REGIONAL SYNTHESIS OF ALGAL COMMUNITY CHANGE IN THE LAKES AND TARNS OF THE WINDERMERE CATCHMENT, LAKE DISTRICT, UK, SINCE THE 19TH CENTURY

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ABSTRACT

The rural Windermere catchment, English Lake District, UK comprises 11 upland and lowland lakes which feed into Windermere, England's largest lake. Palaeolimnological algal records, alongside long-term climate and catchment land use monitoring data from all basins in the catchment were used to quantify the relative importance of regional and local-scale drivers of algal community change. Like many temperate lakes, Mann-Kendall trends showed increased concentrations of total algal production and cyanobacteria accompanied by declines in C/N ratios across the Windermere catchment over the last few centuries. Regression tree analyses suggest that nutrient enrichment has an overarching effect, with temperature playing a secondary role. Synchrony and breakpoint analyses suggested that local forcings led to catchment-wide asynchrony of algal communities after the 1950s. In the lowlands (<100 m.a.s.l), 20th century wastewater treatment installation explained the greatest changes in the algal communities, overriding agricultural intensification, but at sites without point sources, correlations to variables that indirectly explain sewage expansion such as resident catchment human populations were apparent. In contrast, algal community change in upland lakes was more responsive to atmospheric pollutants which caused acidification in the late 19th and early 20th century, alongside climatic variables notably temperature. Evidence for upland atmospheric nitrogen deposition in the 20th century was suggested by decreasing stable $\delta^{15}N_{org}$ isotope values, concurrent with increased concentrations of Chlorophyll *a* (from all algae) but no clear response was found in algal compositional changes. Higher algal community change occurred in lakes with longer residence times overlaying sedimentary geologies typically in the lowlands. However, algal community change was also high in lowland lakes with lower residence times that had point sources, suggesting centennial-scale fertilisation had reduced the ability of local lake characteristics to attenuate environmental change. This work demonstrates that lakes within a few kilometres of one another respond uniquely to environmental change depending on physical characteristics and landscape position. Management measures should focus on reducing nutrients from wastewater effluent and develop local stewardship programmes to increase environmental awareness in the region.

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LIST OF ABBREVIATIONS

1. Site abbreviations

BT…. Blea Tarn
BLE…. Blelham Tarn
CT…. Codale Tarn
EAS…. Easedale Tarn
ELTIN…. Elterwater inner basin
ELTMID…. Elterwater middle basin
ELTOUT…. Elterwater outer basin
EST…. Esthwaite Water
GRA…. Grasmere
LLT…. Little Langdale Tarn
LOU…. Loughrigg Tarn
RYD…. Rydal Water
STI…. Stickle Tarn
WNB…. Windermere north basin
WSB…. Windermere south basin

2. Other abbreviations/formula

Al…. Aluminium
BVG…. Borrowdale volcanic group
C…. Carbon
CA:LA…. Catchment area to lake area ratio
CH_4…. Methane
Chl. a…. Chlorophyll *a*
Chls…. Chlorophylls
CO_2…. Carbon dioxide
C/N ratio…. Carbon to nitrogen ratio, in weight %
CRS…. Constant rate of suppy model
CyanoHABs…. Cyanobacterial harmful algal blooms
DI-TP…. Diatom inferred total phosphorus
DO…. Dissolved Oxygen
DOC…. Dissolved organic carbon

DOM…. Dissolved organic matter
DIC…. Dissolved inorganic carbon
DIN…. Dissolved inorganic nitrogen
GHGs…. Greenhouse gases
H^+…. Hydrogen ions
HABs…. Harmful algal blooms
LDNPA…. Lake District National Park Authority
RT…. Regression trees
N…. Nitrogen
N_2O…. Nitrous oxide
NAO…. North Atlantic Oscillation
NH_4…. Ammonium
NO_3…. Nitrate
NOx…. Nitrogen oxides
NPP…. Net Primary Productivity
OM…. Organic matter
PDA…. Photodiode Array
PVE…. Percentage variance explained
TDN…. Total dissolved nitrogen
TP…. Total phosphorus
TN…. Total nitrogen
r…. Pearson’s correlation coefficient
S…. Synchrony
SAR…. Dry bulk sediment accumulation rate
SIL…. Silurian flags and slates
SO_2…. Sulphur dioxide
SRP…. Soluble reactive phosphorus
SPP…. Species
SSD…. Sum of squared Euclidean distances
P…. Phosphorus
UV…. Ultraviolet radiation
WCRP…. Windermere catchment restoration programme
WFD…. Water Framework Directive
WHO…. World Health Organisation
WRT…. Mean water retention time

95% CI….95% confidence interval

^{210}Pb….lead-210 radioisotope

$\bar{x}$…. Mean

$\delta^{15}N_{org}$…. Ratio of ^{15}N:^{14}N in bulk organic matter

$\delta^{13}C_{org}$…. Ratio of ^{13}C:^{12}C in bulk organic matter

%LOI…. Percentage loss-on-ignition

CHAPTER 1. INTRODUCTION. PAST, CURRENT AND FUTURE STRESSORS ON LAKE ECOSYSTEMS

This chapter provides the background on the current state of lake ecosystems globally and the rationale for the use of catchment-scale investigations when assessing the multiple spatial and temporal scales of past environmental change.

1.1 The importance of lakes as ecosystem service providers

Freshwater ecosystems possess the highest relative species richness in comparison with terrestrial and marine ecosystems (Table 1.1), and contain approximately 21% of global surface water (Gleick, 1989). Lakes are integral components of the hydrological cycle and are highly connected to and influenced by their surrounding catchment (Gleick, 1989). Lakes cover more than 4.2 million km^2 worldwide, and in the UK there are 44,000 lakes and ponds larger than 0.1 ha (Hughes *et al*., 2004). Lakes are composed of three zones: the benthic, pelagic and littoral zones. These zones are closely-coupled and linked to their surrounding terrestrial landscape, making the biota found within lake ecosystems evolutionarily and ecologically unique (Schindler and Scheuerell, 2002).

Table 1.1 Species richness of ecosystems. Modified from McAllister *et al*., (1997).

Ecosystem	**% of Earth's total habitat ecosystem occupies**	**% of known species* each ecosystem contains**	**Relative species richness****
Freshwater	0.8	2.4	3.0
Terrestrial	28.4	77.5	2.7
Marine	70.8	14.7	0.2

*Sum does not add to 100% as 5.3% of known symbiotic species are excluded.

** Calculated as the ratio between the % of known species and the % of area occupied by the ecosystem.

Ecosystem services are the direct, marketable, or indirect, non-marketable, benefits ecosystems provide to humans (Wilson and Carpenter, 1999). Lakes provide a suite of ecosystem services including provision of marketable products such as drinking water and fisheries, and non-marketable services such as being receptors of urban and industrial effluent (Krauze and Wagner, 2007). During the 20th century, the global population quadrupled, the area of agricultural land use doubled, and water use increased nine times (McNeill, 2000). These factors have led to substantial declines in the ability of lakes to provide ecosystem services such as environmental security and water quality. It has also led to increased extinction rates of freshwater flora and fauna at a substantially greater rate than that of terrestrial ecosystems (Ricciardi and Rasmussen, 1999; Krauze and Wagner, 2007).

One of the most important regulatory services provided by lakes is carbon (C) storage. Lakes can store an estimated 30 to 70 Tg of organic C yr^{-1}, not much less than ocean burial at 120-140 Tg organic C yr^{-1}, although their role in the C cycle has received relatively little attention (Downing *et al.*, 2008; Cole, 2013). Most lakes are over-saturated with carbon dioxide (CO_2) and are therefore net CO_2 sources, releasing an estimated ~0.9 Pg C yr^{-1} (range 0.7–1.3). CO_2 is released from both *in situ* oxidation of terrestrially-derived dissolved organic carbon (DOC) and C broken down in terrestrial soils that enters lakes directly as CO_2 (Maberly *et al.*, 2013). Future catchment management and climate change could modify the role lakes play in the global C cycle due to the high connectivity between lakes and their surrounding landscapes (Maberly *et al.*, 2013). Therefore, it is important to understand the complex interactions between lakes and their surrounding catchments.

Lakes provide a wide variety of supporting services such as nutrient cycling and primary production. However, post-industrial anthropogenic activity has led to grossly elevated loadings of nitrogen (N) and phosphorus (P) to freshwaters, changes in nutrient retention and shifts to turbid phytoplankton-dominated systems, which can modify higher trophic level species (Elser *et al.*, 2007). The increase in lake primary production in the early 21st century costs $2.2 billion annually in the USA alone, from losses to commercial fisheries and recreation (Dodds *et al*., 2009). Recovery periods from eutrophication in lakes are typically between 10-20 years, although internal nutrient loading can delay abiotic recovery (Jeppesen *et al*., 2005). Additionally, biological recovery can be much more variable depending on the taxa in question (Verdonschot *et al*., 2013).

Lakes also provide important cultural services. The English Lake District was at the heart of the English romanticism movement in the 18th and 19th centuries, which led to increased tourism in the area in the latter half of the 19th century (Squire, 1988). The 19th century poet William Wordsworth found fame through his descriptions of the region's landscape, while Beatrix Potter's novels attracted adults and children alike to visit the settings of these works (Iwashita, 2006). Their cultural heritage remains and continues to attract visitors from all over the world. Presently, sports events such as the Great North Swim which takes place in Lake Windermere are also major visitor attractions to the region.

Lake management is complex due to multiple stakeholder involvement in the ecosystem services lakes provide and the influence from upstream drainage networks, their surrounding catchments, riparian zones and downstream reaches (Dudgeon *et al*., 2006). Some of the threats to lake ecosystems are discussed in the following section.

1.2 Anthropogenic stressors on lake ecosystems

A natural or anthropogenic stressor is an abiotic or biotic variable which exceeds its normal range and adversely effects individual or population performance in a statistically significant way (Auerbach, 1981). Understanding current and historical stressors of lake ecosystems can provide an appreciation of processes and mechanisms involved in ecological disturbance (Keatley *et al*., 2011). The transfer of energy, water and dissolved substances to the sediments of a lake basin effectively integrates ecological and environmental information from the lake and its catchment into the deposits. As such, lakes are important sentinels of environmental change (McGowan and Leavitt, 2009).

Anthropogenic catchment changes, particularly deforestation and agriculture, have modified lake ecosystems in northern Europe for over 1,000 years, (Keatley *et al.*, 2011). For example, in the English Lake District humans have been extensively modifying lake catchments since the 9th and 10th centuries when Norse invaders first cleared large areas of forest and introduced sheep grazing (Pearsall and Pennington, 1947). Holocene climatic variations occurred alongside human development, with the Medieval Climate Anomaly (~1000-1300AD) and Little Ice Age (~1350-1850AD) modifying energy transfer and interacting with nutrients introduced by anthropogenic activity (Dong *et al.*, 2011). Resultant changes in Holocene catchment vegetation and lake ecology have been identified in pollen and algal assemblages in lake sediment records (Pearsall and Pennington, 1947; Dong *et al.*, 2011). This provides evidence to support the notion that centennial-scale human influence on European lakes explains their current higher trophic status relative to that of North American temperate lakes where agricultural changes are much more recent (Keatley *et al.*, 2011). It also explains the high rates of C-burial in European lowland lakes from centuries of fertilisation and increased eutrophy in recent decades (Anderson, 2014). This highlights the importance of recognising baseline conditions when assessing extent of change and the historical context of the region in question.

Late 19th century global modifications of the water and biogeochemical C, N and P cycles followed the invention of the coal powered steam engine in the late 18th century and modified lake ecosystems on a scale not previously seen (Wolfe *et al.*, 2013). Increased combustion of fossil fuels led to rising emissions of atmospheric greenhouse gases (GHGs) and reactive N compounds (Steffen *et al.*, 2011). This epoch (from c.1800AD onwards) has being widely termed the "Anthropocene" because of the distinct stratigraphic boundaries in stable isotope compositions and palaeobiological markers in lacustrine deposits formed as a result of changes to global biogeochemical cycles (Wolfe *et al.*, 2013). These changes have had detrimental impacts on inland waters (Figure 1.1). During the period after World War II, termed the "Great Acceleration" (sensu Steffen *et al.*, 2007), the global imprint of human activity increased markedly. A rapidly growing global population and technological advances drove further increases in fossil fuel consumption during this time (Steffen *et al*., 2011). This culminated in greater environmental change and substantial losses to global biodiversity via the enhanced efficiency and rate at which humans converted natural ecosystems to human-dominated landscapes (MEA, 2005; Steffen *et al.*, 2011). Anthropocene syndromes and drivers of lake ecosystem change are discussed in more detail in sections 1.2.1-1.2.7.

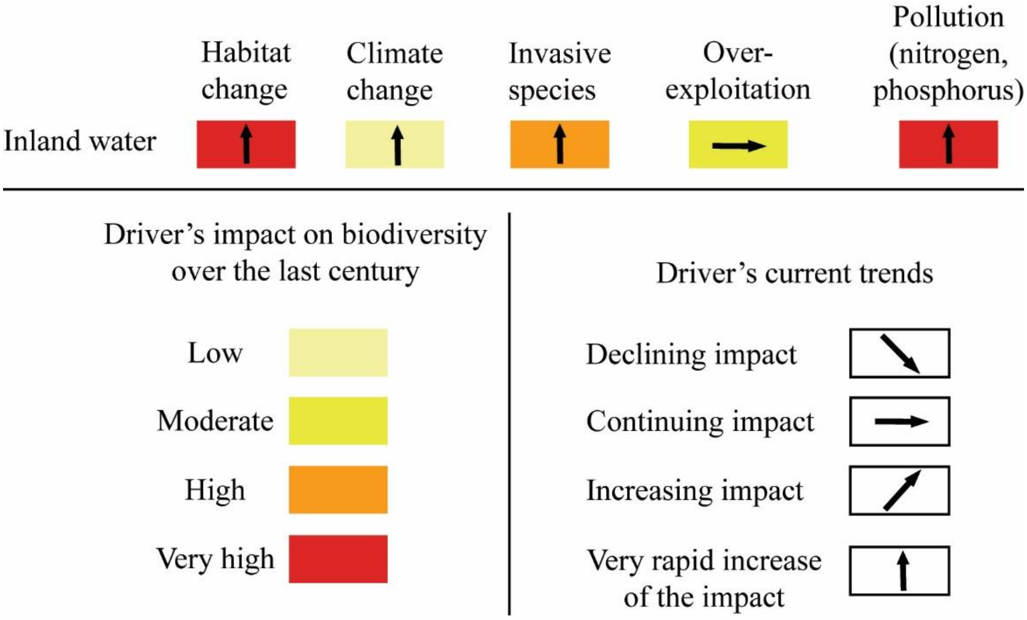


Figure 1.1 Main drivers of global inland water biodiversity and ecosystem change. Taken from the Millennium Ecosystem Assessment (2005).

1.2.1 Eutrophication

The Redfield ratio implies that phytoplankton require C:N:P in a ratio of 106:16:1 for optimal growth (Redfield, 1958). Although interspecific and spatial variance has been found around these values, the Redfield ratio still provides a useful metric to study nutrient stoichiometry (Sterner *et al*., 2008). N and P are in relatively short supply so addition of either of these nutrients enhances productivity and disrupts nutrient stoichiometry and so, the Redfield ratio, which then results in different primary producer communities.

Eutrophication is the fertilisation of waterbodies with N or P that leads to increased photosynthetic organic matter (OM) or algal blooms. Respiration of algal blooms at night and aerobic respiration of microbes that degrade phytoplankton OM can result in either hypoxia or anoxia which suffocate higher aerobic organisms or increase stress and susceptibility to parasitism, respectively (Paerl *et al*., 2001). In the UK, total damage costs of eutrophication are estimated at £105-160 million yr^{-1} via losses in recreation and further treatments required for potable water (Pretty *et al*., 2003). Recovery from eutrophication can take longer in deeper lakes compared to shallow due to longer hydraulic retention which reduces the flushing of nutrients, as well as potential for stronger stratification and so, internal nutrient loading (Jeppesen *et al*., 2005). However, the extent of nutrient loading is often the most important factor in determining recovery length (Jeppesen *et al*., 2005).

Eutrophication may be both natural and anthropogenic. Natural eutrophication is part of lake ontogeny. As sediments infill a lake basin over thousands of years, the hypolimnion becomes gradually anoxic releasing iron (Fe)-bound P into the water column. This internally released P promotes primary production further and leads to further infilling of the lake (Whiteside, 1983). Anthropogenic, or cultural, eutrophication has accelerated the addition of N and P across the globe over a much shorter timescale than natural eutrophication. Cultural eutrophication became a prominent issue during the “Great Acceleration” as the intensification of agriculture resulted in application of synthetic N and P and animal manures to land to support greater crop and livestock production (Steffen *et al*., 2007). This resulted in enhanced delivery of nutrient-rich runoff and sediment to receiving waters. Similarly, urbanisation and development of road networks increased runoff from urban landscapes, and growing human populations increased the volume of wastewater disposed in lakes. Cultural eutrophication has resulted in severe freshwater biodiversity losses and has reduced the resistance of lakes to other stressors such as climate change and invasive species (Smith, 2003). It has altered biogeochemical cycling through high rates of CO_2 and nitrogen-fixation (N_2-fixation), plus storage and transformations of C, N and P (Vitousek *et al*., 1997).

