A steady increase in levels is evident in the 1900s or 20cm to 7cm after which concentrations spike to maximum levels of 57 nmol $g^{-1}$ OM in the 2000s or 4cm. Levels then decline before increasing again into the 21$^{st}$ century at core surface. Concentrations of pheophytin *a* fluctuate throughout the core with three main peaks of 47.8 nmol $g^{-1}$ OM in the 1890s or 25cm, 46.3 nmol $g^{-1}$ OM in the late 1970s or 10cm and 46.4 nmol $g^{-1}$ OM in the 2000s or 4cm.

*Cryptophytes*

Alloxanthin concentrations fluctuate from the bottom of the core to the top with an overall increasing trend evident. Two peaks in concentrations occur with 22 nmol $g^{-1}$ OM in the 1980s or 9cm and 20 nmol $g^{-1}$ OM in the early 1990s or 7cm.

*Chrystophytes*

Fucoxanthin concentrations show a slow gradual increase from the 1800s or base of the core upwards with concentrations of 17 nmol $g^{-1}$ OM in the early 1990s or 7cm to a peak of 57 nmol $g^{-1}$ OM in the 2000s or 4cm. This is followed by a succeeding decrease and a levelling off to the top of the core with c. 20nmol $g^{-1}$ OM into the 2000s.

*Chl b Derivative*

Pheophytin *b* fluctuates along the length of the core with numerous peaks evident. Maxima of 112.5 nmol $g^{-1}$ OM occurs in the late 1970s at 10cm, 111.2 nmol $g^{-1}$ OM around the late 1980s at 8cm and 99.2 nmol $g^{-1}$ OM at the beginning of the 2000s at 4cm. From 3cm to core surface an increasing trend can be observed.

*Siliceous*

Concentrations of the siliceous algae diatoxanthin show increasing trends from the bottom of the core reaching peak concentrations of 21.2 nmol $g^{-1}$ OM around the 1850s and 21.9 nmol $g^{-1}$ OM in the 1850s and 1920s at 29cm and 19cm respectively. A fluctuating decreasing trend in concentration is evident into the mid-1950s and just before the 1990s it reaches its lowest concentrations ending at 7.2 nmol $g^{-1}$ OM at the core surface.

*Grazing senescent diatoms*

Phaeophorbide *a* an indicator of senescent (aging or declining phase of diatom blooms) diatom concentrations start low but increase up core. At the start of the 1900s or 20cm fluctuations become more intense with maxima levels of 351.5 nmol $g^{-1}$ OM around 1960s at 13cm and 419.6 nmol $g^{-1}$ OM into the 2000s at 4cm.

Chl *a*/pheo *a* Ratio

Chl *a*/pheo *a* an indicator of preservation condition steadily fluctuates between 0.4-0.7 until the late 1970s or 10cm. After this an increase to 1.2 is apparent c. 2000 or 4cm followed by a decrease to 0.9 at core surface.

### 5.5.2 Zonation

Three zones of algal pigments were delineated qualitatively by eye in Core 1 (MIC). Zone A marks 150 years or 18cm of sedimentation from 1750-1910. Zone B encompasses 1910-1990 from a depth of 21cm to 7cm. Zone C captures 1990-2015 or 7cm to core surface. Zone C comprises the highest concentrations for some cyanobacteria and chlorophyte pigments while most other pigments have their lowest concentrations. In Zone B pigments show a variety of concentration changes in this zone with some cyanobacteria and chlorophytes exhibiting opposing trends. Total algae shows a clear increase along with cryptophytes, chrystophytes, chlorophyll *b* derivative and grazing senescent diatoms. Siliceous algae decrease in this zone. In Zone C peak concentrations of chlorophyll *a*, echinenone, fucoxanthin, phaeophorbide a and chlorophyll *b* are evident, however the lowest concentrations of zeaxanthin, canthaxanthin, lutein and diatoxanthin are also recorded.

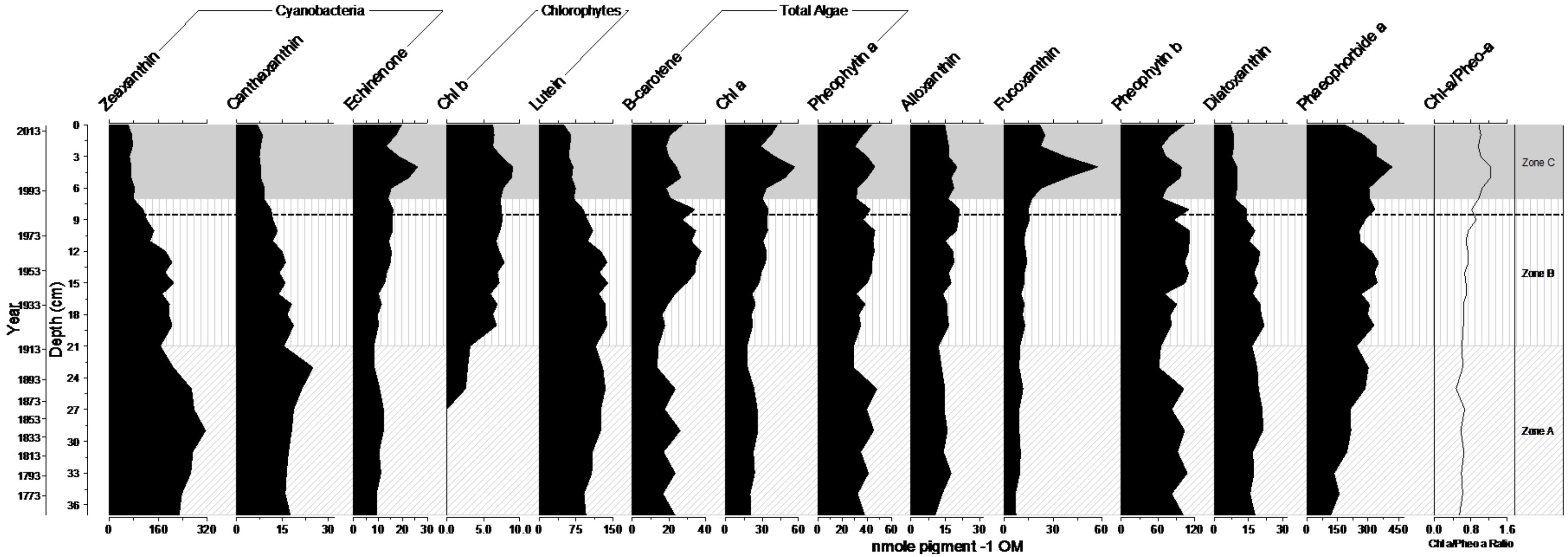



Figure 5:9: Sedimentary chlorophylls, carotenoids and Chl *a*:Pheo a ratio identified in Lough Gur Core 1 (MIC) (dashed line indicates divergence of chronologies at 8.5cm). Zones represent boundaries of key change estimated qualitatively.

## 5.6 Statistical Analyses

### 5.6.1 Correlations

Associations between individual pigments were examined by using Pearson Product Moment correlation with many found to be highly correlated as expected (Table 5.4). Critical values of > +/-0.463 suggest significant correlations between pigments. The highest correlation between pigments was between Chlorophyll a, an indicator of total algae, and the cyanobacteria echinenone (r=1). Siliceous algae and chlorophytes scored the second highest correlation (r=0.93). Cryptophytes and chrystophytes also displayed a strong positive correlation (r=0.65). Cyanobacteria zeaxanthin and canthaxanthin were negatively correlated with cyanobacteria echinenone (r=-0.69).

Associations between individual geochemical concentrations measured by Viaene, (2015) were also examined (Table 5.5). The highest correlation was between Iron and magnesium (r=0.95). Sodium and total nitrogen along with total carbon and total nitrogen both scored the second highest correlations (r=0.92). Total nitrogen and total phosphorus were highly correlated(r=0.90).