Nutrient over-fertilisation and stoichiometric imbalances in lakes can lead to harmful algal blooms (HABs) which cause severe water quality degradation and result in toxicity, taste and odour problems (Paerl *et al*., 2001). Although most algal phyla contain some species that cause HABs or nuisance blooms, cyanobacteria are the most common group causing HABs in eutrophied waters (CyanoHABs) (Paerl and Otten, 2013). Cyanobacteria are ancient, cosmopolitan, prokaryotic organisms and are a common group in algal communities. However, increases in biomass and dominance of cyanobacteria have been noted in recent decades and have been attributed to their physiological adaptations to conditions such as large nutrient and temperature gradients (Kosten *et al.*, 2012; Taranu *et al.*, 2012; Beaulieu *et al.*, 2013).

Anthropogenic nutrient disruption can favour CyanoHABs by reducing N:P ratios which promote heterocystous species (ability to fix atmospheric N_2), or by providing chemically-reduced N such as ammonia (NH_4) which increases growth of low-light adapted, but highly toxic, filamentous taxa (Donald *et al*., 2011). The large biomass and size of many CyanoHABs makes them resistant to high grazing pressure (Paerl *et al*., 2001). In addition, algal blooms rapidly deplete nutrients, and subsequent low P concentrations prompt some species to enter vegetative resting stages so populations can quickly develop once more favourable conditions return (Paerl and Otten, 2013). Toxins produced by cyanobacteria include hepato-, cyto-, neuro-irritants and gastrointestinal toxins (Codd, 2000).

Various management measures have been derived to reduce the negative impacts of CyanoHABs. In response to threats to drinking water supplies, the World Health Organisation (WHO) provided guideline values of 1 μg/l for total microsystin-LR, a hepatotoxin produced by species such as *Microcystis*, *Anabaena* and *Oscillatoria* (WHO, 1997). However, guidelines for other toxins and recreational uses are yet to be developed (Codd, 2000).

The average growing season of algal biomass is strongly related to total phosphorus (TP) content. This recognition led to stringent controls of P on point sources and the construction of P-stripping or tertiary treatments at many large wastewater treatment works (WwTW) in North America and Europe (National Resource Council, 1992). However, the ability of lake sediments to re-release P adsorbed to Fe in anoxic conditions and from other processes such as bacterial mineralization of OM led to many lakes having a long "memory" of acute P loads (Hupfer and Hilt, 2008; Paerl, 2014). It has become more apparent that although point P removal has been effective in some areas, external N loading and diffuse P and N additions continue to promote algal blooms.

Removal of N is much more difficult because it is often diffuse in origin and undergoes complex biogeochemical transformations (Paerl, 2014). The continued abundance of N_2-fixing and non-N_2 fixing cyanobacterial blooms further provide evidence that firstly N_2-fixers are not solely determined by P availability (Paerl, 2014). Further, N enrichment can result in P-limitation which necessitates the need for N control (Paerl, 2014). Lastly, N-enhanced primary production leads to degradation of OM which results in regenerated N and P for further algal growth (Paerl, 2014) (Figure 1.2). Thus, management needs to focus on the reduction of both N and P loads, with catchment-scale investigations which are helpful when assessing diffuse nutrient sources to freshwaters (Soranno *et al*., 2009).

1.2.2 Climate change

GHGs released from fossil fuel combustion, notably CO_2, methane (CH_4) and nitrous oxide (N_2O), have led to disrupted global climate patterns and rapidly increasing average temperatures since the Industrial Revolution. The UK has experienced warmer summer temperatures since 1960 and future projections for the north of the UK indicate continued warmer summer temperatures and increased winter precipitation, with water stress more common in the south of the UK rather than the north (METOFFICE, 2015). However, there is uncertainty around future flood risk in the UK due to uncertainties surrounding climate modelling (METOFFICE, 2015).

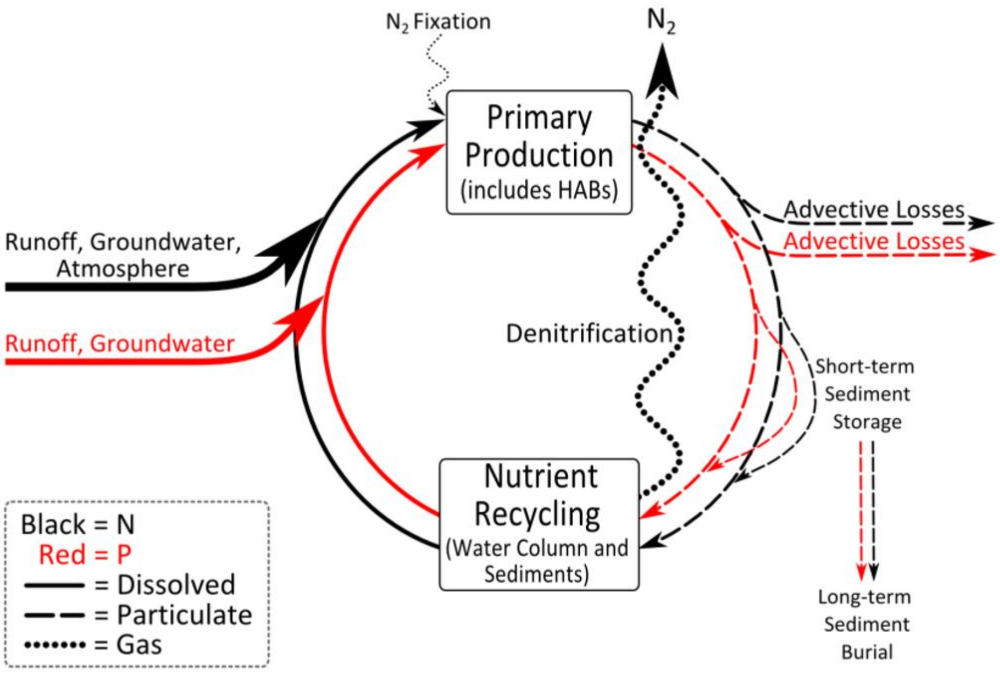


Figure 1.2 Conceptual diagram of N and P inputs, outputs and storage in aquatic ecosystems. Taken from Paerl (2014).

Due to their role in C cycling and their position at the lowest point in their catchments, lakes are important integrators of climate change signals (Williamson *et al*., 2009). Climate change predominantly alters the physical (water level, transparency, stratification, ice cover) and chemical (dissolved organic matter (DOM), nutrients and oxygen delivery and renewal) attributes of lakes which in turn modify biotic community structure, function and geographical ranges (Williamson *et al*., 2009). These responses are amplified by additional stressors such as eutrophication which modify the energy (physical)/mass (chemical) flux ratio (Leavitt *et al*., 2009). As such, un-coupling the effects of gradual, longer-term climate change from recent accelerated nutrient loading is difficult (Taranu *et al*., 2015). Some of the ways in which climate change has been found to modify lake ecosystems are discussed below.

Warming lake temperatures have prolonged thermal stratification, in which temperature differences between the upper epilimnion waters and the lower hypolimnion increases the duration of the thermocline and reduces mixing depth and strength. At Blelham Tarn in the Windermere catchment, UK, prolonged stratification reduced delivery of dissolved oxygen (DO) to the hypolimnion, and thus increased the extent and duration of hypoxic and anoxic zones which can cause stress and death to aerobic organisms (Foley *et al.*, 2012). Anoxia of the hypolimnion has also been found to increase sediment-P release, a process favoured under reduced conditions (Jensen *et al.*, 1992).

In addition, changes to stratification patterns can disrupt algal community composition, with prolonged stratification found to promote CyanoHABs due to their relatively higher temperature growth optima, and their ability to regulate buoyancy and shade out photosynthetic competitors (Figure 1.3) (O'Neil *et al.*, 2012). Thermal stratification has been found to be more important than warming alone in explaining bloom-forming cyanobacterial proliferation (Wagner and Adrian, 2009). Additionally, increased variability of precipitation and storm events predicted in the UK from global climate change (Murphy *et al.*, 2009), could initially prevent bloom-formation from enhanced flushing following heavy rainfall. But the delivery of terrestrial nutrient loading and turbidity once high discharge subsides could subsequently promote shade-adapted CyanoHABs (Paerl and Otten, 2013). Contrastingly, in microcosms mimicking shallow well-mixed lakes, warmer temperatures had little impact on algal communities with no increase in cyanobacteria, but changes to nutrients and fish abundances did (Moss *et al.*, 2003). Thus, lake morphometry plays an important role in "filtering" the effects of temperature increases and thermal stratification.

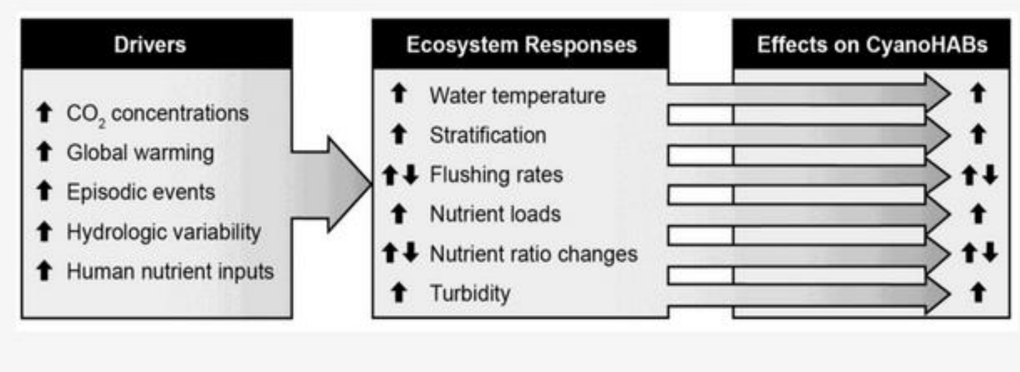


Figure 1.3 Linkage between climate and anthropogenic drivers on CyanoHAB dynamics. Taken from Paerl (2014).

Hydromorphological modifications that increase mean water retention times (WRTs) promote similar responses, and coupled with warmer temperatures enhance the effects of thermal stratification. Cyanobacteria can survive in high pH and low dissolved inorganic carbon (DIC) conditions that result from elevated atmospheric CO_2 levels caused by anthropogenic activity (Qiu and Gao, 2002). Ozone depletion from atmospheric pollutants has increased ultraviolet (UV) radiation that can cause stress and mutations in aquatic communities. Cyanobacteria have UV-screening compounds and an ability to respond and recover from UV damage from ozone depletion (Vincent and Roy, 1993). In conclusion, these prokaryotes have wide environmental tolerances and adaptions that allow them to thrive under multiple stressors and to survive short- and long-term environmental change (Paerl *et al*., 2001). Most research on cyanobacteria has focussed on contemporary datasets, so gaps remain in knowledge about long-term, regional trends in cyanobacterial growth (Taranu *et al*., 2015).

Through temperature and hydrological variability, climate change will alter catchment vegetation structure and attendant OM delivery to lakes. Experiments on upland soils in Cumbria found leaching of DOM increased with warming, followed by rainfall induced export (Tipping *et al*., 1999). Elsewhere in the UK, DOC concentrations in upland lakes have increased, attributed to warming and reversing trends of atmospheric deposition of acidic compounds released from fossil fuel combustion (Evans *et al*., 2005). Coloured lakes i.e. those with higher concentrations of DOM and DOC, attenuate harmful UV-B radiation and so have lower temperature fluctuations and greater water column stability than clear lakes (Snucins and John, 2000).

The impact of climate change on catchment vegetation and cycling of OM as mentioned above, highlights the importance of understanding the role of catchment area:lake area (CA:LA) ratios and land cover type. CA:LA is a usefool tool to understand the chemical composition of a lake (Schindler, 1998). Generally, the larger the catchment and the smaller the lake; the faster the hydraulic renewal and the greater uptake of nutrients by catchment vegetation (Schindler, 1998). Land cover type also alters the chemistry of the receiving water body, with inverse correlations between P-limitation and pasture and N-limitation and rough grazing (Maberly *et al.*, 2003). Thus, CA:LA and land cover type could work synergistically in magnifying and attenuating energy and mass influx from climate change by altering terrestrial-aquatic OM transfer and changing surface runoff chemistry and subsequently lake biotic communities.

Climate change will cause the geographical ranges of species to alter, favouring those species with higher temperature optima and wider temperature ranges. It is therefore predicted that climate change in the UK will favour CyanoHABs and prolong there growing season, particularly in thermally-stratified eutrophic waters (Elliot, 2012). Many studies point to the importance of nutrient management in reducing the effects of climate change (e.g. Jeppesen *et al*., 2009).

Climate change could lead to un-coupling of species interactions as many aquatic organisms use environmental temperature cues throughout their life cycles. In Windermere, UK, warmer temperatures and increased food availability have advanced the spring diatom bloom and their vernal *Daphnia* zooplankton grazers (Thackeray *et al*., 2013). Elsewhere, long-term declines in *Daphnia* have been recorded due to temporal mismatches between their life cycles and those of vernal algal blooms (Winder and Schindler, 2004). Although food availability is often cited as more important for these earlier phenological changes, climate warming has complicated annual trophic synchronisation between these predator-prey relationships (Thackeray *et al*., 2013). Reviews on case studies across the globe acknowledge that such trophic interactions are complex, nonlinear, and are amplified by multiple stressors (Walther, 2010). The spatially explicit effects of climate change and its interactions with additional stressors such as eutrophication necessitates the need to look more broadly and so understand the different ways such multiple stressors may interact within a region, and the different response of shallow to deep and upland to lowland lakes (Taranu *et al*., 2015).

1.2.3 Acidification and atmospheric deposition

Palaeolimnological investigations have shown that many UK upland lakes with base-poor bedrock have experienced acidification as a result of deforestation-induced vegetation changes from post-glacial to Holocene periods (Pennington, 1984). However, in the late 1970s palaeolimnologists began to recognise the extensive and rapid effects of acidification from the mid-19th century, ascribed to wet and dry atmospheric deposition of acidic sulphur and N gases released via industrial activity (Battarbee, 1984) (Figure 1.4).

Lakes exhibited different spatial and temporal responses to recent acidification across the UK. The lowering of pH was more prominent in lakes in regions of high deposition and poorly buffered catchments, which are typically small, acid-sensitive catchments overlying base-poor geology with thin, undeveloped acidic soils (Davies *et al*., 2005). This catchment buffering capacity also explained the difference in timings of notable diatom-inferred pH decreases across the UK (Battarbee, 1984). The upland lakes in the English Lake District were considered at less risk of notable declines in pH to lakes elsewhere, due to the already slightly acidified waters however, biological evidence of acidification in several Lake District tarns was found (Battarbee, 1984; Whitehead *et al.*, 1997).

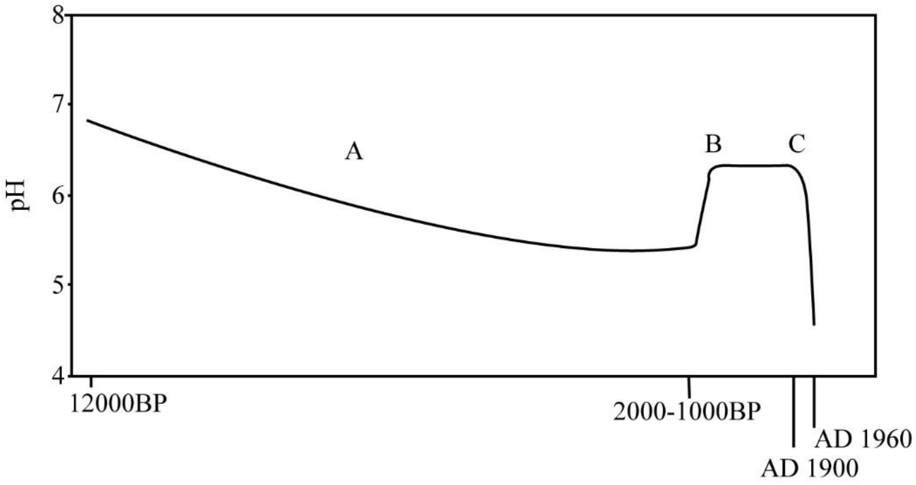


Figure 1.4 Schematic timeline of pH changes in acid-sensitive lakes in Sweden. A= natural acidification, B= increased pH from forest clearance and agricultural development and C= recent acidification. Modified from Renberg *et al.*, (2009).

Direct and indirect effects of acidification caused considerable biological deterioration. For instance, lower pH caused shifts in diatom community assemblages to more acid-tolerant species at the expense of sensitive taxa (Birks *et al.*, 1990). Higher trophic level organisms such as fish, in particular Salmonids in the UK, suffered reproductive, recruitment and spawning failure due to increases in hydrogen ion (H^+) concentration and the consequent effects of acute and chronic heavy metal toxicity notably Aluminium (Al), which leached from acidified catchment soil (Battarbee, 1984). Other secondary effects of low pH recorded in Canadian lakes included precipitation of humic substances, specifically DOC, from the water column which increased water transparency and attendant, harmful UV-B radiation penetration (Vinebrooke *et al*., 2002). UV-B radiation caused physiological damage to aquatic DNA and altered community structure by favouring species with habitat refuges such as deep, large, inedible epipelic algae and benthic algae which led to deeper chlorophyll *a* (Chl. *a*) maxima, and algae with photo-protective pigments (Vinebrooke and Leavitt, 1999; Vinebrooke *et al.*, 2002).

UK reductions in emissions of Sulphur dioxide (SO_2) by 94% and 58% for Nitrogen oxides (NO_x) from 1970-2010 were observed, owing to the use of abatement technologies and switching from coal to natural gas (RoTAP, 2012).

However, the relationship between emissions and deposition in the UK exhibits important non-linearities. For instance, whilst emissions of oxidised N have decreased by 58%, deposition has declined by only 23% owing to continued fossil fuel reliance, and in many areas, reduced forms of N deposition is increasing (RoTAP, 2012). One of the main sources of NH_4 or reduced N is agricultural activity, and control of such emissions is required to reduce the environmental effects of N deposition (RoTAP, 2012).

Most lakes in the UK acid monitoring networks have experienced increased DOC concentrations due to increasing pH, a factor which enhances lake buffering to acidification (Monteith *et al.*, 2005). In all but the most acidified lakes, reductions in labile Al have been observed (RoTAP, 2012). Biological response to acidification recovery however, has been modest and geographically patchy across the UK, although subtle shifts towards circumneutral taxa have been recorded (Monteith *et al*., 2005).

New trajectories and the lags in ecological recovery may be caused by continued N deposition and/or climate change (RoTAP, 2012). Nitrate (NO_3) concentrations have shown little evidence of decline and have increased in many upland waters, which could not only be slowing the rate of recovery from acidification but acting as a nutrient at these oligotrophic N and co-limited N and P sites (RoTAP, 2012). Evidence that NO_3 entering upland surface waters is often microbially processed prior, indicates N-export to these waters will continue regardless of the oxidised or reduced forms of N deposited on the catchment (Curtis *et al*., 2012). In addition, palaeolimnological evidence from Loch Coire Fionnaraich, Scotland, UK, noted declines in stable sedimentary N isotopes and spheroidal carboniferous particles as a proxy of industrial atmospheric N deposition, and corresponded to diatom compositional changes indicative of N enrichment (Pla *et al*., 2009). Recommendations for future work involve uncoupling the effects atmospheric N deposition on changing nutrient balances, climate change and the subsequent impacts on primary production (AWMN, 2015). These studies highlight the importance of regional studies to help identify the causes of spatial differences in lake response to acidification, recovery and atmospheric deposition.

1.2.4 Hydromorphological modifications

Hydromorphological alterations to lakes have included modifications to water levels from dam building, changes to depth regimes from shoreline modifications and inflow re-alignment, all of which have modified lake ecosystems. In the UK, the construction of dams grew rapidly in the 19th century and peaked by 1950 before declining after 1990 (EEA, 2008). The total number of dams in the UK is 486 (EEA, 2008). Such impoundments have caused impacts beyond the local-scale in downstream lakes and rivers by increasing turbidity and altering seasonal primary production dynamics (McCully, 1996; Finger *et al.*, 2007). In impounded lakes, the longer WRTs and water level changes have increased algal blooms and, in extreme cases most notable in tropical ecosystems, hyper-scums of toxin-producing species have developed (Zohary, 1985; Chen *et al.*, 2015). At Lake Thirlmere in the English Lake District, the damming and water abstraction of this deep, oligotrophic lake, could have caused adverse effects on the indigenous Arctic Charr *Salvelinus alpinus* from water level variation. Water level variation alters littoral habitat, causes temperature fluctuations, alters flow, disrupts trophic interactions and impedes upstream and downstream migration, factors known to effect the survival and recruitment of Salmonids (Jonsson and Jonsson, 2009).

Channel modifications to rivers in the UK have been undertaken over several centuries, but the most intense period of activity over substantial lengths of rivers occurred after 1930 following the Royal Comission on Land drainage in 1927 (Brookes *et al.*, 1983). Inflow channel modifications led to improved transport of alluvium and urban and agricultural runoff to lakes which increased turbidity and siltation, and shifted macrophyte dominance to phytoplankton (Romanescu and Stoleriu, 2014). Climate-induced WRT changes have led to further nonlinear responses in lakes that have already undergone hydromorphological modifications (Michalak *et al.*, 2013). Regional long-term studies could help assess the relative importance of hydromorphological alterations to other stressors, and whether they have had impacts beyond the site-scale.

1.2.5 Future stressors

Current predictions suggest rapid and continuing impacts of multiple stressors on freshwaters in the near future (Figure 1.1) (MEA, 2005). The global population is predicted to rise to 9.6 billion people by 2050 and, as a consequence, 40% of the world's population will live in water scarcity by 2025 due to increased demand and degradation of potable water (Foster and Chilton, 2003; WWAP, 2006). Agricultural intensification will probably continue in order to meet the demands of the growing population, resulting in N saturation of soils, distortion of N and P cycling and continued reinforced interactions between diffuse and urban pollutants (Heathwaite, 2010). UK climate projections predict a continued increase in mean daily temperatures, winter precipitation and decreased snow cover (Murphy *et al*., 2009). These changes will lead to unpredictable, complex interactions between hydrological connectivity, diffuse pollutants and C, N and P biogeochemical cycling in lakes and their catchments (Heathwaite, 2010). Thus, understanding different spatio-temporal scale responses of lakes to multiple stressors could help forecast the impacts of changing nutrient delivery and biogeochemical cycling in a future of climatic variability and greater anthropogenic demand (Heathwaite, 2010).

1.2.6 Landscape-scale studies to address multiple stressors acting on lakes

As previously mentioned, stressors often co-occur and interact to produce either synergistic, non-additive or antagonistic responses on biodiversity and ecosystem services (Vinebrooke *et al*., 2004). This results in unpredictable ecological responses and uncertainty surrounding future global change (Christensen *et al*., 2006). Studies investigating multiple stressors have revealed huge variability across ecosystems of impact and response, as well as discrepancy between the terminology and evidence of regime shifts, lags and non-linear biotic responses (Capon *et al.*, 2015; Nõges *et al.*, 2016). Such studies are still rudimentary and lack quantitative evidence on multi-stress impacts on lakes (Ormerod *et al.*, 2010; Nõges *et al.*, 2016). Futhermore, the interaction of stressors at different spatial and temporal scales and sensitivity of ecosystems to different stressors has been understudied (Hering *et al*., 2015).

Landscape-scale palaeolimnology has been identified as an ideal approach to study the effects of past multiple stressors on lakes because of its ability to study different temporal and spatial distributions of pollutants and assessment of the effects of these on biotic communities over long timescales (Smol, 2010).

The landscape filter concept has been used as a tool to assess how landscape characteristics modify freshwater responses to multiple stressors, so that no single site behaves the same. More specifically, landscape-scale limnology can help elucidate the extent to which the terrestrial and human contexts of a lake and its connectivity to other freshwaters shape in-lake physical, chemical and biological characteristics (Figure 1.5) (Soranno *et al*., 2009). These factors exhibit a hierarchal scale, with regional factors defining and constraining the local-scale factors (Soranno *et al*., 2009). This relates and is developed by the conceptual model of Blenckner (2005), which describes both a landscape filter (taking into account the geography, characteristics and morphology of a lake and its catchment) and an internal lake filter (taking into account the history and biotic and abiotic interactions within a lake). This model acknowledged the need to understand the range of variability of lake ecosystems over longer timescales, and develop baselines of change as necessary to determine whether a system has been altered significantly (Kratz *et al.*, 2003; Blenckner, 2005). In doing so, it promotes the use of palaeolimnology in landscape-scale studies as a means to help assess the extent of environmental change.

Many landscape-scale studies have shown that lakes within the same geographical position exhibit synchronous inter-annual variability of lake variables, often most pronounced for physical and less for biological (Baines *et al.*, 2000; George *et al.*, 2000; Quinlan *et al.*, 2003). Distinctions have been further made between the chemical composition of lakes that have a higher elevation to those with a lower, which are often smaller, clearer, have a higher ability to dilute pollutants and are subject to less direct anthropogenic influence (Kratz *et al*., 2003). However, some studies have found no discernible pattern between nutrient concentrations, anthropogenic activity and lake order, attributed to upstream lakes as buffers and landscape and in-lake filtering effects of eutrophication (Dixit *et al.*, 2000; Quinlan *et al.*, 2003). This highlights that different landscapes exhibit disparate hierarchies of spatial characteristics, thus necessitating the need to investigate and expand our understanding of these landscape-scale interactions.

In terms of landscale-scale studies on algal synchrony, authors have reported synchrony for algal biomass (as Chl. *a*) for lakes with similar degress of thermal stratification and so, timing of complete mixing and internal nutrient supplies (Baines *et al*., 2000; George *et al*., 2000). However, studies which have focussed on both algal biomass and community dynamics differ in their findings. For example, since the 1970s, long-term biomass changes were not synchronous to TP reductions or climatic changes, but community compositions were to climatic changes only in four peri-alpine lakes (Anneville *et al*., 2005). Another study found in 35 lakes across Europe, shallow and deep lakes had distinct algal community compositions to one another during re-oligotrophication spanning 5-35 years (Jeppesen *et al*., 2005). Over longer timescales (134 years), inter-decadal increases in algal abundance were highly synchronous with changes in human population, agriculture and climate influences, but not on inter-annual scales or between different algal groups in lakes with homogenous characteristics (Patoine and Leavitt, 2006). These studies highlight discrepancy between spatial and temporal behaviour of algal communities within landscapes to different drivers, and that more studies are needed to understand these scale effects.

More specifically, recent and future anthropogenic stressors are heterogeneous across a landscape (such as land use and atmospheric deposition), so understanding their impacts requires an appreciation of the spatial context of both the stressors and the receiving water body (Soranno *et al*., 2010). Furthermore, understanding how lake functional groups respond to landscape features such as catchment topography and lake physical characteristics such as maximum depth (max. depth), alongside anthropogenic stressors will help prioritise management on systems that are more amenable to action (Soranno *et al*., 2010).

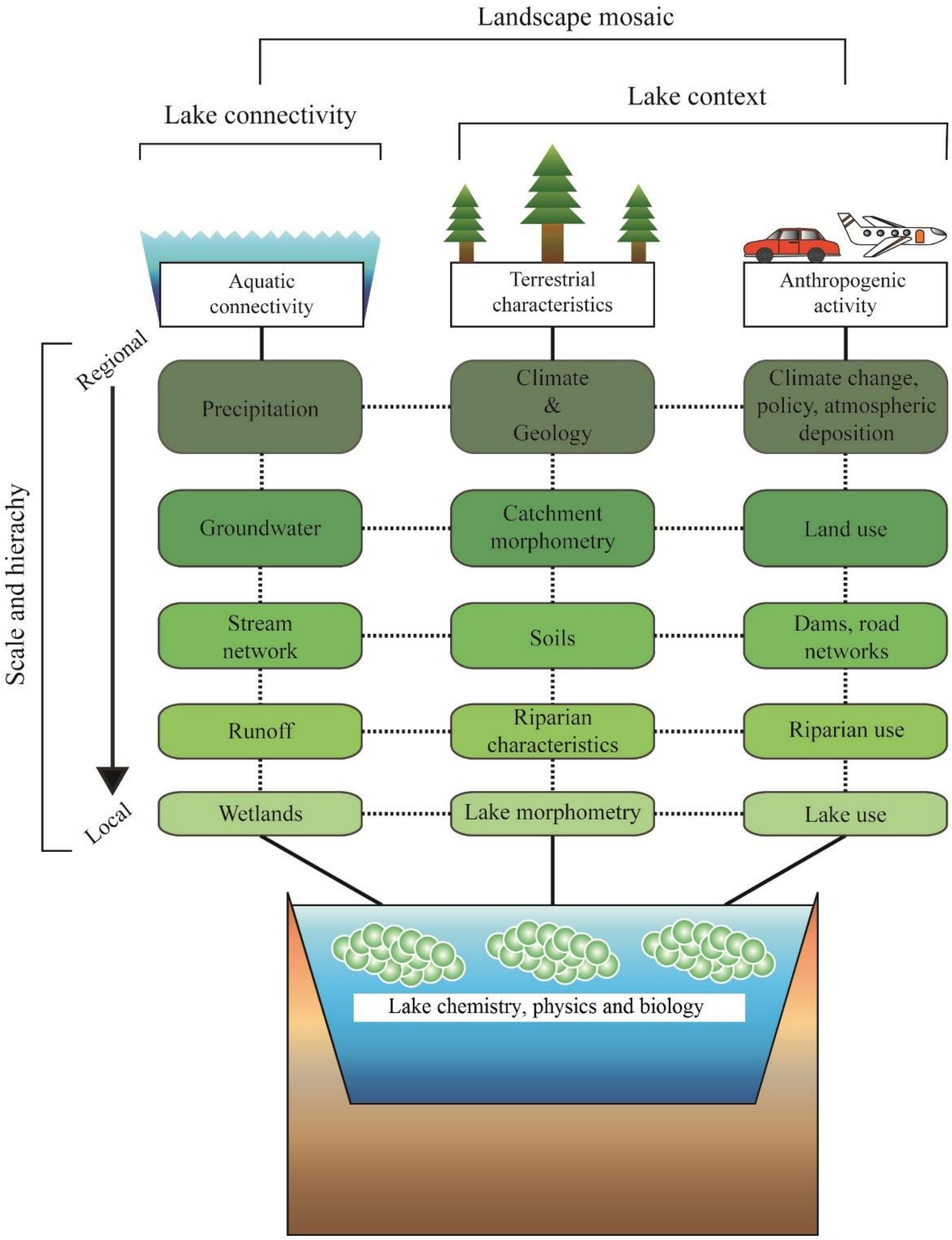


Figure 1.5 Conceptual diagram of regional to local aquatic, terrestrial and anthropogenic drivers that modify limnological variables. Modified from Soranno *et al*. (2009).

1.3 The EU Water Framework Directive and palaeolimnology

The EU Water Framework Directive (Directive 2000/60/EC) (WFD) is the main legislative driver of water management in the UK (European Union, 2000). It requires that all EU Member States achieve good ecological status for all surface water bodies by 2015 with the option to defer until 2027. The difference from previous legislation is the shift of focus to biotic structure and function rather than on pollutant monitoring (Hering *et al*., 2010). Supporting elements include hydromorphology and physico-chemistry but the final judgement is made on ecological status derived by measuring the extent to which the biological community of a site deviates from its reference condition; a condition absent of anthropogenic impact (European Union, 2000). 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 (European Union, 2000). Palaeolimnology is one approach recommended to determine reference conditions.

Analyses of lake sediment characteristics permits detailed environmental reconstructions of pre-disturbed or reference conditions for the WFD. However, as previously noted, the long history of anthropogenic activity in European lake catchments has altered terrestrial, atmospheric and aquatic processes and so determining and achieving appropriate reference conditions is a major challenge (Bennion and Battarbee, 2007). Other challenges include those more specific to palaeolimnology itself such as sediment disturbance, diagenesis of proxies, and error associated with chronostratigraphic, laboratory and numerical analyses which can result in inaccurate interpretations. Multi-proxy studies, calibration of proxies and their methods, and understanding modern lake ecosystems can, however, improve the accuracy of palaeolimnological reconstructions (Battarbee *et al*., 2002a).

1.3.1 Catchment-scale palaeolimnology

The WFD reorganised water management to the catchment-scale rather than administrative borders using the rationale that freshwaters are influenced by the land and water in the drainage area (Hering *et al*., 2010). River Basin Management Plans required by the WFD, must focus on the ecological integrity of the catchment as a whole rather than on discrete, isolated sites (Hering *et al*., 2010). The aim is to capture the importance of regional processes or pollutants that influence the surface waters of a catchment. This provides catchment-scale palaeolimnological studies with a unique advantage, with their ability to capture the relative importance of scale-dependent drivers of ecological change, such as regional diffuse pollutants, to local-scale point drivers at different timescales.