Table 5.4: Correlations between individual pigments. Significant correlations (≤ -0.463 to ≥0.463 1, df=(n-2) 99% confidence interval) are emboldened.

| | Alloxanthin | β carotene | Canthaxanthin | Chl a | Chl b | Diatoxanthin | Echinenone | Fucoxanthin | Lutein | Phaeophorbide a | Pheophytin a | Pheophytin b |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| β carotene | **0.56** | | | | | | | | | | | |
| Canthaxanthin | -0.36 | -0.21 | | | | | | | | | | |
| Chl a | **0.61** | 0.42 | **-0.74** | | | | | | | | | |
| Chl b | **0.64** | 0.41 | **-0.58** | **0.64** | | | | | | | | |
| Diatoxanthin | -0.13 | 0.09 | **0.88** | **-0.62** | -0.39 | | | | | | | |
| Echinenone | **0.61** | 0.42 | **-0.74** | **1.00** | **0.64** | **-0.62** | | | | | | |
| Fucoxanthin | 0.41 | 0.03 | **-0.68** | **0.88** | **0.56** | **-0.68** | **0.88** | | | | | |
| Lutein | -0.07 | 0.09 | **0.85** | **-0.60** | -0.23 | **0.96** | **-0.60** | **-0.63** | | | | |
| Phaeophorbide a | **0.60** | 0.22 | -0.27 | **0.50** | **0.82** | -0.17 | **0.50** | **0.58** | 0.01 | | | |
| Pheophytin a | 0.44 | **0.75** | -0.04 | **0.48** | 0.16 | 0.18 | **0.48** | 0.20 | 0.13 | 0.12 | | |
| Pheophytin b | 0.39 | **0.81** | 0.04 | 0.29 | 0.05 | 0.29 | 0.29 | -0.05 | 0.21 | -0.07 | **0.88** | |
| Zeaxanthin | -0.34 | -0.10 | **0.87** | **-0.69** | **-0.75** | **0.86** | **-0.69** | **-0.69** | **0.78** | **-0.48** | 0.12 | 0.23 |

Table 5.5: Correlations between individual geochemical elements. Significant correlations (≤ -0.463 to ≥ 0.463 1, df=(n-2) 99% confidence interval) are emboldened.

| | Cadmium (cd) | Iron (Fe) | Potassium (K) | Magnesium (Mg) | Manganese (Mn) | Sodium (Na) | Total Carbon | Total Nitrogen |
|---|---|---|---|---|---|---|---|---|
| Iron (Fe) | 0.43 | | | | | | | |
| Potassium (K) | **0.54** | **0.89** | | | | | | |
| Magnesium (Mg) | **0.53** | **0.95** | **0.84** | | | | | |
| Manganese (Mn) | 0.16 | -0.36 | 0.03 | -0.46 | | | | |
| Sodium (Na) | **0.50** | -0.05 | 0.35 | -0.11 | **0.90** | | | |
| Total Carbon | **0.62** | -0.18 | 0.13 | -0.13 | **0.70** | **0.82** | | |
| Total Nitrogen | **0.72** | 0.12 | **0.46** | 0.11 | **0.72** | **0.92** | **0.92** | |
| Total Phosphorus | **0.67** | 0.43 | **0.75** | 0.38 | **0.62** | **0.86** | **0.66** | **0.90** |

### 5.6.2 Algal pigments PCA

Ordinations scores were used to summarise the main algal floristic changes across the sediment samples. PCA axis 1 captured 67% of the variance with chl b having the highest positive score (1.69) and zeaxanthin having the highest negative score (-1.67) (Figure 5.10). Axis 2 explained 17% of the variance where chlorophyll *b* again had the highest positive score (2.33) and fucoxanthin had the highest negative score (-0.31).

This represents a floristic gradient change from fossil algal pigment assemblages dominated by zeaxanthin in the 1700-1800s to chlorophyll *b* from the 1900s into the 2000s (r=-0.75) (Figure 5.11). Chlorophyll *b* concentrations were not identified until the 1890s (25cm), after which levels quickly increased and peaked c. 2000 (4cm). Zeaxanthin concentrations were highest at the base of the core with maximum concentrations c. 1850 (29cm) after which concentrations decline to core surface.

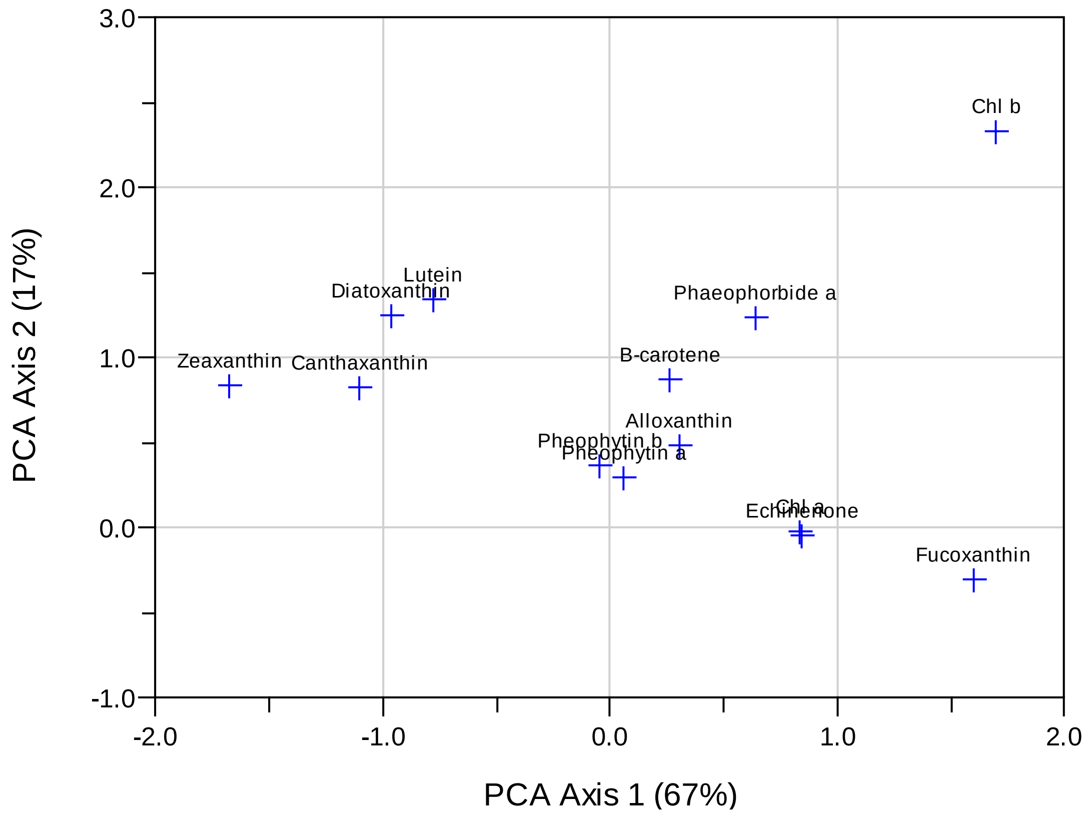



Figure 5:10: PCA bi-plot of axis 1 and 2 scores for algal pigments.

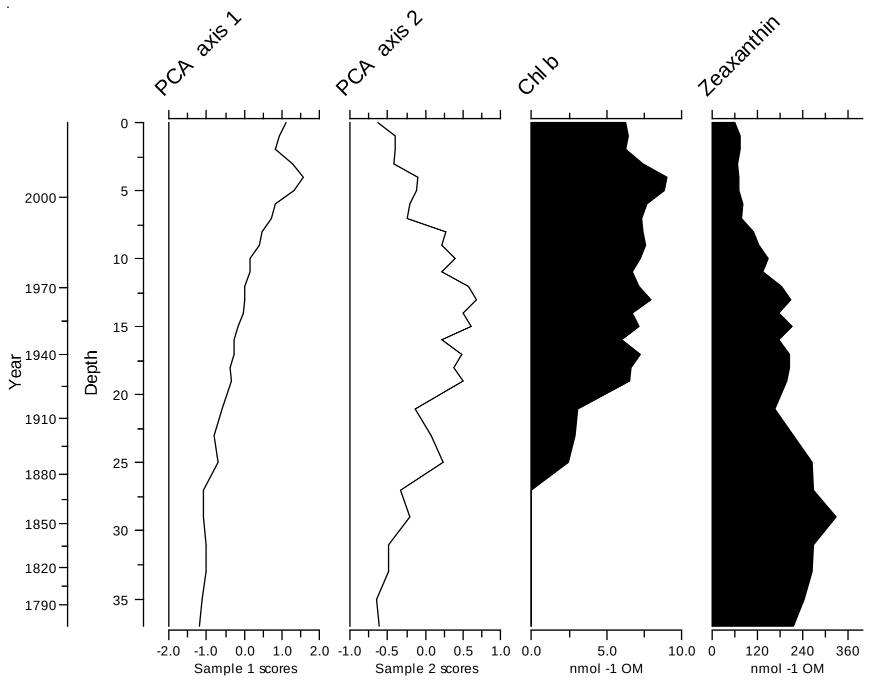



Figure 5:11: PCA sample scores for axis 1 and 2 with main algal drivers (chlorophyll *b*, zeaxanthin).