Previous catchment-scale palaeolimnological studies have often been focussed on the regional assessment of a single stressor. For example, in lakes of the Adirondacks, USA, changes in composition of sedimentary diatoms and chrysophytes implied a decline of pH in 80% of the study lakes from post-industrial (1850AD) sediments (Cumming *et al*., 1992). In contrast, diatom-inferred TP (DI-TP) transfer functions and cladoceran remains from 21 Danish lakes revealed deviation from 1850AD due to nutrient loading (Bjerring *et al*., 2008). This was developed by a study which used diatoms to assess environmental change in 257 lakes from several ecoregions in north eastern USA and found a dominant single stressor for each region e.g. acidification in the Adirondacks and eutrophication in the Coastal Lowlands/Plateau (Dixit *et al*., 1999). On a similar note, in four shallow lakes in the Norfolk Broads, DI-TP did not equate to the eutrophication histories of these lakes due to the dominance of three benthic species, highlighting the limitations of relying on a single algal group to infer environmental change (Bennion *et al*., 2001). Although these studies provide excellent evidence and guidance for where management should focus in a region, they overlook the role of other stressors and the complex responses of individual lakes to such stressors within the same region (Smol, 2010).

The assessment of a single stressor was developed by other authors who noted that responses varied according to landscape characteristics. For instance, in British Columbia, Canada, six lakes responded differently according to catchment size and extent of anthropogenic activity in the catchment (Reavie *et* *al*., 1995). Whereas in Iowa, USA, geochemical proxies revealed 91% of study lakes had undergone agricultural-derived eutrophication, but DI-TP did not correspond and diatom floristic changes were driven by other factors including lake depth (Heathcote *et al*., 2015). The observations of these studies point to the recognition of landscapes as filters, but do not statistically quantify these effects or go into detail beyond observations.

There are several catchment-scale palaeolimnological studies that have sought to disentangle the role of multiple stressors and landscape filters using spatial synchrony. In the northern Great Plains, Canada, spatial synchrony was highest in years when evaporation was high, as it induced synchrony of lake chemistry and the susceptibility of the lakes to the effects of urban and agricultural effluent as shown by elevated cyanobacterial pigments and $\delta^{15}N_{org}$ values (Pham *et al*., 2008). However, the patchiness of precipitation and groundwater replenishment reduced coherence (Pham *et al*., 2008). In shallow lakes of southern Alberta, Canada, an investigation into multiple stressors found asynchronous algal pigment changes due to differences in both timing of eutrophication and basin hydrology at each site (Maheaux *et al*., 2015). This was despite an overall increase in total algal abundance and purple sulphur bacteria in most study lakes since 1850AD (Maheaux *et al*., 2015). Although these studies investigate both multiple stressors and the catchment filter hypothesis, both study areas are fairly homogenous in terms of catchment and lake characteristics (in particular catchment elevation) and the regional drivers of change.

One study that has focussed on heterogeneous lakes by Leira *et al*., (2006) assessed multiple stressors across Irish lakes using geochemical variables and sedimentary diatoms, to find acidification and nutrient enrichment caused deviation from the reference condition in 68% of study lakes. However, the lakes had fairly similar trophic statuses (meso- to oligotrophic) and only top and bottom samples of each sediment core were studied, which may have missed more significant changes in variables in between those two samples (Leira *et al*., 2006). Again, this points to a gap in the literature for a catchment-scale, community palaeolimnological investigation into multiple stressors in a heterogeneous landscape. In doing so, the extent that landscape characteristics filter different drivers may be more clearly examined and will provide results more likely to be applicable to other landscapes and/or lakes of similar features and drivers. Notwithstanding these gaps in knowledge, the usefulness of the aforementioned catchment studies in assessing the response of lakes to stressors and facilitating management must be acknowledged.

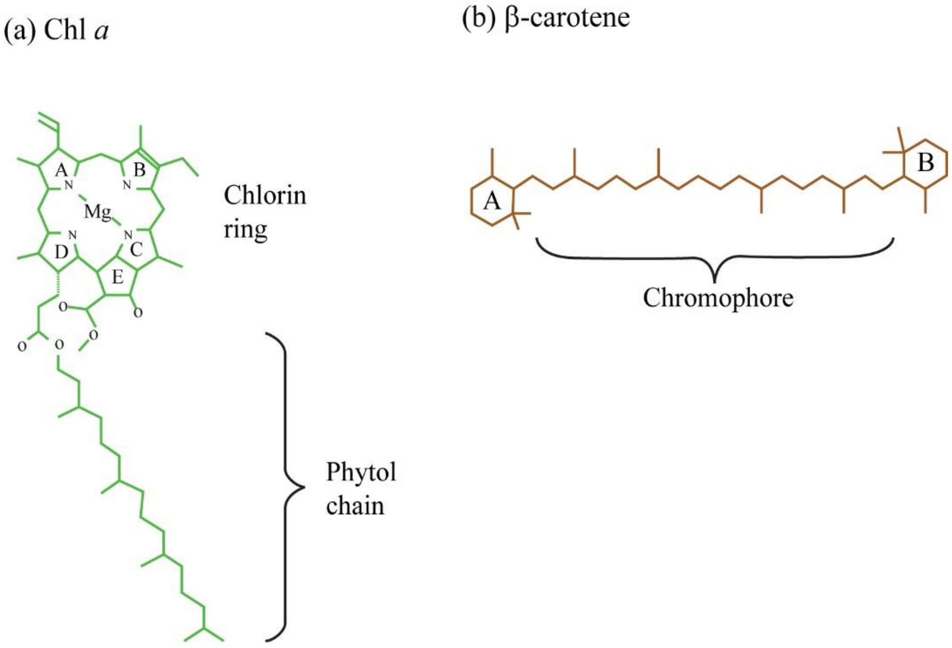
1.3.2 Surface water typologies and the WFD

The WFD demands that ecological assessments must account for natural differences in aquatic communities and does so by grouping surface waters into "types" according to physical, chemical and morphological differences including salinity, alkalinity, lake altitude and depth (Hering *et al.*, 2010). This typology system recognises that different lake characteristics can shape the baseline and current ecological condition of surface waters, as well as its response to anthropogenic impacts. However, typologies are often coarse delineations which overlook natural gradients and the multiple environmental parameters which influence ecosystems (Hering *et al.*, 2010). As such, typologies can oversimplify the dynamic processes of freshwater ecosystems in a landscape (e.g. Magnuson *et al.*, 1990). Palaeolimnology has often focussed on one lake in a catchment as a sentinel for determining baseline conditions, and overlooks the spatial interactions of multiple lakes in a landscape with their catchments and differences in lake response to environmental change within a region (Anderson, 2014). Thus, there remain gaps in the knowledge about the role of lake and catchment characteristics in shaping lake ecosystem response to long-term change, and how this may vary between sites within a region.

1.4 Sedimentary algal pigments as biomarkers of past environmental change

Algal pigments are the light-absorbing chlorophylls (Chls) and carotenoids and their breakdown products, and UV photo-protective compounds of phototrophic organisms (McGowan, 2013). They are often the only biochemical compound remains of such organisms that are preserved in aquatic sediments, especially for non-siliceous algae and bacteria (Hodgson *et al.*, 1997). Algal pigments can be taxonomically specific e.g. the pigment alloxanthin is attributed to cryptophytes and zeaxanthin to cyanobacteria (McGowan, 2013). However, in most cases the taxonomic group a pigment belongs to can be attributed to either several phytoplankton groups e.g. the pigment fucoxanthin is found in diatoms, chrysophytes, haptophytes and some dinoflagellates, or all phosynthesisers such as the Chls i.e. Chl. *a* and its degradation product pheophytin *a* (Leavitt and Hodgson, 2001). Algal pigments are particularly useful due to their ability to capture snapshots of primary production from the entirety of the water column, often overlooked by contemporary monitoring (McGowan, 2013).

All Chls contain a central magnesium atom within a complex of four pyrrole units (an organic compound composed of four C atoms, one N atom, with a single H atom in the ring: C_4H_5N) cyclically arranged around it, with this being the defining feature of a Chl molecule (Figure 1.6) (McGowan, 2013). Chls are susceptible to oxidative degradation. The loss of the magnesium atom from Chls forms pheophytins, whereas the loss of the phytol chain creates chlorophyllides (McGowan, 2013). These degradation products are also readily detectable in pigment extracts and can be used to interpret degradation and past lake conditions (McGowan, 2013). Carotenoids are composed of a long chain of eight isoprene units (C_5H_8), also known as the chromophore, which have two functional groups at both ends. Carotenoids are separated into two distinct groups due to differences in chemical structure; carotenes, such as β-carotene found in most algae and higher plants, are composed of C and H atoms, whereas xanthophylls such as alloxanthin, found in cryptophytes, carry one or more oxygen atoms (McGowan, 2013). In both Chls and carotenoids, it is the chromophore which is responsible for light absorption.


(a) Chl *a*

(b) β-carotene

Figure 1.6 Chemical structure of (a) Chl. *a* with tetrapyroles with fifth isocyclic ring (E) and phytol chain, (b) β-carotene with characteristic carotenoid structure of double bond chromophore bound at each end by two functional groups (A-B). Modified from McGowan (2013).

All pigments are subject to degradation under exposure to oxygen, heat and light, which varies in most aquatic systems from differences in lake depth, morphometry, habitat preference and compound chemical structure (Leavitt, 1993; Cuddington and Leavitt, 1999). More than 95% of pigments are lost before reaching the sediments, particularly in the first few hours or days after death, during which time pigments may undergo grazing and digestion, chemical or microbial oxygenation, and cell lysis and metabolism during senescence or sinking (Figure 1.7) (Leavitt, 1993; Cuddington and Leavitt, 1999). Grazing can actually improve preservation due to quicker sinking in heavy faecal deposits. Once in the superficial sediments, degradation is typically much slower (years) but this is governed by the conditions of the sediment-water interface and microbial activity (Leavitt and Hodgson, 2001). Labile pigments such as fucoxanthin or Chl. *a* often increase exponentially with decreasing depth of sediment, particularly in the top few centimetres of the sediment record, but below this zone degradation is over millennial timescales (McGowan, 2013). Therefore, lakes with anoxic waters and shallow depths rapidly incorporate pigments into sediments, particularly benthic algal pigments comparable to planktonic pigments (Hurley and Armstrong, 1990; Hodgson *et al.*, 2004). In addition, compounds with complex structures and functional groups often degrade at a higher rate than those with simple structures and are therefore less common in sediments (Leavitt and Carpenter, 1990b; Leavitt and Carpenter, 1990a).

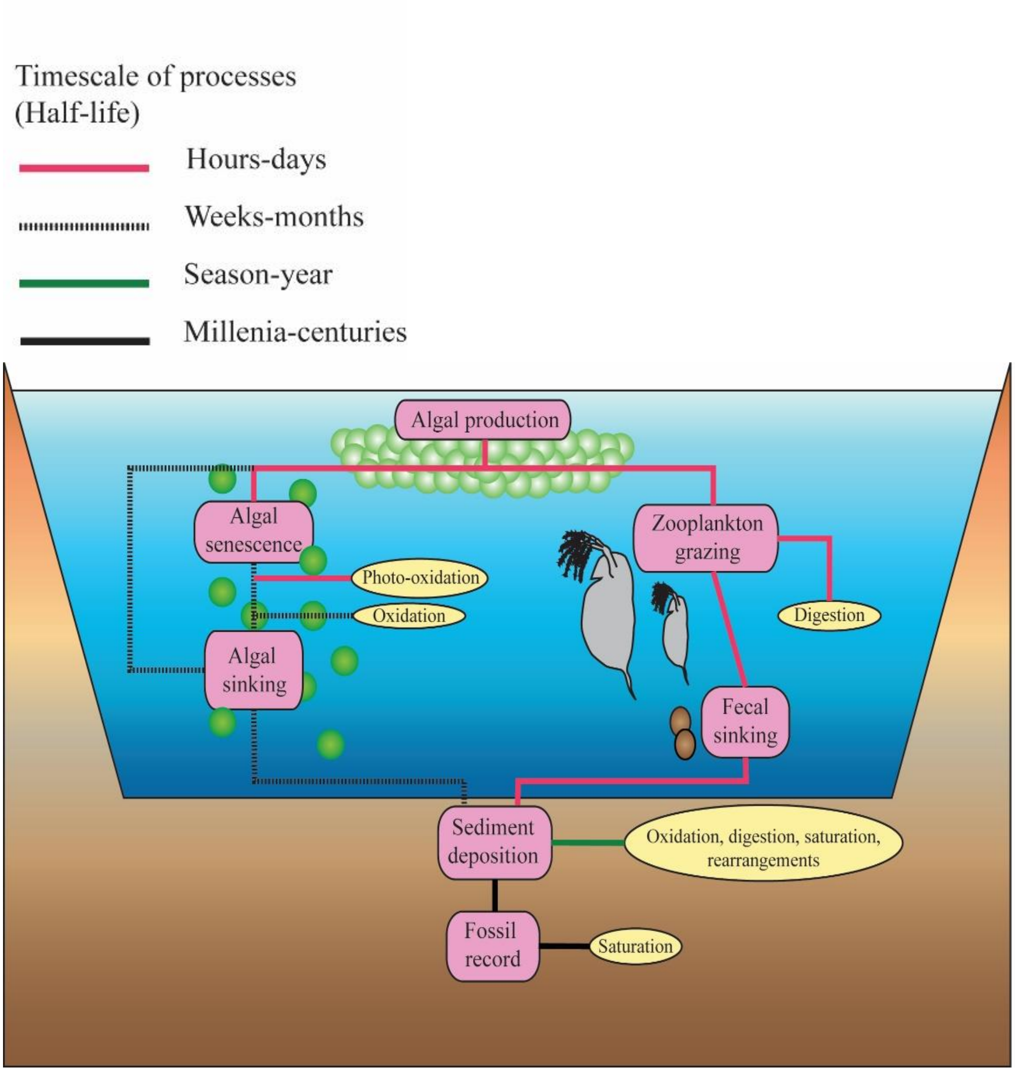


Figure 1.7 Pathways and rate of pigment degradation during deposition from the water column to the sediments. Modified from Leavitt (1993) and Cuddington and Leavitt (1999).

Nonetheless, most lakes have well-preserved pigment records and provide a useful insight into algal and lake development and environmental conditions during pigment deposition, as well as being good indicators of total algal biomass and dominant algal groups (e.g. diatoms, cryptophytes, cyanobacteria)

(Marchetto *et al*., 2004). For example, in Lough Neagh, fossil concentrations of the colonial cyanobacterial pigment myxoxanthophyll were strongly correlated with monitored water column Chl. *a* which was driven by the cyanobacteria *Planktothrix agardhii* (Gomont) Anagnostidis and Komárek (1988) (>70% of the algal community) during historical eutrophication (Bunting *et al*., 2007). Sedimentary pigments have also been shown to correspond well with monitored climatically-driven chemical changes which regulate production and community assemblage changes (Lami *et al*., 2010).

Primary producers are direct mediators of energy and mass inputs which make algal pigments useful biomarkers to study environmental perturbations. In addition, different groups have preferential conditions or characteristics and so their abundance can be used to explore changes in nutrients, habitat and other ecosystem variables (Paerl *et al*., 2003). For instance, concentrations of total algal and cyanobacterial fossil pigments typically increased in response to historical eutrophication (Leavitt and Findlay, 1994). On the other hand, other taxa responded more variably due to localised diversity of algal taxonomy and morphology which led to different nutrient uptake and grazing pressure (Watson *et al*., 1997). Pigments have recorded past changes in climate including increased chlorophyte (lutein) and diatom (diatoxanthin) pigment concentrations from drought induced salinity increases (Vinebrooke *et al*., 1998). Variable UV protective pigment concentrations recorded past warming and cooling-induced catchment vegetation changes and consequent changes in inputs of DOC and so, water transparency (Pienitz and Vincent, 2000). Acidification, symptomatic of mid/late 19th century atmospheric deposition, resulted in more complex pigment stratigraphies, although increased concentrations of benthic or deep-blooming taxa such as cryptophyte (alloxanthin) and chlorophyte (lutein) pigments and UV protective compounds were often greater (Leavitt *et al*., 1999). Sedimentary pigments have been used in conjunction with monitoring data to derive the importance of nutrient inputs to that of climate, and have shown eutrophication resulted in distinct algal community modifications to increased cyanobacterial production relative to other phytoplankton (Taranu *et al*., 2015). Thus, fossil pigments are a useful tool to detect not only environmental disturbances but the relative importance of co-occurring stressors.

1.5 Gaps in knowledge of landscape-scale palaeolimnological investigations into multiple stressors

There remain four major gaps in our knowledge of past multiple stressors on landscape-scale primary production.