### 5.6.3 Geochemical PCA

PCA was also carried out on the geochemical results from Core 2 which were analysed in Viaene (2015). PCA axis 1 which captured 69% of the geochemical variance (Figure 5.12). PCA scores initially decline reaching a low at c. 1760 (36cm) and then steadily increases 6cm and peaks at the core surface. Sodium (Na) and Total Nitrogen (TN) had the highest scores on axis 1 scoring 1.48 and 1.37 respectively. Na levels increase steadily from the base of the core to c. 1990 (6cm) and peak at the core surface. TN levels also rise up core. PCA axis 2 captured 24% variance in the dataset and shows a decreasing trend up core. This is driven principally by Fe and K which have geochemical scores of 1.75 and 1.41 respectively. Both elements show relatively similar up core profiles.

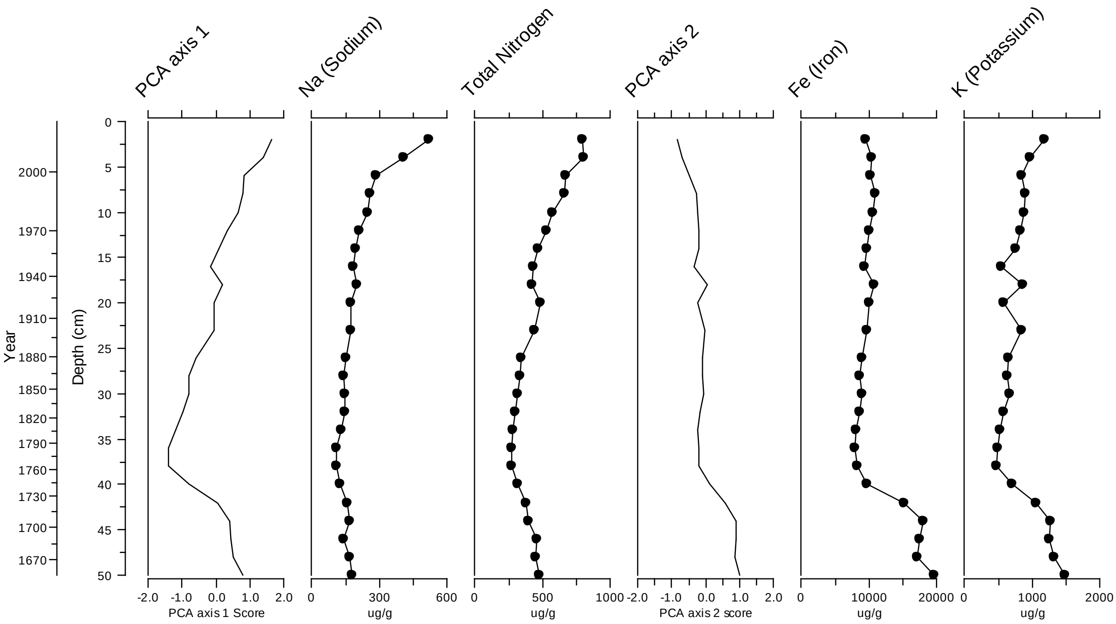



Figure 5:12: PCA of sample scores for axis 1 and 2 with main geochemical drivers (Na, TN, Fe and K).

# CHAPTER 6 DISCUSSION

Sediments deposited in Lough Gur were investigated for lithological, geochemical and biological changes in an attempt to identify periods of increased lake productivity associated with catchment activities. Two sediment cores were collected and analysed in two Master's projects in separate institutions. The adjacent cores were cross correlated, thus allowing for a multi-proxy study. This chapter will discuss Lough Gur's catchment and lake characteristics as well as trends in sediment chronology, physio-chemical and biological proxies.

## 6.1 Catchments

It was initially envisaged that the groundwater catchment area was potentially far greater than the surface water drainage catchment given the underlying limestone bedrock and thus a potential factor in explaining the water quality of Lough Gur. The lake is located in a hierarchy of catchments, Lough Gur surface water catchment, Ballycullane, Camouge River, Maigue and the Shannon Estuary South catchment. The larger Maigue catchment is delineated based on topography and river flow, while river sub-basins have recently been altered to more effectively represent environmental monitoring points and data (www.catchments.ie). Gur is situated within sub-basin BALLYCULLANE24_010. Natural geomorphic factors have resulted in the formation of Lough Gur's surface and ground water catchments. The surface water catchment is bounded by a series of topographical high points enclosing a depression containing the lake. The lakes positive water balance is due to both surface runoff and ground water inputs, however it also results in Lough Gur's shallow depth and low water volume. An estimated surface water catchment area of 5.38km$^2$ was suggested by King and O'Grady, (1994) however the current estimate is 3.68km$^2$ (Langford and Gill, 2016). Limestone geology can create complex hydrological networks making it difficult to establish ground water catchment source areas (Ford *et al.*, 2007; Shaw *et al.*, 2013). Gur is primarily underlain by karstic limestone which enables a substantial ground water contribution. Ball, (2004) estimated a ground water catchment area of 4.68km$^2$ for Gur, however a more recent investigation has reduced this to 3.48km$^2$ thus suggesting that the surface drainage area is similar in size to the groundwater catchment (Langford and Gill, 2016). Lough Gur's small surface water catchment area and low water volume may mean it is more susceptible to nutrient enrichment as it has limited the capacity for dilution of pollutants (Moses *et al.*, 2011).

### 6.2 Water Temperature

Initially it was envisaged that both dissolved oxygen (DO) and temperature loggers would be positioned in Lough Gur to profile both DO and temperature variations in the water column. DO loggers can provide an insight in DO levels throughout the water column identifying differences between the epilimnion and hypolimnion. Xu *et al.,* (2010) investigated eutrophication events in the shallow, hypereutrophic Lake Taihu, China in which DO loggers were used to identify periods of high algal growth in the epilimnion which were associated with increases in DO levels. The hypolimnion DO loggers reported aerobic conditions due to the weak thermal stratification caused by the lakes shallow depth, and wind induced mixing which led to large short term pulses of nutrients being released to overlying water (Xu *et al.*, 2010). It is possible that similar events are occurring in the shallow water of Lough Gur while deeper waters may have anaerobic conditions. Anaerobic conditions allow for the resuspension of soluble phosphorus from sediments into the water column which can contribute to nutrient enrichment and subsequent eutrophication of lake waters (Wang *et al.,* 2008). Unfortunately problems with DO logger calibration prevented collection of data.

Results from temperature logger's show that the lake has very weak thermal stratification during summer months even at its deepest point which is consistent with shallow polymictic lakes (Boehrer and Schultze, 2008). The temperature range of Lough Gur suggests that the lake is suitable for algal growth as surface waters reached optimum temperature of 20–30°C for photosynthesis of blue green algae (cyanobacteria) in July (Singh and Singh, 2015). Thermal stratification can allow for resuspension of nutrients and can lead to increased internal loading (Dokulil, 2014).

### 6.3 Timeline of sediment core chronology

Establishing a chronology is an essential element of palaeolimnological studies as decadal or even annual changes in sediment can be identified. Chronologies established using $^{210}$Pb give accurate dating for the last 150 years, although after equilibrium of $^{210}$Pb is reached dates can be extrapolated to provide a longer timeframe (Kirchner, 2011). Short sediment cores reveal timeframes of variable chronologies depending for example on sedimentation rates as low sedimentation rates can lead to older chronologies.

Liverpool University (LU) and University College London (UCL) radiometric laboratories were utilised to establish the recent chronology of the Lough Gur sediments. Two chronologies were initially hypothesised by LU for the longer 50cm core (Viaene, 2015). This resulted in the adjacent slightly shorter 40 cm core being sent to UCL for dating as part of this Master's project. As a result the hypothesis of surface sediment loss was discounted. A sediment chronology from 2015 to the mid-1980s was established and validated by the two independent radiometric laboratories. Pre-1985 however the LU and UCL chronologies diverge suggesting dates of 1945 and 1883 at 15.5 cm when equilibrium of $^{210}$Pb is reached and extrapolated core basal dates of 1732 and 1350 at 41 cm. An increase in sediment deposition is modelled post-1985 compared to pre-1985 with the UCL model. The calculated mean SARs were 0.020 g cm$^{-2}$ y$^{-1}$ (0.20 cm y$^{-1}$) with the LU model and 0.010 g cm$^{-2}$ yr$^{-1}$ (0.12cm y$^{-1}$) with the UCL model. The Liverpool University chronology was subsequently adopted as the preferred chronology due to its relatively higher radionuclide measurements (36 compared to 19 Bq/m$^2$/yr).

Both cores in this study show evidence of poor quality radionuclide concentrations which are far below the expected range (Appleby, 1971) suggesting that the site is a weak accumulator of atmospheric deposition. This could possibly be due to catchment characteristics and resuspension of sediments. Bennion *et al.*, (2001) also encountered similar poor quality radionuclide records when dating four shallow lakes in the Norfolk Broads in England. It was suggested that dating of shallow lake cores stretches $^{210}$Pb dating to its limits and results can often have large uncertainties. Leira *et al.,* (2006) reported that similar issues with $^{210}$Pb concentrations arose when dating a core from Lough Atedaun, a small shallow lake in Co. Clare. While $^{210}$Pb is the preferred method of dating for lake sediment studies, it appears that there are specific problems encountered when dating in shallow lakes. It may be that studies of shallow lakes which have encountered complications with $^{210}$Pb chronologies have remained largely unpublished therefore the area remains understudied. $^{14}$C dating of basal sediments of both cores may provide some clarity on chronology however this was outside the remit of this Masters project.

The SARs calculated for Lough Gur are in line with some of the lower values present in related Irish literature. Taylor *et al.,* (2006) calculated sedimentation rates for six productive lakes in Ireland including Egish Lake, Co. Monaghan and Sillian Lake, Co. Cavan. Egish Lake, a lake similar in size and mean depth as Lough Gur returned a SAR of 0.017 g $cm^{-2}$ $y^{-1}$ which resulted in a comparable chronology while Lough Sillian, a deeper, larger lake returned the highest SAR of 0.053 g $cm^{-2}$ $y^{-1}$. Carson *et al.,* (2014) reported a SAR of 1.71 cm $y^{-1}$ in Milltown Lake, a small, deep lake with a much larger catchment area than Lough Gur which has under gone eutrophication since the 1970s due to increased agricultural activities. Lough Gur's SAR is at the lower end of the recorded SAR of five small, shallow lakes in Poland which had surface water catchment areas ranging from 1.5 – 14$km^2$. SAR varied between 0.019 – 0.064 g $cm^{-2}$ $y^{-1}$ and variable chronologies of between 150-250 years in 50cm of sediment (Gąsiorowski, 2008). Rose *et al.,* (2010) describes sediment accumulation rates of 17 small, shallow lowland European lakes and estimated a mean SAR of 0.099 g $cm^{-2}$ $yr^{-1}$ for the year 1850. Ten of the seventeen lakes displayed an accelerating trend in SARs to core surface which was attributed to changes in land use, agricultural practices and eutrophication (Rose *et al.,* 2010). Mc Gowan *et al.,* (2012) reported SARs of the north (0.12g $cm^{-2}$ $y^{-1}$) and south (0.080 g $cm^{-2}$ $y^{-1}$) basins of Windermere Lake, U.K., a large, deep lake in which eutrophication occurred due to nutrient enrichment from domestic and agricultural activities. The lack of sediment inflow from riverine sources to Lough Gur means limited allochthonous material inputs. Low SAR was calculated for a small, shallow enclosed lake in Cumbria which was only fed by groundwater springs, similar to Lough Gur (Pennington, 1979). Therefore it appears that small catchment areas, low catchment to lake surface areas and shallow lakes in general appear to result in low SAR. A more comprehensive evaluation of all radiometrically dated sediment cores is necessary to verify this conclusion.

## 6.4 Temporal trends in physical, biological and geochemical parameters

Poor diatom preservation throughout the sediment core prohibited the use of diatoms to infer historical water quality. However, quantitative and qualitative examination of organic matter, geochemical elements and algal pigment assemblages revealed synchronous and asynchronous change points in the Lough Gur sediment (Figure 6.1).

These periods and change points are now outlined in an effort to reconstruct recent environmental change and associate change with known catchment events.

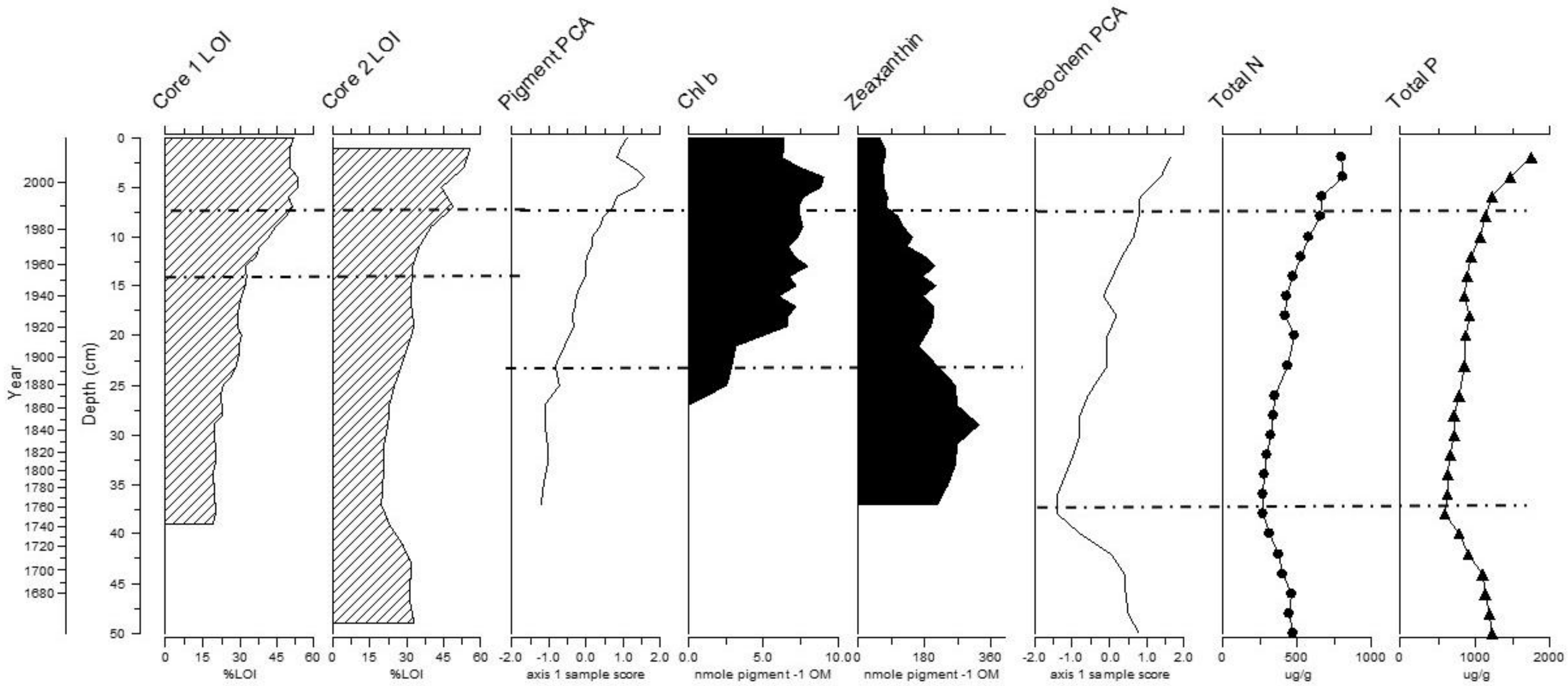



Figure 6:1: Synthesis plot of lithostratigraphical, biological (this project) and geochemical proxies (source: Viaene, 2015) (dashed lines mark qualitatively estimated change points).