First, most regional palaeolimnological studies, unlike their contemporary limnology counterparts, overlook the importance of catchment characteristics or environmental heterogeneity when investigating spatio-temporal drivers of ecosystem change (Anderson, 2014). Few palaeolimnological studies have sought to quantify the role landscapes play in filtering environmental change, particularly on a regional-scale (see section 1.3.1). Similarly, few palaeolimnological studies exist from heterogeneous landscapes such as lowland to upland lakes (see section 1.3.1). Further, in light of the WFD's typology classification, there is growing recognition of the need to understand the role landscape characteristics have played in shaping past ecosystem dynamics and response to environmental stressors.

Second, past regional palaeolimnological studies have often focussed on the impacts of a single stressor (see section 1.3.1). The growing recognition that lakes with and without human catchment activity have been impacted by multiple stressors, makes any study that seeks to quantify the relative importance of these stressors invaluable (Smol, 2010; Taranu *et al*., 2015).

Third, broad generalisations are often used to predict lake ecosystem trajectories before and after disturbance (Turner, 2010). This is because information has only been available from palaeolimnological investigations of single sites, or top-bottom core profiles or from limnological monitoring programmes which generally only cover post-disturbance periods (Taranu *et al*., 2015). Both of these approaches tend to overlook the importance of gradual, longer-term, wider-scale stressors such as climate change or historical diffuse fertilisation in shaping more recent ecological responses to disturbance (Bunting *et al.*, 2007; Thies *et al.*, 2012). Consequently, the idea of appropriate scales to deliver effective science for sustainable water management has been questioned (Heathwaite, 2010). Thus, in order to understand the "ecological surprises" from multiple stressors, longer-term, regional palaeolimnological studies are required to elucidate the importance of stressor scale and how it can shape baseline inference, trends in response variables and the comparative importance of ecosystem stressors (Anderson, 2014; Taranu *et al.*, 2015). In addition, catchment-wide management of multiple ecosystems and an improved understanding of the degree of deviation from baseline conditions are required in order to meet the objectives of the WFD.

Finally, regional-scale community studies are still relatively rare when investigating multiple stressors (Turner, 2005). Palaeolimnological studies often focus on one species (e.g. diatoms) (see section 1.3.1), which although useful, community-wide studies are more likely to be sensitive to wider environmental changes. The sensitivity of lake algal communities to environmental change and their ability to modify both their habitat and higher trophic levels makes them ideal communities to investigate across a given region.

1.6 Aims and objectives

The aim of this thesis is to address the knowledge gaps outlined in section 1.5, specifically to examine how and when algal communities changed across the Windermere catchment in the 19th and 20th centuries, and to identify the primary mechanisms driving these changes. The justification of the Windermere catchment as an important site choice is discussed in Chapter 2. The broader spatio-temporal scales of algal community change (centennial and catchment) are to be investigated to assess the relative importance of regional and local-scale stressors that have altered lake primary production. Further, investigating how catchment and lake characteristics could have modified community drivers and response should help prioritise and define mitigation measures for the Windermere Catchment Restoration Programme (WCRP).

Attaining the stated aim required that six specific research objectives be achieved. These are to:

1. Establish centennial-scale changes to algal communities in the Windermere catchment using sedimentary algal pigments as biomarkers in Lead-210 (^{210}Pb) dated sediment cores.
2. Identify changes to sedimentary OM sources and cycling using lithological proxies (e.g. % Loss-On-Ignition) and stable and bulk C and N isotopes.
3. Develop sediment core chronologies using ^{210}Pb dating in order to derive timings of algal community change over the 19th and 20th centuries.
4. Compare changes in sedimentary algal communities with environmental records collated from historical and instrumental sources to identify environmental drivers of algal community change over the 19th and 20th centuries.
5. Use various statistical approaches to create a regional synthesis of centennial and catchment-scale algal community drivers and response which will involve the following:
    I. Establish centennial-scale trends and whether or not algal community compositional changes were synchronous across the catchment.
    II. Identify key timings of community change using breakpoints.
    III. Determine the relative importance of regional and local-scale drivers of lake environmental change using regression trees.
    IV. Assess how landscape characteristics could have altered drivers and response of algal communities by using linear regression models to look for gradients of community change and t-tests to distinguish whether landscapes can be characterised into distinct types in accordance with community response.
6. Assess the role of catchment-scale palaeolimnological studies on determining the impacts of multiple stressors on lake ecosystems.
7. Interpret the research findings in the context of management concerns and derive effective remediation measures through the understanding

of the relative importance of regional and local-scale stressors of environmental change.

1.7 Thesis outline

The structure of this thesis is designed to address the aims and objectives outlined in section 1.6 and are depicted schematically in Figure 1.8.

Chapter 2 justifies the use of the Windermere catchment and 19th and 20th centuries as an appropriate spatio-temporal study. Chapter 3 describes the individual sites and coring locations and 4 describes the laboratory and historical collection methods used. Chapter 5 describes the statistical analyses used. Chapter 6 presents the individual multi-proxy core stratigraphies and describes site-specific environmental change in order to support and interpret the results of the regional synthesis. Chapter 7 addresses how algal communities have changed and how similar these changes were across the catchment. Chapter 8 addresses when the key timings of algal community change occurred, and what environmental drivers caused these changes. The role that landscape characteristics played in shaping algal response is also investigated here. Results and interpretations of stable isotopes in Chapter 9 look at changes to OM sources and cycling, and so, autochthonous production in the catchment. Chapter 10 summarises the results of this thesis and provides management recommendations derived from the results and suggests future studies that could build on the work presented herein.

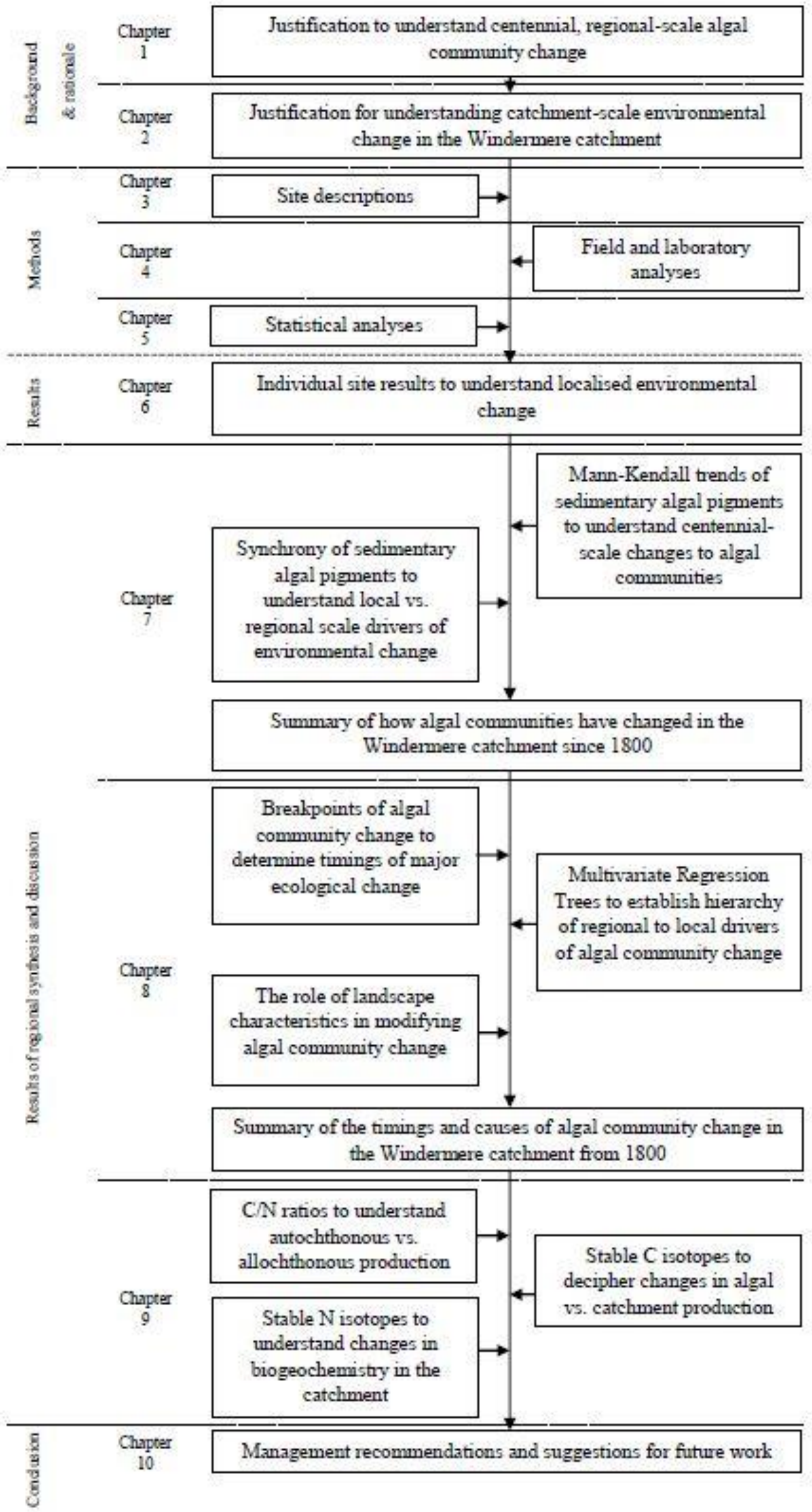


Figure 1.8 Thesis structure

CHAPTER 2. SITE DESCRIPTION AND ENVIRONMENTAL HISTORY OF THE WINDERMERE CATCHMENT, ENGLISH LAKE DISTRICT, UK

This chapter aims to contextualise the past and current environment of the Windermere catchment in order to provide reasoning behind its selection as a study catchment within the timescale[1] needed to address the aims of this thesis outlined in section 1.6.

2.1 Geographical context

The Windermere catchment (54°18′ N; 2°54′ E) is situated in the Lake District National Park, in North West England, UK (Figure 2.1). It is 235km^2 and comprises 11 lakes and tarns (a colloquial term for small mountain lakes) which feed into Windermere, England's largest (area: 14.7km^2) and longest (17km) lake. Windermere itself is split into a deep mesotrophic north basin (area: 8.1km^2, max. depth: 64m) and a relatively shallow eutrophic south basin (area: 6.7km^2, max. depth: 42m) by an area of shallows (mean depth: 10m) near the centre. The largest in-flowing rivers to the north basin are the Rivers Brathay, Rothay and Trout Beck, and to the south Cunsey Beck which drains Esthwaite Water (McGowan *et al.*, 2012). The main outflow is the River Leven at the southern end of the south basin.

2.1.1 Conservation designations

The Windermere catchment is a region of international and national importance for its habitats and biodiversity. The Lake District National Park was designated in 1951, with the aim of conserving and enhancing the natural and cultural heritage of the region while also promoting public enjoyment. There are several other national and international conservation designations in the catchment, including Sites of Special Scientific Interest (SSSIs) such as Blea

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[1] This thesis will use the Gregorian calendar to express years as AD (Anno Domini). Those that are Before Christ (BC) will be stated in the main body of text.

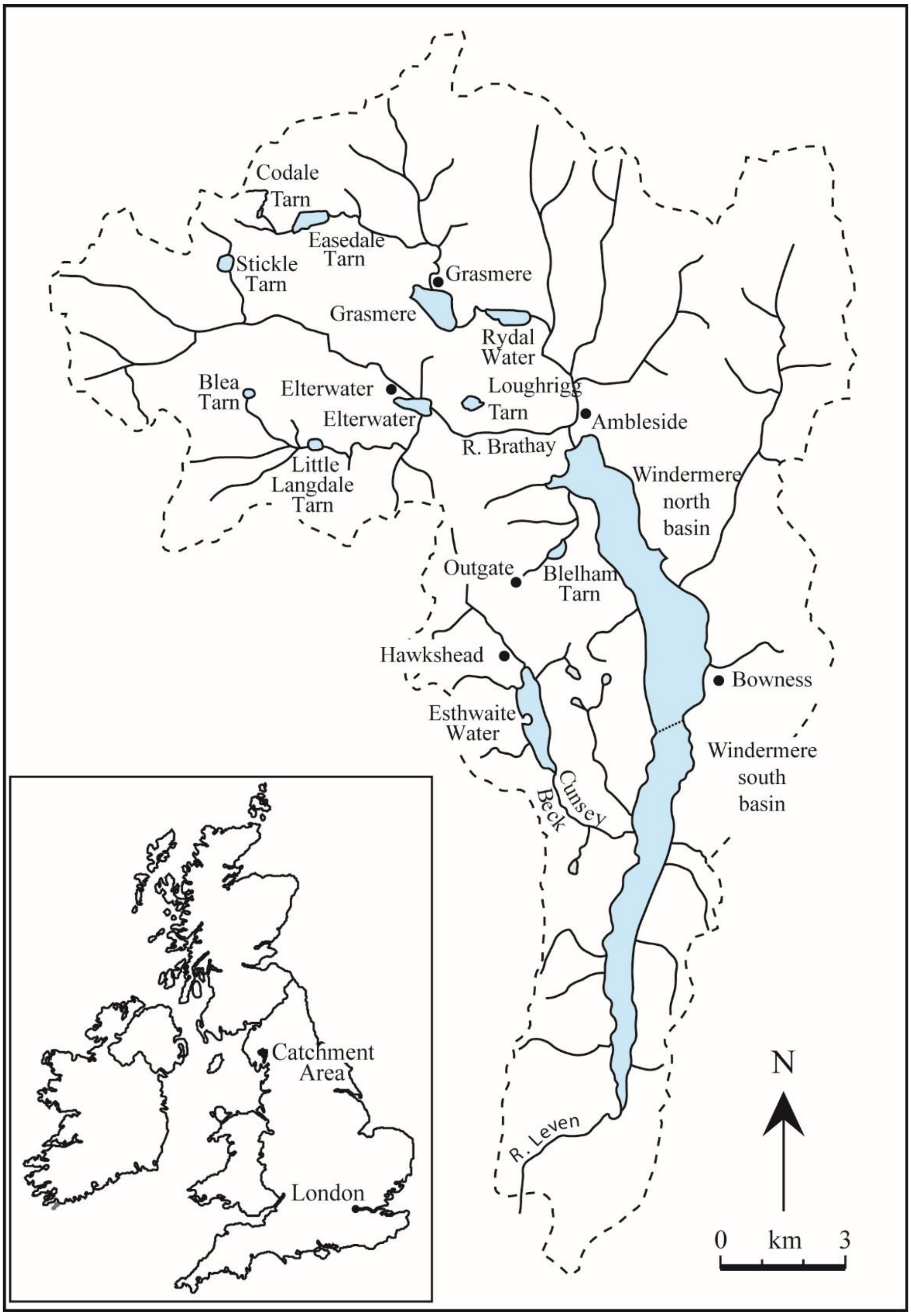


Figure 2.1 Map of Windermere catchment. Modified from McGowan *et al*., (2012) .

Tarn, Blelham Tarn and bog, Elterwater, Esthwaite Water, and Little Langdale Tarn on account of several rare plant species and habitats such as wetland fens (NE, 2015). Esthwaite Water is also a Ramsar site: an area of internationally important wetlands.

2.2 The physical landscape of lakes and tarns in the Windermere catchment

Lakes of the English Lake District were formed at the end of the last ice age (14,000-15,000 years ago) when the glaciers receded from an upland dome, carving deep valleys, peaks and ridges, and formed a pattern of large lowland lakes centred around the high ground (Pearsall and Pennington, 1947). As the glaciers retreated they deposited morraines, created high fells and excavated smaller tarns (Pearsall and Pennington, 1947). This led to the lakes and their individual sub-catchments in the Windermere catchment being highly variable in morphometry (Table 2.1).

2.2.1 Relief

Catchment elevation is highly varied and ranges from 40-902 m.a.s.l. (Pearsall and Pennington, 1947) (Figure 2.2). As a result, rainfall leads to rapid sediment runoff, particularly in upland areas where mean annual precipitation is higher (~3m/yr^{-1}) than in the lowlands (~1.2m/yr^{-1}) (McClean, 1940; Pearsall and Pennington, 1973; Chiverrell, 2006).

Table 2.1 Physical characteristics of lakes in the Windermere catchment with altitude shaded in light grey. BVG = Borrowdale Volcanic Group. SIL = Silurian flags and slates.