### 6.4.1 Pre-1850s

Lough Gur is steeped in a rich history of human settlement dating back to 5000 BP with archaeological evidence of human settlement from the Neolithic period through to the Bronze Age and also in the last two millennia suggesting the lake has been an important settlement location for thousands of years (Ó Ríordáin and Ó Danachair, 1947; Ó Ríordáin, 1948). Initial palaeoecological reconstructions of Lough Gur focused on long term Holocene change and used proxies such as pollen and stable isotopes to identify periods of human occupation and land use change (Mitchell, 1954; Ahlberg *et al.*, 2001). These studies suggested that an increase in human settlement and agricultural activities had occurred around Lough Gur predominantly in the last two thousand years. Before the 1850s, the Irish population was primarily rural and a population of 330,029 was recorded for Co. Limerick in 1841 (Central Statistics Office, 2017). The exact human settlement pattern in the Maigue catchment is unknown but it assumed that it will have been influenced by this large rural population. During this time, 95% of land in Ireland was controlled by 5,000 landlords and the farming method employed was tenant farming, in which small areas of land (0.1 – 0.8 ha) were rented to farmers for seasonal use. A farming method like this was most likely employed around Lough Gur and evidence of small farming settlements in the 1600s have been found around Knockadoon hill (Ó Ríordáin and Ó Danachair, 1947). No references to water quality in Lough Gur exist before the 1850s, however, it is believed the lake was approximately 2.1m higher, covering a larger area. In 1847, the lake level was lowered by the construction of an artificial outlet (O'Kelly and O'Kelly, 1978). This event was recorded in a core collected by (Mitchell, 1954) and was thought to have disturbed the sediment chronology established for this period, and thus constrained interpretation of recent sediment history. This reduction in size and depth may also have reduced nutrient loading capacity of Gur.

Medium levels of OM (approximately 30 %LOI) are initially evident between the core base at 1650 and the early-1700s. These levels are concurrent with high PCA geochemical scores from 1650-1700 and high levels of TN and TP (Viaene, 2015). This suggests that Gur was productive as early as the 1600s. After this, low %LOI and high %$CaCO_3$ are confirmed in both Lough Gur sediment cores and indicates that OM deposition subsequently declined into the 1700s and mid-1800s. Geochemical PCA scores illustrate a decreasing trend from 1700-1750 after which they demonstrate a small increase in the mid-1800s (Figure 6.1). Taylor *et al.,* (2006) presented a study of six lakes across Ireland, Egish, a hypertrophic lake, was the only lake to possess a chronology dating to the late-1700s, Egish also showed declining levels of %LOI to the mid-1800s. Gąsiorowski, (2008) presented OM for three small, shallow Polish lakes, with only one lake having a chronology for this period which demonstrated similar low levels of OM. Individual concentrations of TN and TP are at their lowest in Gur during the late-1700s and remain low to 1850 (Viaene, 2015). This reduction in nutrients possibly slowed growth in Gur and most likely indicates that there were no external inputs of N or P to the lake in this period.

Algal pigment ordination scores from the 1750s to 1850s illustrates little variation and parallels trends in OM. Concentrations of 12 algal pigments are identified and display a wide range of pigment concentrations suggesting that lake was moderately productive during this time. High concentrations of cyanobacteria zeaxanthin indicate it was the abundant algae assemblage in Lough Gur from 1750-1850. Mc Gowan *et al.,* (2012) measured concentrations of zeaxanthin, one third that of Lough Gur, for the same period in the south basin of Windermere Lake and suggested they were not indicative of nutrient enrichment. Concentrations in Lough Gur are twice as high as peak concentrations found in Milltown Lake, Co Monaghan during a period of nutrient enrichment in the 2000s (Carson *et al.,* 2014) and also higher than peak levels in the north and south basins of Windermere Lake during periods nutrient enrichment (Mc Gowan *et al.,* 2012). Hall *et al.,* (1997) investigated fossil pigments of Williams Lake, a large, deep, eutrophic lake in Canada and also reported lower concentrations of zeaxanthin for the same period. Concentrations of lutein are also high pre-1850, and are similar to those present during a period of nutrient enrichment in Windermere, however, they are only a quarter that of a period of nutrient enrichment in Milltown Lake. Bunting *et al.,* (2007) measured much lower sediment concentrations of both zeaxanthin and lutein in a study of Lough Neagh, Northern Ireland, however up core increases were still attributed to nutrient enrichment.

It appears therefore that OM and geochemical measurements were higher in the late-1600s and subsequently declined into the 1700s. Although sediment P and N concentrations and OM deposition were low from 1750-1850 algae concentrations suggest the lake was relatively productive. OM and geochemical concentrations therefore suggest that catchment activities had affected Lough Gur in the late 1600s and mostly likely long before then as the lake has long been a focus for human settlement (Mitchell, 1954). High levels of cyanobacteria from the 1750s onwards are indicative of enrichment. Evidence of human impact on lake productivity has been well establish across Europe (Lotter, 2001; Enters *et al.,* 2010) and Ireland since the Neolithic Age through to the Bronze Age (Mitchell, 1954; Stolze *et al.*, 2012) with even more intensive land use evident in Ireland since the Medieval Age (Cole and Mitchell, 2003).

### 6.4.2 1850s-1950s

The 1850s-1950s represents a period in Lough Gur's rich historical background when the majority of the population of Ireland lived in rural areas and agriculture was of paramount importance both socially and economically (Bell and Watson, 2008). The population of Co. Limerick fell from 262,132 in 1851 to 142,559 in 1946 which may have reduced human activity in the Maigue river catchment (Central Statistics Office, 2017). Living conditions were rudimentary and houses around Lough Gur lacked running water or adequate sewerage systems (Fitzgerald, 2015). Bell and Watson, (2008) state that in 1911, 84% of farms were under 50 acres and the provision of a basic living wage was the main priority for farmers. Large farms over 50 acres were few in number and had just started to adopt new methods such as metal ploughs and reaping machines while small farms still relied on shovels and manual labour. This period directly succeeds the lowering of water level in 1847 suggested by (O'Kelly and O'Kelly, 1978) which may have consequently altered lake characteristics. The late 1840s marks a relatively minor change point in the short core sediments with an increase in OM and a peak in Axis 1 pigment scores reflecting a change in pigments from zeaxanthin to chlorophyll *b*. No obvious change is apparent in the geochemical measurements (Viaene, 2015).

From 1850-1950 levels of %LOI show a gentle increase up core, while %$CaCO_3$ exhibits an opposing trend, however both remain at medium levels (c. 30% and 20% respectively). Taylor *et al.,* (2006) demonstrated fluctuations of between 20% - 35% in %LOI for the same period in Egish Lake and suggested that levels did not signify nutrient enrichment, however, Crans Lake, a small, deep lake in Northern Ireland showed higher OM between 1850-1950 which was attributed to catchment disturbance and nutrient enrichment. Mc Gowan *et al.*, (2012) measured lower levels of %LOI in both basins of Windermere Lake for the same period. Lake Głębokie which is classed as a phytoplankton-macrophyte dominated lake also showed a similar slow steady increase in %LOI in this same period, while Lake Rotzce, a macrophyte dominated lake had %LOI in the range of 45-65% (Gąsiorowski, 2008). The increase in OM content matches the main geochemical axis of variation which also shows a slow but steady upward trend between 1850 and 1950 with a slight peak c. 1920 (Viaene, 2015) (Figure 6.1). Increasing levels of TN and TP suggest more nutrients may have been available during this period.

A varying range of concentrations of algal pigments continues to be observed into the late-1800s and early 1900s. Concentrations of zeaxanthin decline through this period possibly due to altered lake characteristics but it still remains abundant in the sediment record. Concentrations of cyanobacteria canthaxanthin peak c. 1900 which might explain the poor aesthetic water quality noted by (Praeger, 1900) Towards the mid-1900s concentrations of Total Algae (β-carotene, chlorophyll *a* and pheophytin *a*) indicators of overall algae production show increases with β-carotene in particular displaying a rapid increase between 1920 and 1940. Similar trends in concentrations of β-carotene were found in both the north and south basins of Windermere Lake between 1800 and 2000, in response to nutrient enrichment (Mc Gowan *et al.,* 2012). Bunting *et al.,* (2007) identified concentrations of β-carotene in Lough Neagh which were only one quarter that of Lough Gur between 1920 and 1940 and suggested they were not indicative of nutrient enrichment. Concentrations of chlorophytes (chlorophyll *b*/lutein) are also high around this time with the appearance of chlorophyll *b* in the pigment profile from 1870 onwards while lutein reached peak concentration in the 1920s. Mc Gowan *et al.,* (2012) reported similar concentrations of chlorophyll *b* for both basins of Windermere Lake in the late 1940s. The peak in lutein and increases in β-carotene and chlorophyll *b* in the 1920s may related to the small peak in TN and TP.

So therefore the premise for this period is that catchment activities may have been reduced due to a reduction in population however continued land use was now more effectively impacting the shallower Gur as its nutrient loading capacity was reduced. Small increases in OM and geochemical measurements and increases in some algal pigments towards the mid-1900s suggest productivity was increasing in Lough Gur and bouts poor water quality may have persisted.

### 6.4.3 1950s – Present

After the mid-1900s, Ireland experienced rapid economic and social growth. Farming practices became specialised and mechanization began to take hold. Events such as the First World War (1914-1918) the and Second World War (1939-1945) led to greater government intervention in farming including protecting farmer's incomes by the means of guaranteeing prices (Bell and Watson, 2008). Following Ireland's accession to the EU in 1973, farming processes of specialisation and intensification were adopted resulting in increased agricultural activity across the country (Crowely *et al.,* 2008). Farmers became more reliant on external inputs such as mechanical farm equipment and chemical fertilisers in order to meet demand for produce. These chemical fertilisers often consisted of N or P being added to the soil to increase growth. Between 1950 and 1990, the average P soil value increased by 900% which has led to an accumulation of P in Irish soils (Tunney, 1990). This saturation of P in soils can lead to both surface and groundwater contamination (Brogan *et al.,* 2001) and when N and P accumulate in lakes it can lead to increased autochthonous growth and internal sediment loading (Smol, 2008). From the 1950s onwards Ireland also witnessed a trend of counter urbanisation take hold (Gkartzios and Scott, 2013). People opted to move from urban areas to more scenic rural locations giving rise to increased demand for detached rural housing. Between 1951 and 2011, the population of Limerick grew from 141,239 to 191,809 (Central Statistics Office, 2017). This population increase combined with counter urbanisation may have resulted in an increase in the population of the Maigue River rural catchment. The Lough Gur visitor centre and toilet facilities were built in 1981 which would have attracted more visitor numbers.

Substantial increases in %LOI of Lough Gur sediment cores signify an increase in the deposition of organic matter from 1950s onwards. Parallel gradual increases in TN and TP are also evident from 1950-1990 (Viaene, 2015) . This increasing trend of %LOI is in line with that of the majority of lakes studied during this period. For example, Taylor *et al.,* (2006) reported that five of six lakes in Ireland examined for %LOI show increasing trends from the 1950s onwards which was ascribed to nutrient enrichment from catchment disturbance, in particular Mullagh Lake, a highly eutrophic lake displays results similar to Lough Gur with %LOI increasing to >45% in the 1990s into the 2000s. Both basins of Windermere Lake recorded increases in %LOI from 1950 to 2000s, however levels are only half those measured in Lough Gur, and is probably representative of deep basins and larger surface areas (Mc Gowan *et al.,* 2012). Gąsiorowski, (2008) demonstrated increasing trends in %LOI from 1950s onwards and attributed this to anthropogenic eutrophication caused by the high (>80%) agricultural land use. Lough Gur's increasing OM could be due to increases in both autochthonous and allochthonous materials. Due to the small and enclosed nature of the lake it is most likely from autochthonous sources, however further analysis to determine sediment provenance would be useful in future palaeolimnological investigations of Gur.

The majority of algal pigments illustrate an increasing trend in concentrations from 1950 to the core surface. Concentrations of Total Algae (β-carotene, Chlorophyll *a* and Pheophytin *a*) indicators of overall algae production show increases with β-carotene in particular reaching sustained elevated concentrations throughout the 1950s-1970s. Mc Gowan *et al.,* (2012) presented similar increases of β-carotene concentrations for the same period in the north basin of Windermere Lake. Concentrations in Lough Neagh, a lake found to be nutrient enriched due to excessive loading of N and P from agricultural activities were slightly lower for the same period but similarly displayed an increasing trend up core (Bunting *et al.,* 2007). Concentrations of chlorophytes chlorophyll *b* and lutein are also high in the 1960s. Concentrations of chlorophyll *b* and lutein resemble concentrations found in Milltown Lake from 1970-1990 however after this Milltown lake exhibits much higher concentrations possibly due to larger amounts of nutrients entering the lake as a result of its larger catchment size. Contemporary lake investigations of phytoplankton's response to nutrient enrichment reported increases in chlorophytes as a characteristic of nutrient enriched in lakes (Cottingham and Carpenter, 1998). No obvious changes in OM, geochemical or algal pigment concentrations is evident after the construction of the visitor centre and toilets in the early 1980s possibly suggesting that it did not have an impact on lake water quality at this time.

Throughout the 1990s and into the 2000s, Ireland's social and economic growth continued to accelerate. Urban areas grew faster than that of any other European state at a rate of 3.1% per annum (European Environment Agency, 2005), while the trend of counter urbanisation persisted across Ireland resulting in even more rural houses being built. The lack of sewer networks in rural areas meant that the use of onsite septic tanks was required to clean waste water and in 2004 it was estimated that over 400,000 households nationally were using onsite septic tanks to treat their waste water (EPA, 2004). Previous studies have highlighted the ineffectiveness of septic tanks to deal with waste in an effective manner and have suggested that many only transform organic P into inorganic P with consequences for runoff waters and aquatic ecosystems (Dudley and May, 2007; European Environment Agency, 2005). In 2007, a total of 83 residential dwellings were identified in the 3.7km$^2$ surface water catchment with P loading calculated at 0.3kg per day from the accumulative households (LCC, 2009). Twelve houses were surveyed directly to the south of Lough Gur on account of the extreme vulnerability to contamination of bedrock aquifers in this area. All 12 septic tanks were found to be noncompliant with statutory regulations and it was suggested septic tanks be either replaced or improved (LCC, 2009).

In the late 1990s agricultural activities continued to apply inorganic sources of P to soils through fertilisers and increased organic P through slurry spreading. The effects of this P overload were linked to eutrophication of freshwaters (Ulén *et al.,* 2007). Ireland aimed to reduce P fertiliser application per unit area from 138,000 tonnes in 1981 to 115,000 tonnes in 1999 (European Commission, 2002). Despite efforts to reduce the use of P it has continued to remain high in the soils as other organic sources of P enter from agricultural waste, slurries and grazing animals defecating (Brogan *et al.,* 2001). In 2010, Teagasc, a semi state body responsible for agricultural food industry reported that 32% of 32,874 soil samples analysed from grazed land across Ireland had P concentrations which exceeded agricultural requirements (Lalor *et al.,* 2010). The vast majority of land (98.3%) in the Camouge catchment is used for agricultural purposes. This land use can contribute to diffuse nutrient pollution through land spreading of fertilisers and organic manure as well as point sources of pollution from farmyards (Langford and Gill, 2016). The Lough Gur Environmental Management Study, (2009) states that the P loading to soil from the 17 farms in Lough Gur catchment was enough to contribute to the nutrient enrichment of the lake.

In 2009, Lough Gur's potential to attract tourists was revisited in the Lough Gur Environmental Management Study and in an attempt to revive local communities, promote tourism and further protect the lakes heritage, the Lough Gur visitor centre was refurbished and reopened in 2013. The Lough Gur visitor centre septic tank which was reported to pose a direct threat to groundwater has reportedly been decommissioned since 2013 and effluent is now tankered off site (Langford and Gill, 2016). This may help reduce the waste water entering the lake system, however the exact nature of the works carried out are unknown and it may still pose a threat if it was not correctly decommissioned. Visitor numbers have increased substantially from 2,800 in 2006 to 135,000 in 2016 with 45,000 recorded entering the heritage centre. Attracting tourists is good for the promotion of the heritage of Lough Gur, however uncontrolled conventional tourism has been cited as a threat to many natural areas worldwide including causing nutrient enrichment of lake environments (Dokulil, 2014).