Site	Geology	Mean depth (m)	Max depth (m)	Length (km)	Area (km^2)	Catchment area (km^2)	Catchment to lake area ratio (CA:LA)	Volume (10^6 m^3)	Altitude (m.a.s.l)	Mean catchment altitude (m.a.s.l.)	Mean Retention time (days)	Human population per 10^6 m^3 lake volume	Source
Blea Tarn	BVG	7	8	-	0.038	1.16	30.5	-	192	-	-	-	Haworth (1969), Haworth *et al*., (2003)
Blelham Tarn	SIL	6.8	14.5	0.67	0.1	4.0	40	0.69	42	105	50	8.7	Jones *et al*., (1979), George *et al*., (2007)
Codale Tarn	BVG	3.3	7	-	0.013	0.40	30.8	-	467	610	12	-	Tipping *et al*., (2000a), Tipping *et al*., (2002), Haworth *et al*., (2003)
Easedale Tarn	BVG	10.5	22.5	-	0.106	2.7	25.5	-	279	510	55	-	Tipping *et al*., (2000a), Tipping *et al*., (2002), Haworth *et al*., (2003)
Elterwater Inner Basin	BVG	2.3	7.4	1	0.036	1.0	27.9	0.89	55	08	106	-	Beattie *et al*., (1996), Goldsmith *et al*., (2003), George *et al*., (2007),
Elterwater Middle Basin	BVG	2.3	6	1	0.074	1.0	13.5	1.5	55	108	26	-	Beattie *et al*., (1996), Goldsmith *et al*., (2003), George *et al*., (2007)
Elterwater Outer Basin	BVG	2.5	7.5	1	0.083	1.0	12	2.05	55	108	20	-	Beattie *et al*., (1996), Goldsmith *et al*., (2003), George *et al*., (2007)
Esthwaite Water	SIL	6.4	15.5	2.5	1	17.0	17	6.4	65	148	100	9.7	Jones *et al*., (1979), George *et al*., (2007)

Table 2.1 Continued

Site	Geology	Mean depth (m)	Max depth (m)	Length (km)	Area (km^2)	Catchment area (km^2)	Catchment to lake area ratio (CA:LA)	Volume (10^6 m^3)	Altitude (m.a.s.l)	Mean catchment altitude (m.a.s.l.)	Mean Retention time (days)	Human population per 10^6 m^3 lake volume	Source
Grasmere	BVG	7.74	21.5	1.6	0.644	30.2	46.9	4.987	62	328	25	9.7	Hall *et al*., (1978), Reynolds and Lund (1988), George *et al*., (2007)
Little Langdale Tarn	BVG	2.7	9.5	0.375	0.065	12	184.6	-	102	520	3.3	-	Tipping *et al*., (2000a), Tipping *et al*., (2002), Haworth *et al*.,(2003)
Loughrigg Tarn	BVG	6.9	10.3	0.4	0.07	0.95	13.6	0.5	94	175	117	-	Tipping *et al*., (2000a), Tipping *et al*., (2002), Haworth *et al*.,(2003)
Rydal Water	BVG	4.4	19	1.2	1.5	33	22	4.4	53	312	9	-	Jones *et al*., (1979), George *et al*., (2007)
Stickle Tarn	BVG	8	14	-	0.083	1.8	21.7	-	469	610	39	-	Tipping *et al*., (2000a), Tipping *et al*., (2002), Haworth *et al*., (2003)
Windermere North Basin	SIL	25.1	64	7	8.1	175	21.6	201.8	39	231	180	-	McGowan *et al*., (2012)
Windermere South Basin	SIL	16.8	42	9.8	6.7	200	37.3	112.7	39	231	100	-	McGowan *et al*., (2012)

This thesis will use the term upland to refer to lakes found above 100 m.a.s.l and lowlands as those below 100 m.a.s.l. here on in (Figure 2.2; Figure 2.3). Although technically the distinction is made on whether the lakes are found above or on the alluvial plain, 100 m.a.s.l. follows the classification by Curtis *et al.*, (2014) which described upland sites as “waters located upstream of direct human disturbance and intensive land use through industry, agriculture and urbanisation”. The 100 m.a.s.l. grouping was considered to be a more useful tool to help address the aim of this thesis which seeks to elucidate the relative importance of global and local stressors, and the spatial scales on which they influence lake catchments. This is because different pressures have acted on lowland to upland lakes over different timescales, with lowland lakes impacted by agriculture and human settlement since the Neolithic period and upland lakes impacted by atmospheric pollutants from the Industrial Revolution (Bennion *et al.*, 2011a). The spatio-temporal differences of these environmental drivers necessitated the need for distinction between the two lake groups.

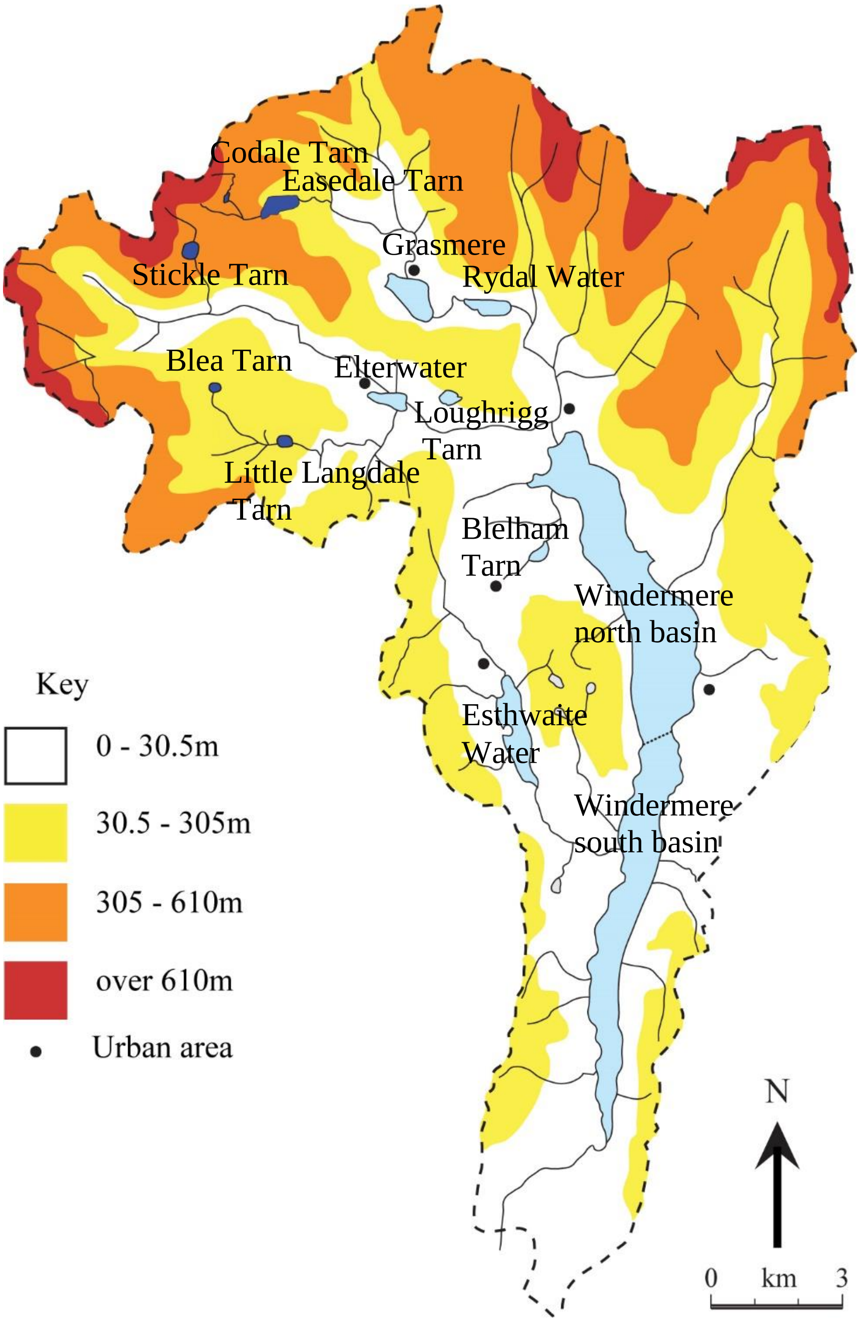


Figure 2.2 Low resolution relief map of Windermere catchment. Lakes shaded dark blue are upland sites (>100 m.a.s.l.) and lowland sites (<100 m.a.s.l.) are shaded light blue. Modified from Pickering (2001).

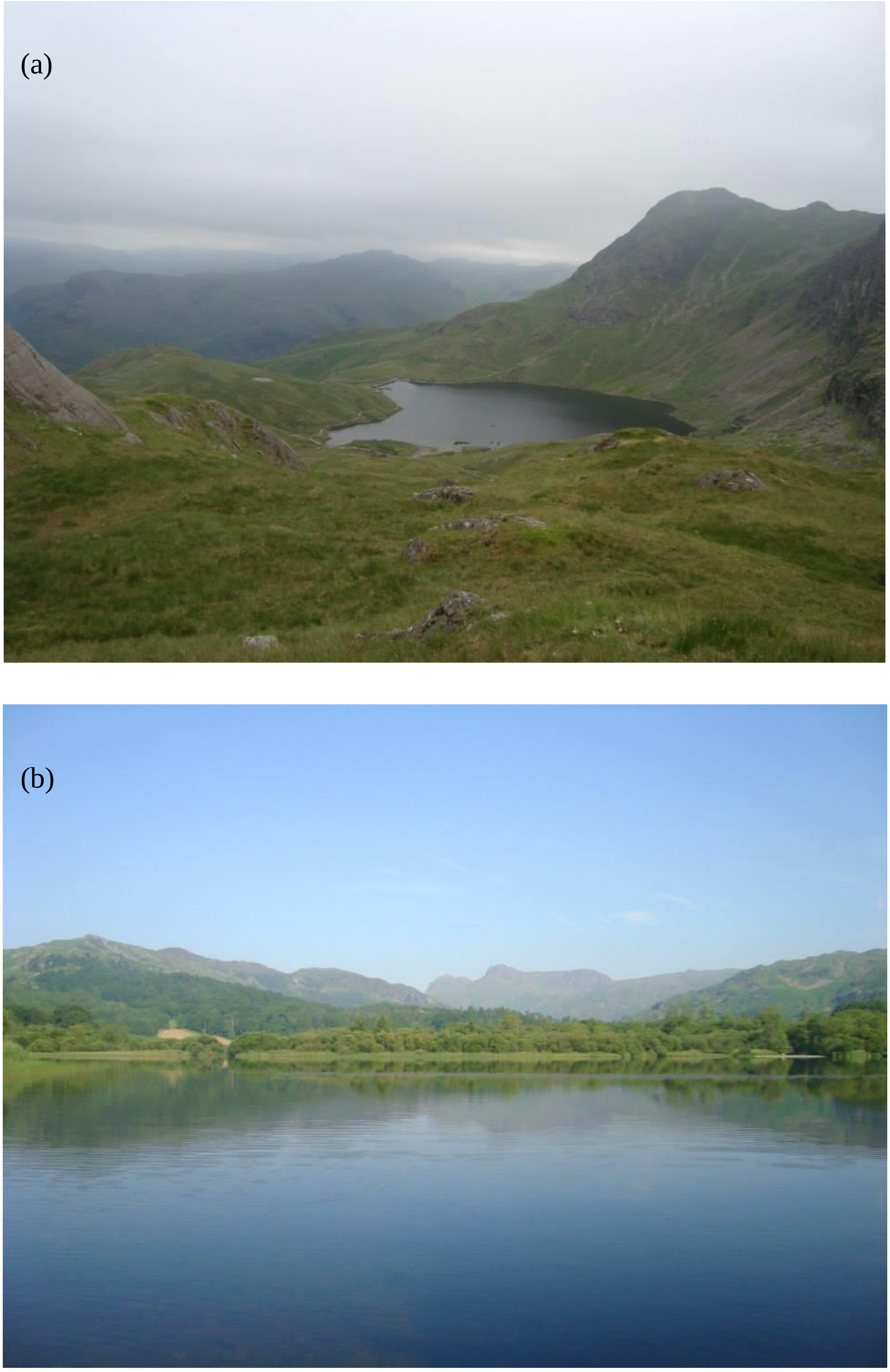


Figure 2.3 Photos (taken by the author) showing different catchment characteristics of (a) Stickle Tarn, with its rocky, moorland upland catchment and (b) Grasmere located in the valley bottom.

2.2.2 Geology

The catchment is split into two distinct geological regions (Figure 2.4). The bedrock of the north catchment is Mid-Ordovician (~470 million years old) Borrowdale Volcanic Group (BVG) strata, which are hard, slow-weathering extrusive lavas (Sutcliffe and Carrick, 1983). The rocks of the BVG are green slates and porphyries which impart low amounts of major ions (e.g. sodium, potassium, magnesium) to the overlying surface waters meaning that lake water has a similar ionic composition to precipitation (Sutcliffe *et al.*, 1982). The shallow mineral soils in the north catchment are thinly covered by acidic podsols (Pickering, 2001).

The southern catchment bedrock is composed of Silurian Coniston Flags and Slates (SIL) which are younger (~443 million years old) marine sedimentary rocks of flags, grits and shales. SIL rocks are easily weathered resulting in surface waters with higher ionic content and greater buffering capacity to acidification than the BVG group (Thornton and Dise, 1998). Between the BVG and SIL bedrock there is a thin band of Coniston Limestone, which further increases the hardness of those waters draining below it (Sutcliffe and Carrick, 1983). The south catchment soils are unproductive deep alluvial soils, composed of free-draining loams and brown earths, with patches of peaty-gleys (Sutcliffe and Carrick, 1983; George *et al.*, 2007).

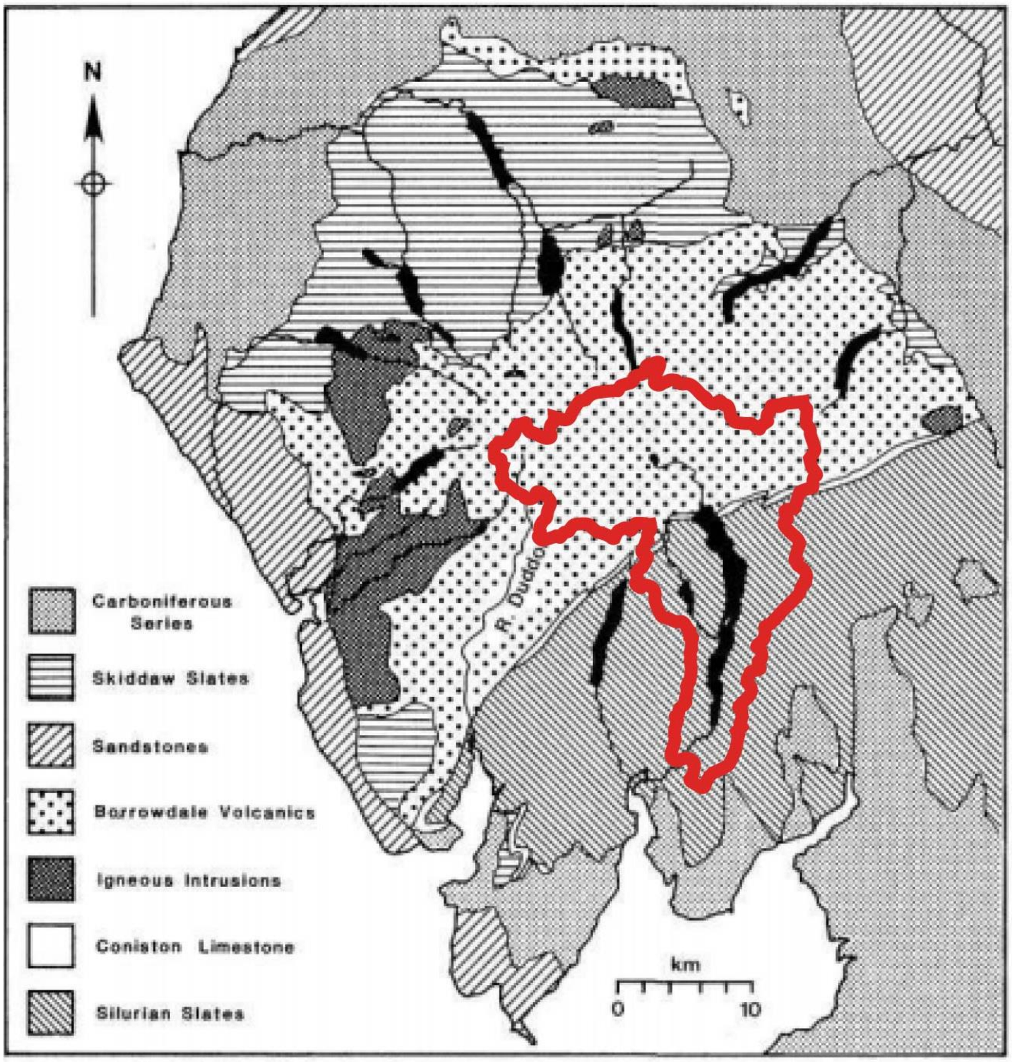


Figure 2.4 Geology of English Lake District. Windermere catchment highlighted in red. Modified from Sutcliffe and Carrick (1983).

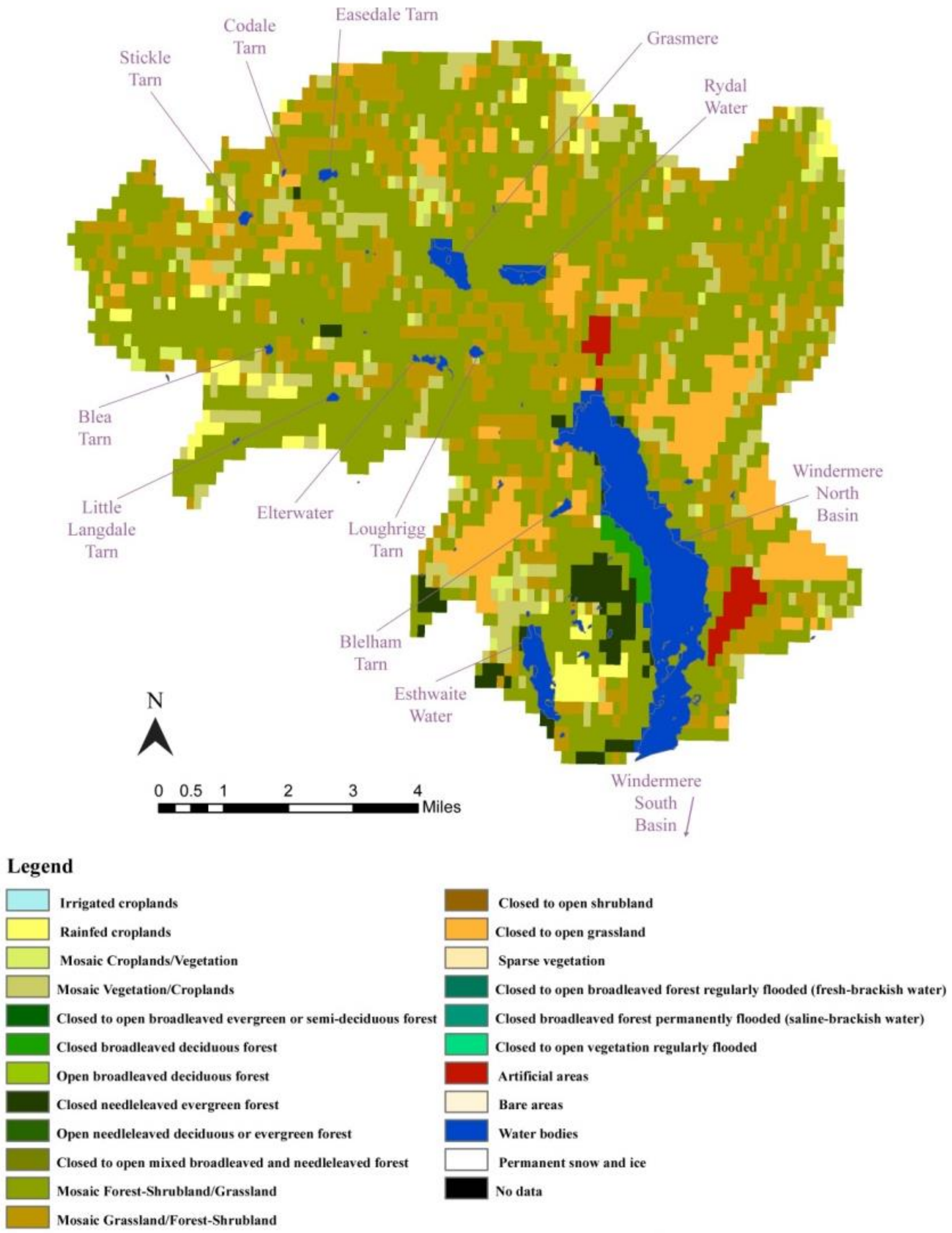
2.2.3 Land cover

After the last glaciation the region was rapidly colonised by vegetation as the climate became milder. Although intermittent cold and warm spells shifted vegetation from scrub to trees, afforestation resulted in a community of oak and elm woodland on well-drained slopes, ash on the limestone and valley bottoms, and alder and willow on wetter soils (Pickering, 2001). Deforestation and other agricultural vegetation changes from the 9th century onwards disrupted the natural vegetation succession and are described in section 2.4.1.

Present day land cover is largely unimproved grassland in the north of the catchment, with shrub land on steeper, denudated slopes, and native broad-leaf and conifer woodland and improved grassland to the west of Windermere (Pickering, 2001) (Figure 2.5). The east contains the largest urban settlements of Ambleside and Bowness-on-Windermere. The dominant land class in the catchment is rough pasture (Maberly *et al.*, 2003).

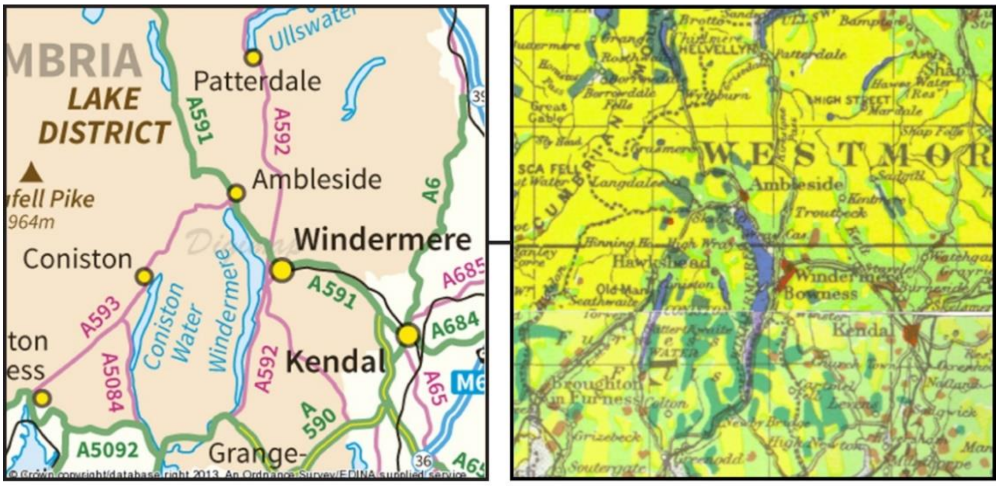
Comparison between present and historical land-cover (1931-35) (Figure 2.5; Figure 2.6) reveals relatively little expansion of urban and improved grassland cover over the last 80 years, although different resolution and vegetation classifications prevent a more accurate assessment. It implies that intensification rather than expansion of human activity within the catchment has been responsible for altering lake trophic status over the last century, with distinct differences in status found between lakes in cultivated and uncultivated catchments (George *et al*., 2000). It also implies significant land cover change prior to the 1930s as described in section 2.4.1.

The morphology of both the catchment and lakes, coupled with heterogeneous geology and land use, has resulted in lakes that exhibit considerable differences in chemistry and ecology despite their close proximity in space (Talling, 1999).



Dataset: Globcover2009
Supplier: ESA and Universite catholique de Louvain
Source: © ESA 2010 and UCLouvain

Figure 2.5 Globcover2009 300m resolution land cover map of the Brathay/north Windermere catchment. © European Space Agency (ESA) and Université catholique de Louvain (UCL). Modified from Arino *et al*., (2012).



(scale 1:625 000)

Key:
Land Use

🟦 Forest & Woodland

🟫 Arable Land

🟩 Meadowland & Permanent Grassland

🟨 Heathland, Moorland & Rough Pasture

🟥 Chief Urban Areas

🟪 Orchards and Nursery Gardens

Figure 2.6 Current Ordnance Survey map (2013) and the Dudley Stamp Land Utilisation Survey Map and key (1931-35) of Windermere catchment (50.1°N, 30.8°E). Scale 1:625,000, © Crown copyright: Ordnance Survey, GB and L. Dudley Stamp/Geographical publications ltd, Audrey N. Clark, Environment Agency/DEFRA and Great Britain Historical GIS. Using: EDINA Digimap Ordnance Survey Service. Created May, 2014

2.3 The climate of the Windermere catchment

2.3.1 Drivers of inter-annual climate

Since the catchment lies close to the west coast, it is influenced by the quasi-cyclical patterns of atmospheric pressure systems from the Atlantic, resulting in a broadly mild and wet climate. The mountains also have an important impact on the climate of the Lake District. The shading effect of the mountains reduces temperatures and sunlight in the uplands, and rainfall is predominantly orographic (George *et al.*, 2007; Kenworthy, 2014). Further, temperatures can decrease by 0.7°C per 100m of altitude (METOFFICE, 1971). In winter, air temperature and rainfall determine lake physical characteristics, with typical winter air temperatures reaching -10°C, resulting in smaller lakes freezing over (George *et al*., 2007). In summer, wind-mixing is important in governing the transfer of heat particularly in the larger lakes (George *et al*., 2007). To summarise, the smaller upland lakes are subject to greater rainfall, lower temperatures, sunlight and wind-mixing, and in winter, the occurrence of ice cover, compared to the larger lowland lakes of the Lake District.

Several authors have found a relationship between the atmospheric pressure gradient known as the North Atlantic Oscillation (NAO) and its underlying physical mechanism known as Rossby Wave Breaking, and winter weather characteristics in the Windermere catchment and elsewhere in Europe (George *et al.*, 2004; Strong and Maberly, 2011). A low pressure system over Iceland and a high pressure system over the Azores control the strength and direction of westerly winds over Europe, with large differences causing a high NAO index/positive phase and small differences causing low/negative index years (Hurrell, 1995). When the NAO index is low/negative, winters are colder and drier, dissimilar to the milder, wetter winters caused by strong westerly air flows when the NAO index is high/positive (George *et al.*, 2004). Milder, wetter winters correspond to lower winter Chl. *a* biomass in the catchment's lakes particularly in small, well-flushed lakes such as Grasmere, from increased hydraulic flushing and turbidity (George *et al*., 2004). Thus, coherent lake physical and biological properties have been linked to the NAO, which is further enhanced by landscape factors such as altitude, lake depth and trophic status (Straile and Adrian, 2000).

2.3.2 Late Holocene climate variability

The Holocene Interglacial period since the last ice age has consisted of cooling and warming periods which have influenced human-mediated catchment vegetation changes and lake algal communities (Dong *et al*., 2011). For instance, at Esthwaite Water, the cooler period between ~780 and 880AD prior to the Medieval Climate Anomaly was characterised by expanding agriculture and deforestation which resulted in greater nutrient delivery and the first appearance of the mesotrophic diatom *Asterionella formosa* Hassall (1850) in the lake (Dong *et al*., 2011). During the Medieval Climate Anomaly (~850-1350AD), however, terrestrial nutrient uptake increased due to the proliferation of woodland in the absence of human activity and warmer temperatures, and oligotrophic diatom taxa were more typical (Dong *et al*., 2011).

2.3.3 19th and 20th century climate warming

Within the last two centuries the global climate has warmed by ~0.6°C beyond the relatively stable temperatures of the late Holocene (disregarding the anomalies of the Medieval Climate Anomaly and Little Ice Age). This has modified both regional (NAO) and local weather patterns and has consequently disturbed ecological functioning in lakes of the Windermere catchment (Kovats *et al*., 2014). For example, warmer spring temperatures have adjusted phytoplankton phenology in lake Windermere, with the advancement of spring diatom *Cyclotella* spp. peak biomass due to earlier thermal stratification (Thackeray *et al*., 2008). However, changes in both nutrient levels and climate shown by monitoring data in the 20th century in the lowland lakes of the catchment make it difficult to determine the extent to which each has altered lake algal communities because of their similar effects and inter-connectedness (Smol and Stoermer, 2010; Dong *et al*., 2012).

Further, the lack of instrumental data and the highly heterogeneous metereological nature of the upland regions make it difficult to characterise the climate the upland lakes have or will be subject to (Orr *et al*., 2008). Observed rainfall in the Lake District found winters were wetter within the 1970s to 1990s, and heavy precipitation events during this period were more marked at high altitude sites (Malby *et al*., 2007). Evidence of more rapid warming in upland regions of the North Peninnes and reduced snow cover and duration in Scottish uplands could indicate similar trends have been experienced in the uplands of the English Lake District (Harrison *et al.*, 2001; Holden and Adamson, 2002).

2.4 A brief anthropogenic history of the Windermere catchment

Humans have shaped the nature of the Windermere catchment since Neolithic times (~4000-2400BC) as evident from the extensive Neolithic axe factory at the Great Langdales near Stickle Tarn (Pickering, 2001) (Figure 2.1). Following this, settlement revolved around agriculture and mining industries, whilst tourism and industrialisation began much later, in the 18th century. These industries are summarised in sections 2.4.1-2.4.3.

2.4.1 Agriculture and human settlement

The longest direct impacts of human activity on the catchment have been from agriculture and associated human settlement, which began in the Neolithic period (Table 2.2). Deforestation was relatively small-scale until the arrival of Norse settlers in the 9th century, whose mass clearance and animal husbandry of Herdwick sheep and enclosures built from dry-stone walls were the beginnings of the present-day landscape of the Lake District. Arable farming was typical in the valley bottoms until the 18th and 19th centuries when agriculture became mechanised with the invention of the plough and arable production shifted to livestock (Pickering, 2001). Farmers also experimented with sewage slags and liming to help create more fertile pastures in which to increase stocking densities (Pickering, 2001). Presently, rough grazing of sheep is the dominant form of livestock production in the catchment, with some limited cattle farming (Figure 2.7). The use of artificial fertilisers and overstocking is common, although numbers of cattle have declined since the Foot and Mouth crisis in 2001 (McGowan *et al.*, 2012).

Prior to the 19th century, agricultural impacts on lake ecosystems stemmed from the attendant effects of deforestation and associated soil erosion. Allochthonous OM delivered nutrients to the lakes which stimulated algal production (Moorhouse *et al.*, 2014). However, later 19th and 20th century intensification of agriculture is believed to have accelerated nutrient loading and led to the proliferation of cyanobacteria in lowland lakes, specifically Windermere and Blelham Tarn (Moorhouse *et al*., 2014). The wider impacts of agriculture across the catchment during this time will be investigated in this thesis.

Figure 2.7 Herdwick sheep grazing at Dungeon Ghyll, valley bottom of Stickle Tarn. July 2013. Photo taken by author.

Table 2.2 Historical records of agricultural activity in the Lake District and Windermere catchment. Sources: Rollinson (1967), Pennington (1984), Thornton and Dise (1998), Pickering (2001) and Lear (2007).

Date	Historical agricultural activity and human settlement in the Lake District
1950s	Liming related to raised base cation and alkalinity of SIL lakes.
19th century onwards	Farming switched from arable to livestock production in the valleys, using "slag" to enrich the pastures.
1899	Rev Rawnsley and son help establish Herdwick Sheep Association, dedicated to the preservation of the rare Herdwick breed.
Late 18th-early 19th century	Afforestation in hillsides due to demand for timber from the mining and industry in West Cumbria.
1780's	John Christian Curwen planted larches on Belle Isle in the centre of lake Windermere and on the slopes surrounding the lake. Wordsworth acknowledged his distaste for the introduction of exotic larch species.
1763-1800	Enclosure movement responsible for 50,000 acres of land enclosed by drystone walls in Cumberland and Westmorland.
Post-1750	Large-scale amenity planting and woodland conservation in the Lake District. Grazing rapidly expanded.
17th-18th centuries	Increased farm buildings and houses built, owned by independent Dalesmen who held land by customary tenure.
17th century	Use of liming on grassland in Rydal documented.
16th-17th centuries	Cultivation of arable crops such as oats (variety known as skegg) and barley. Limited to what could grow on thin acidic soils and under heavy rainfall. Pack horses used for transport. Farm equipment primitive with no documentation of horse drawn ploughs. Livestock put out to graze stubble after harvest. Livestock was predominantly sheep (Herdwick) and dairy cattle.
16th century	Growing number of small-scale landowners, land divided into grounds which were then named after family who owned it.
16th century	Building of chapels and grammar schools in region signified increasing human population.
1537	Furness Abbey dissolved, land fell into secular hands
14th century	Furness Abbey produced 40 sacks of wool per year.
12th-13th centuries	Monasteries were major landowners and used uplands for sheep pasture. Most extensive landowner was Furness Abbey (includes land around Little Langdale and Elterwater)
12th-13th centuries	Fells cleared of forest, valley floors drained and improved. Small villages and hamlets grew larger.
1092	Norman invasion reached Cumbria, establishment of monasteries in region.
9th-10th centuries	Norse settlers brought over Herdwicks and built dry stone walls.
9th-10th centuries	Scandinavian settlements named tarn/dale/fell/beck, kept sheep but also cattle and pigs. Grasmere named after Scandinavian word for pig=griss. Pigs kept in woodland which reduced regeneration and corresponded to decline in tree pollen.
~600AD	Anglian settlers identified by names of settlements ending in ingham/ham/ington
400AD	Romans retreated marking beginning of dark ages with Pictish and Scottish raids devastating settlements in Lake District.
100-400AD	Roman road built from Ambleside to Ravenglass, Hardknott castle built believed to be roman.
100-120AD	Roman fort built at head of Windermere at small delta of Rothay and Brathay, attacked in 197, 296, 367AD.
77-84AD	Cumbria invaded by Roman troops and used as a military zone not for building of settlements.
1st-2nd centuries	Clearing of forests and improvements to agricultural implements such as ploughs.
~4000-2400BC	Elm decline. Neolithic forest clearance began which increased transfer of acidic organic soils to lake sediments.