Sediment maxima in OM and algal pigment concentrations occurs from 2000. Pigment concentrations are often high in the surface sediments and have been attributed to both preservation and environmental conditions (Leavitt, 1993). Concentrations of six algal pigments increase dramatically during the 1990s and peak c. 2000 which is further demonstrated by a peak in the PCA scores (Figure 6.1). Chlorophyll *a* and pheophytin *a* reach maximum concentrations in this period possibly due to the increase in nutrients suggested by the high concentrations of N and P (Viaene, 2015). However, concentrations of both pigments are significantly less that those observed in both Windermere Lake and Milltown lake for the same period (Mc Gowan *et al.,* 2012; Carson *et al.,* 2014). In contrast lutein begins to decrease. The exact cause of the decrease is unknown but it has previously been attributed to natural variations in the algal community composition rather than preservation issues as lutein is a very stable pigment used in many palaeolimnological studies (Hall *et al.,* 1997; Leavitt and Hodgson, 2001; Carson *et al.,* 2014). Two other pigments with similar stabilities, fucoxanthin and diatoxanthin also diverged during this time with concentrations of fucoxanthin spiking as diatoxanthin declines. This decline in diatoxanthin, an indicator of siliceous algae, may have been due to a number of environmental factors for example temperature change, salinity, silica depletion and pH levels (Barker, 1992b; Gibson *et al.,* 2000; Ryves *et al.,* 2006; Flower and Ryves, 2009). Previous studies on Lough Neagh and Milltown lake have suggested it might be the result of biogenic silica ($SiO_2$) limitation, as increases in algal blooms are initially driven by P increases but a reduction in $SiO_2$ due the algal blooms reduces diatom production thereafter (Gibson *et al.,* 2000; Carson *et al.,* 2014). Lough Gur could therefore be following a similar series of events with initial increasing P concentrations driving diatom growth but Si depletion restricting it thereafter. The poor fossil diatom preservation discovered in Lough Gur sediments was unforeseen. The impoverished diatom flora is a further indicator of unique local conditions potentially related to the unique site hydrology, high alkalinity and may also potentially be attributed to $SiO_2$ limitation. Further analysis is required to help derive a conclusion on the matter. Fucoxanthin contrarily, displays a peak in concentrations in the 1990s. Similar concentrations and peaks are evident in Milltown Lake (Carson *et al.,* 2014) and Windermere Lake (Mc Gowan *et al.,* 2012) during the same period.

Concentrations of phaeophorbide *a* and the cyanobacteria echinenone spike during the 1990s suggesting that nutrient availability in Gur may have increased in this recent period. Increasing concentrations of echinenone are similar to those observed in both basins of Windermere Lake for the same period. An increase in Chl a:pheophytin ratio during the 1990s indicates improved pigment preservation, and is often observed when algal production increases (Leavitt, 1993).

The increase in OM and algal pigments in the surface sediments also coincides with a spike in K, and further increases in TN and TP throughout the 1990s and into the 2000s (Viaene, 2015). These increases are probably the result of increased agricultural and human activities in the catchment in the last 30 years. The co-limiting nutrients nitrogen and phosphorus have been shown to be the main controlling factors in algae growth (Yang *et al.,* 2008; Xu *et al.,* 2010). Therefore, the increased concentrations of these elements coinciding with increased fossil algal pigments concentrations from the 1950s onwards, and subsequent rise in OM deposition all suggest a sediment signal of nutrient enrichment. The relationship between the availability of limnetic N and P and increased algal growth has been well established in previous studies (Waters *et al.*, 2005; Ulén *et al.,* 2007). It is likely that the increases in water column N and P in Lough Gur during the 1990s created optimum conditions for increased algal growth which resulted in increasing deposition of Total Algae fossil pigment and incorporation of N and P in the sediment record in the 1990s and into the 2000s. This recent peak is in P is also recognised in the lake water monitoring data (Limerick County Council) as average levels of P were found to be elevated between 2004 and 2016.

# CHAPTER 7 CONCLUSION

The intensification of lake eutrophication events around the world has been attributed to increased human activities in catchments. The predominant cause is increase in agricultural activities which give rise to increased amounts of N and P entering surface and ground water through both point and diffuse pollution. Lough Gur is one example of a range of Irish lakes that have demonstrated signs of eutrophication in recent years raising concerns over water quality. Lough Gur provided the opportunity to examine a unique lowland shallow lake system that has been classed as hypereutrophic in recent water quality monitoring programmes. The lakes unique morphological and hydrological characteristics appear to make it prone to internal loading and the lack of a surface water in-flow restricts flushing of nutrients. The construction of an artificial outlet in 1847 reduced the size and depth of the lake potentially affecting the ecological balance.

Our study aimed to reconstruct historical trends in Lough Gur's water quality and identify onset and timing of periods of increased productivity from sediment core data. This research aimed to situate the current poor lake quality in a historical palaeolimnological context. Our palaeo-data demonstrates that Lough Gur has a complex nutrient history with evidence of both natural and anthropogenic nutrient loading. The timing of change in sediments has been verified to an extent by $^{210}Pb$ dating of two sediment cores which was based on low radionuclide concentrations. An approximate chronology with a basal date of 1650 at 50 cm was adopted based on its higher radionuclide concentrations and also its appropriateness to lithological, biological and geochemical signals. The chronology estimated a low SAR, which was surprising given the lakes current enriched status but which possibly reflects Lough Gur's shallow depth, groundwater inputs and small surface catchment area. Before the 1950s OM content and geochemical measurements suggest that periods of potential natural nutrient loading did occur. Fossil algal pigments display variable concentrations indicating the lake was productive while high levels of cyanobacteria zeaxanthin and canthaxanthin are suggestive of earlier periods of poor water quality. Synchronous change in all proxies however was greatest from the 1950s onwards. Increases in algal pigments particularly Total Algae coincides with a parallel increase in geochemical measurements including TN and TP while OM content rose by 20% from 1950-2000. A distinctive peak in OM and algal pigments is evident c.2000 and is coincident with continued increases in sediment TN and TP. Increased availability of N and P originating from diffuse anthropogenic sources in the surrounding catchment such as residential development, tourism and agricultural activities are potential drivers. Taylor *et al.,* (2006) demonstrated that productive lakes in Ireland often have complex, locally specific and often long histories of enrichment which appears to be the case in Lough Gur. It is also important to note that this study was not a straightforward sediment reconstruction. The study demonstrated issues in establishing a sediment chronology and encountered poor sediment diatom preservation thus complicating the inferred history of Lough Gur.

The WFD initiated investigation into the identification of reference conditions for lakes around Ireland and in the EU. The aim was to use reference condition to define an appropriate set of goals to be met for future conservation and restoration management policies (Dearing, 2013). Lough Gurs complex hydrology means that it is difficult to identify the diffuse source of pollutants and thus even harder to tailor prevention or mitigation measures. A possible reference condition for Lough Gur could be suggested as any time before the 1950s as the most substantial anthropogenic nutrient loading appears to have occurred after this, however this may only succeed in reverting the lake back to a eutrophic state. Future conservation efforts at Lough Gur must acknowledge that lake responses to human influences are complex and multidimensional meaning some lakes may never fully return to reference conditions (Whitmore and Riedinger-Whitmore, 2014). Future management policy must recognise that the higher the trophic state of a lake the faster it will react to increased nutrient loading and the slower it will respond to limiting nutrient load (European Commission, 2002). Previous studies of shallow European lakes reported recovery times of 10 to 20 years after external loading was reduced (Sondergaard *et al.,* 2001; Schindler, 2006b). It will also be important that future climate change will need to be accounted for in lake management decisions. It is expected that climate change will exacerbate eutrophication events in mesotrophic and eutrophic lakes as a result of physio-chemically and biologically induced higher internal loading (Jeppesen *et al.,* 2014). Our study shows that there is a need for careful nutrient management if increased human activities and improvement in water quality in Lough Gur are to develop in harmony.

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# APPENDIX 1

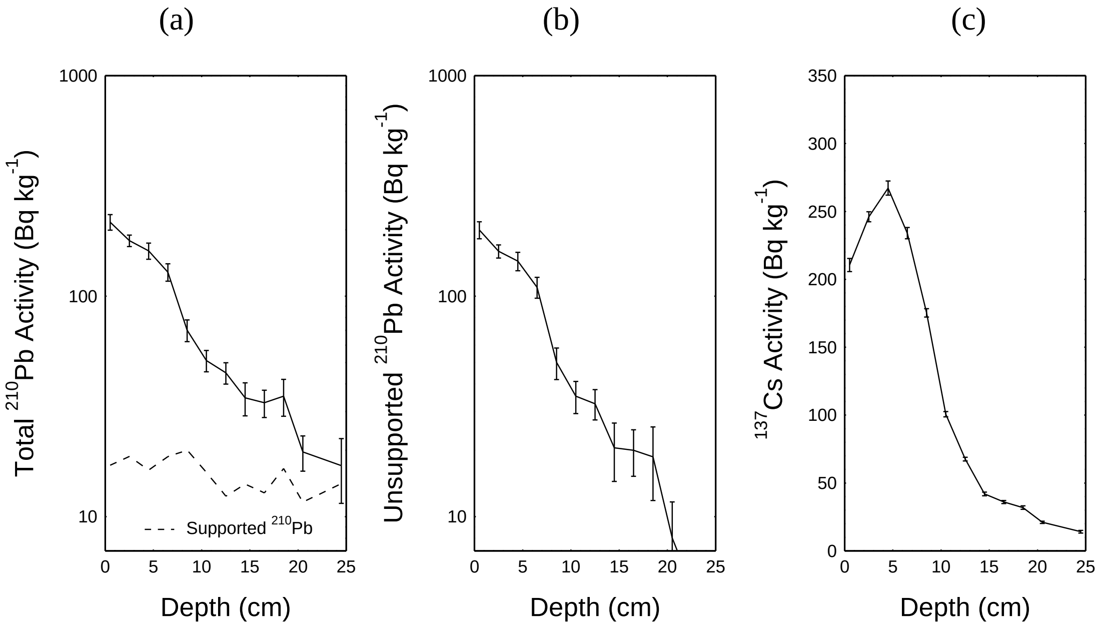


Figure 1. Fallout radionuclides in the Lough Gur sediment core showing (a) total and supported $^{210}$Pb, (b) unsupported $^{210}$Pb and (c) $^{137}$Cs concentrations versus depth.

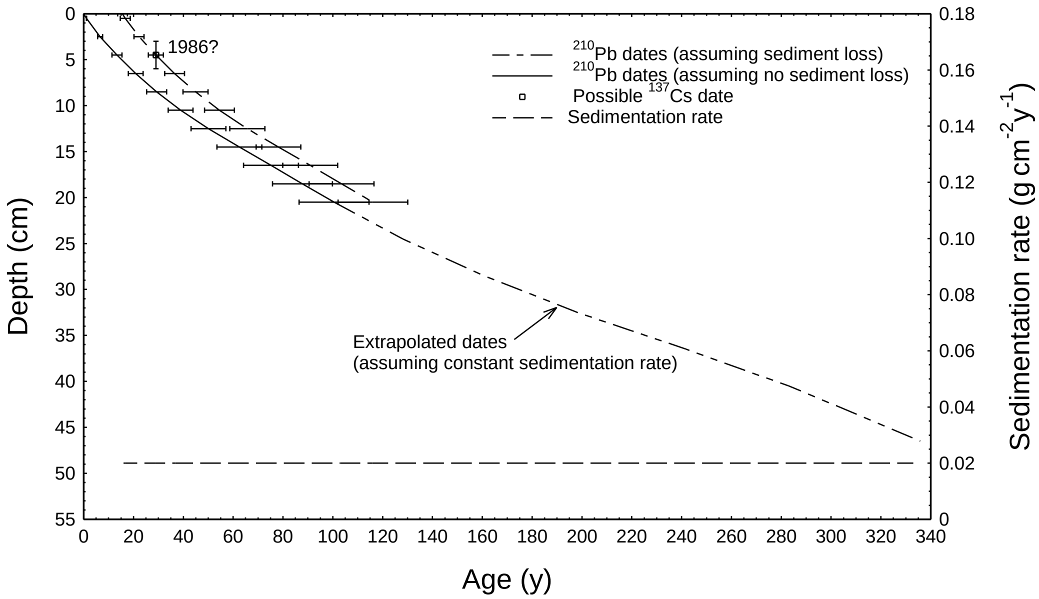


Figure 2. Radiometric chronology of the Lough Gur sediment core showing the possible 1986 depth suggested by the $^{137}$Cs record, the $^{210}$Pb dates and sedimentation rates assuming both a small loss of sediment from the top of the core consistent with the possible $^{137}$Cs date, and also the $^{210}$Pb dates assuming no sediment loss and that the core is intact. Also shown is an extrapolation of the $^{210}$Pb chronology assuming no sediment loss and a constant (dry mass) sedimentation rate.

## APPENDIX 2

Table 1. $^{210}$Pb concentrations in sediment core GURL taken from Lough Gur.

| Depth | Dry Mass | Pb-210 | | | | | | Cum Unsupported | |
|---|---|---|---|---|---|---|---|---|---|
| | | Total | | Supported | | Unsupp | | Pb-210 | |
| cm | g cm$^{-2}$ | Bq Kg$^{-1}$ | ± | Bq Kg$^{-1}$ | ± | Bq Kg$^{-1}$ | ± | Bq m$^{-2}$ | ± |
| 0.5 | 0.0211 | 139.78 | 39.63 | 55.26 | 9.52 | 84.52 | 40.76 | 17.8 | 6.1 |
| 2.5 | 0.1149 | 142.31 | 26.39 | 29.97 | 6.89 | 112.34 | 27.27 | 109.5 | 27.4 |
| 4.5 | 0.2013 | 103.09 | 33.17 | 39.86 | 8.32 | 63.23 | 34.2 | 183.3 | 37.8 |
| 6.5 | 0.287 | 124.53 | 16.12 | 14.74 | 3.87 | 109.79 | 16.58 | 255.6 | 46.2 |
| 7.5 | 0.335 | 111.66 | 15.95 | 44.02 | 4.54 | 67.64 | 16.58 | 297.4 | 47.2 |
| 8.5 | 0.3829 | 115.31 | 17.65 | 30.96 | 4.52 | 84.35 | 18.22 | 333.7 | 48 |
| 9.5 | 0.4532 | 90.9 | 9.21 | 15.79 | 2.39 | 75.11 | 9.52 | 389.7 | 49.2 |
| 10.5 | 0.5236 | 65.35 | 13.55 | 18.4 | 4.62 | 46.95 | 14.32 | 431.8 | 49.8 |
| 11.5 | 0.6194 | 46.12 | 8.19 | 14.68 | 2.17 | 31.44 | 8.47 | 468.9 | 51.1 |
| 12.5 | 0.7152 | 52.74 | 8.1 | 17.01 | 2.22 | 35.73 | 8.4 | 501 | 51.8 |
| 13.5 | 0.8244 | 28.89 | 8.42 | 12.51 | 1.92 | 16.38 | 8.64 | 528.1 | 52.6 |
| 14.5 | 0.9335 | 33.39 | 7.8 | 17.74 | 1.83 | 15.65 | 8.01 | 545.6 | 53.4 |
| 15.5 | 1.0579 | 39.8 | 7.28 | 14.67 | 2.39 | 25.13 | 7.66 | 570.5 | 54.3 |
| 16.5 | 1.1824 | 26.22 | 7.49 | 19.05 | 1.97 | 7.17 | 7.74 | 588.3 | 55.1 |
| 17.5 | 1.3133 | 18.05 | 6.39 | 11.79 | 2.21 | 6.26 | 6.76 | 597.1 | 56 |
| 19.5 | 1.5874 | 17.86 | 5.85 | 14.77 | 2.03 | 3.09 | 6.19 | 609.4 | 58.1 |

Table 2. Artificial fallout radionuclide concentrations in core GURL.

| Depth | Cs-137 | | Am-241 | |
|---|---|---|---|---|
| cm | Bq Kg$^{-1}$ | ± | Bq Kg$^{-1}$ | ± |
| 0.5 | 194.28 | 9.41 | 0 | 0 |
| 2.5 | 218.3 | 7.51 | 0 | 0 |
| 4.5 | 181.36 | 8.12 | 0 | 0 |
| 6.5 | 205.12 | 4.88 | 0 | 0 |
| 7.5 | 230.68 | 4.9 | 0 | 0 |
| 8.5 | 220.32 | 4.91 | 0 | 0 |
| 9.5 | 184.91 | 2.95 | 0 | 0 |
| 10.5 | 166.87 | 5.03 | 0 | 0 |
| 11.5 | 110.23 | 2.24 | 0 | 0 |
| 12.5 | 111.82 | 2.49 | 0 | 0 |
| 13.5 | 59.84 | 1.9 | 0 | 0 |
| 14.5 | 70.31 | 1.97 | 0 | 0 |
| 15.5 | 56.28 | 2.19 | 0 | 0 |
| 16.5 | 38.39 | 1.55 | 0 | 0 |
| 17.5 | 33.05 | 1.74 | 0 | 0 |
| 19.5 | 0 | 0 | 0 | 0 |