2.4.2 Mining

Since the 16th century, the region has been mined and quarried for its abundant mineral resources (Table 2.3). Mining expanded in the 1800s as larger private companies took ownership (Miller *et al.*, 2014). Copper, lead and iron were mined most extensively in the 19th century but declined towards its end (Pickering, 2001). Quarrying for slate and other stones and aggregates largely ceased in the early 20th century, with only a few small quarries now remaining open (Millward *et al.*, 2000).

Evidence of heavy metal pollution and associated impacts on biota have been recorded in sediments of lakes downstream of mining activity. These included Windermere, Elterwater and Little Langdale Tarn (Figure 2.8) (Oswald *et al.*, 2001; Miller *et al.*, 2014). In the early 20th century, a copper peak in the sediments at Little Langdale Tarn corresponded with an increase in the copper resistant diatom taxa *Brachysira vitrea* (Grunow) Ross (1966) (Oswald *et al.*, 2001). In 1979, the Greenburn reservoir dam burst upstream of the tarn and an increase in allocthonous OM sedimentation and lower autochthonous production were recorded in the tarn's sediments, which implied that increased turbidity suppressed primary production (Oswald *et al.*, 2001). Although sediment mineral compositions are not investigated in this thesis, the effects of erosion on lake biota from 19th century historical mining activity will be attempted.

Table 2.3 Historical records of mining activity in the Lake District and Windermere catchment. Sources: Rollinson (1967), Adams (1988) and Oswald *et al*., (2001).

Date	Historical mining activity in the Lake District
1906-1917	Work undertaken at Greenburn but on a smaller scale.
End of 19th century	Coniston copper mines ceased production, began by German miners in 17th century, left spoil tips and disused mine shafts.
1885	Engine shaft abandoned at Greenburn Copper mine.
1845-1865	Greenburn copper mine active (although potentially in operation from the late 17th century onwards).
1845	Greenburn reservoir was built for Greenburn Copper mine.
1840-1920	Copper mining in the Greenburn valley upstream of Little Langdale Tarn.
19th century	Gunpowder works at Black Beck, Low Wood and Elterwater.
19th century	Honister and Coniston most productive slate quarries.
By 1830	Greater development of textile manufacturers, mining, shipping in the Lake District
18th century	Regular charcoal boats on Windermere. Clappersgate near Ambleside became a port for the shipment of slate and charcoal.
1630	Water supplied from Little Langdale and Blea Tarn's to Stamp mills at Hackett.
1623	Iron smelting near Sawrey.
1564	Founding of the Company of Mines Royal signalled expansion of copper and lead mining in Lake District, which in turn increased demand for charcoal and subsequent deforestation in region.
1564	Lead mine opened in Greenhead Gil, Grasmere but closed in 1573.
15th-16th centuries	Fulling mills expanded in catchment linked to woollen cloth industry of Kendal.
14th century	Furness fells site of charcoal manufacture and iron smelting.
13th century to 1946	Mining of coal since the monks of St Bees Abbey supervised the opening of coal mines at Arrowthwaite until the closing of the last deep coal mine at Haig Pit in 1946.

Figure 2.8 Little Langdale Tarn. Downstream of Greenburn copper mine. July 2013. Photo taken by author.

2.4.3 Tourism and urban expansion

The Romantic Movement of the 18th – 19th centuries sparked the beginnings of national and international interest in the Lake District, which promoted the area as one of inspirational natural, wild beauty (Table 2.4). Mass tourism began from 1847 following the opening of a railway from Manchester to Windermere, which rapidly increased visitor numbers, urbanisation and sewerage development (Rollinson, 1967). Concerns about the threats to the region's natural beauty from urban development were first voiced by the poet William Wordsworth in the 19th century, a forerunner of the Romantic Movement and later in the century by the children's author Beatrix Potter. This "opening up of the Lake District" was recorded in the sediments of Windermere by a shift in diatom ecology to dominance of *A. formosa* from the mid-19th century onwards (Pennington, 1943). Presently, 15.8 million tourists visit the Lake District annually, most of whom stay in or visit the Windermere catchment, and spend over £1 billion, making tourism the most important economy in the region (Figure 2.9) (Harvey *et al.*, 2013).

The dominant, indirect effect of tourism and urbanisation on the catchment lakes was the increased delivery of treated and untreated effluent and attendant nutrient enrichment in lowland lakes close to urban areas. At Windermere, wastewater was first treated in 1886 at Ambleside WwTW, and treated effluent was released into the north basin which stimulated marked increases in phytoplankton growth (McGowan *et al.*, 2012). A similar trend was seen in the south basin after the development of Beemire WwTW in 1888, but the centralisation of wastewater treatment in the 1960s increased nutrient loading further, particularly in Windermere and the other receiving waterbodies of the large WwTWs in the catchment, specifically Grasmere, Elterwater and Esthwaite Water (Figure 2.10) (Talling, 1999). A P budget at Windermere in 1991 revealed 68% of the P delivered to the lake was from sewage effluent (Tower Wood WwTW=30% (south basin), Ambleside WwTW=27% (north basin), Elterwater WwTW=2% (north basin), Grasmere WwTW=2% (north basin), and Hawkshead WwTW=7% (south basin)) (Reynolds and Irish, 2000). Palaeolimnological studies in Windermere, Grasmere, and Esthwaite Water revealed shifts in community structure to enhanced filamentous cyanobacteria production, nutrient-rich diatom taxa and reduced hypolimnetic oxygen, of particular concern for Windermere's population of *S. alpinus* (Sabater and Haworth, 1995; Barker *et al.*, 2005; Winfield *et al.*, 2008; Dong *et al.*, 2011; McGowan *et al.*, 2012). Long-term comparable changes in phytoplankton production and community structure related to sewage loading have not been investigated on a wider catchment-scale and will be addressed in this thesis.

Figure 2.9 Stickle Tarn. Troops of fell-walkers line the hills and have been linked to severe footpath erosion in certain locations in the Windermere catchment. November 2012. Photo taken by author.

Table 2.4 Historical records of tourism and urbanisation activity in the Lake District and Windermere catchment. Sources: Rollinson (1967), Thompson (1971) and Lear (2007).

Date	Historical tourist and urban development in the Lake District
1957	Foxfield to Coniston railway closed.
1952	Alfred Wainwright began work on the first page of his "Pictorial Guide to the Lakeland Fells" on 09/11/52. He spent 13 years completing this book.
1951	Lake District National Park designated.
1943	Death of Beatrix Potter. She bequeathed her properties and holdings to the National Trust including 14 farms (which included Yew Tree farm, Coniston and Hill Top Farm, Near Sawrey), Sheep (she was an expert Herdwick sheep breeder and the first female president designate of the Herdwick Sheep breeders Association) and 4000 acres of land.
1930s	Friends of the Lake District campaign against aesthetically unpleasing re-afforestation in Lake District.
1934	Formation of "Friends of the Lake District".
1911	Beatrix Potter involved in local campaign against construction of aeroplane factory at Cockshott Point on Windermere and the use of hydroplanes on the lake.
1907	National Trust registered under special act of parliament. Presently owns much of land in Lake District.
1895	Reverend Rawnsley and others establish the National Trust for Places of Historic Interest or Natural Beauty. Based on legal premise of a non-profit entity being entitled to land/buildings for the enjoyment of the entire nation.
1887	Plans to extend railway from Windermere to Ambleside abandoned.
1883	Reverend Rawnsley (friend of Beatrix Potter) proposed the formation of Lake District Defence Society in order to prohibit "injurious encroachments upon the scenery….from purely commercial or speculative motives".
1882	Reverend Rawnsley (vicar at Wray) campaigned against a railway that would have been through Borrowdale along the pristine shores of Derwentwater.
1860	Coniston water - steamer "Gondola" operating.
1847	Lancaster-Carlisle line at Oxenholme via Kendal to Windermere station opened.
1846	Two steamers "Lady of the Lake" and "Lord of the Isles" operating.
1810	Wordsworth published his "Guide to the Lakes" which went into its 5th edition in 1835. Described Lake District as "…a sort of national property in which every man has a right and an interest who has an eye to perceive and a heart to enjoy".
1800-1831	Increase in human population by 36% in Furness and Cartmel.
Early 19th century	Expansion of inns to cater for travellers in Grasmere, Ambleside and Hawkshead.
End of 18th century	Regattas held on Windermere.
1778	Thomas West published the first guidebook to the lakes and dubbed Stickle pike "an inaccessible pyramidal rock".
1769	Poet Thomas Gray considered first genuine tourist of the Lake District. Described Grasmere as an "unsuspected paradise".
1757	Dr John Brown published "Description of the Lake and Vale of Keswick" signifying the beginning of the 'Romantic' movement.
1752 onwards	Turnpike roads constructed in Cumbria. Improved road travel and communications.

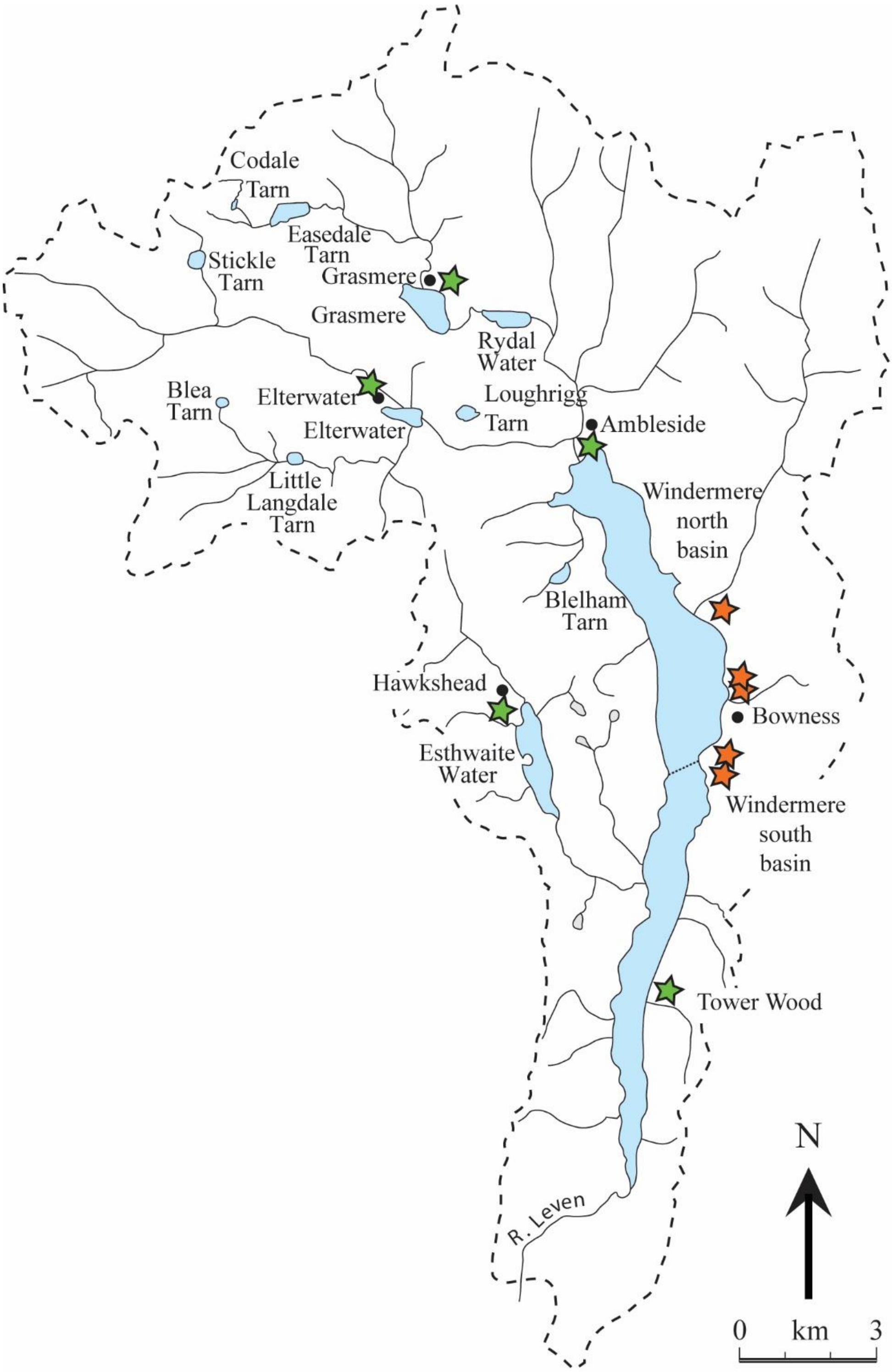


Figure 2.10 Location of present Wastewater Treatment Works (WwTWs) in the Windermere catchment (green stars) and disused (red stars). Modified from McGowan *et al*., (2012).

2.5 History of long-term monitoring and palaeolimnology

In 1929, the Freshwater Biological Association (FBA) was founded by W. H. Pearsall amongst others, and housed its laboratory at Wray castle on the western shores of Windermere. Limnological monitoring began in ~1945 when J.W.G. Lund realised that it was imperative to study lake physics and chemistry in order to understand the effects of habitat and food resources on algal ecology (Maberly and Elliott, 2012). Today, systematic two-weekly sampling is carried out by the Centre for Ecology and Hydrology (CEH), who use these long-term limnological records (~65 years) to answer questions on lake ecosystem functioning and drivers of change (Maberly and Elliott, 2012).

Palaeolimnology originated on the shores of Windermere in 1937, when Clifford Mortimer hammered a steel tube into the sediments and studied the lithological composition of the core (Mortimer and Worthington, 1938; Battarbee, 2012). Palaeolimnology in the region then focussed on testing Pearsall's theory of post-glacial lake evolution, in which he ordered the Lake District lakes from "primitive" to "evolved" (Pearsall, 1921). In the late 1970s, Pennington used diatoms and pollen to interpret post-glacial climate and human-mediated vegetation changes and their effects on lake ecology, and in doing so, marked a shift in the focus of the region's palaeolimnology (e.g. Pennington, 1984). Below brief overviews are given into the nature of investigations into three key environmental drivers within the Windermere catchment.

2.5.1 Eutrophication

In the mid-1970s, Lund's pioneering mesocosm experiments at Blelham Tarn, using the "Lund tubes", showed the effects of N and P fertilisation on phytoplankton community structure (Lund *et al.*, 1975). Lund also investigated the effects of eutrophication on phytoplankton community changes at Windermere, Blelham Tarn, Esthwaite Water and Grasmere, and determined the nutrient sources to be sewage, artificial fertilisers and P-detergents (Lund, 1981). Palaeolimnological investigations supported Lund's findings, with increased eutrophic diatom spp. in lowland lakes such as the peak in the eutrophic diatom *Stephanodiscus astraea* var. *minutula* (Kützing) Grunow. in the sediments of Blelham Tarn dated to 1973, attributed to increased sewage delivery (Haworth, 1984). The effects of eutrophication on algal communities in Windermere was developed further by McGowan *et al*., (2012), which attributed increased cyanobacterial pigments and algal production from the early 1900s onwards to treated and untreated sewage effluent and increasing agricultural intensification.

2.5.2 Acidification

In the 1960s, palaeolimnological studies included fossil diatoms from Blea Tarn showed natural acidification from the early to mid-Holocene (Haworth, 1969), and the chemical composition of sediment mineral matter to reconstruct base cation impoverishment in lakes and their catchments over time (Mackereth, 1966). By the 1980s, the acid rain debate, improvements to dating techniques, and development of transfer functions from diatom compositional changes to reconstruct lake chemistry such as pH, saw an increase in palaeolimnology as a tool to study recent (Industrial Revolution onwards) anthropogenically-driven acidification of the upland lakes (Battarbee, 2012). Sedimentary diatoms were used to reconstruct pH changes in three upland tarns elsewhere in the Lake District, and found different timings and degrees of anthropogenic pH changes since 1850 due to the different neutralising abilities of each tarn’s catchment (Whitehead *et al*., 1997). More recently, palaeolimnological studies have tried to determine the extent of recovery from acidification in the upland lakes in the Windermere catchment (e.g. Tipping *et al*., 2002).

2.5.3 Climate change

Early palaeolimnology in the catchment was interested in the changing physical and chemical sediment composition of long sequences between periods of glacial to temperate states (Pennington, 1991). Whereas recent palaeolimnology has primarily focussed on un-coupling climate-nutrient impacts on lake primary producer communities in the lowlands lakes of the catchment (Barker *et al.*, 2005; Dong *et al.*, 2011; McGowan *et al.*, 2012).

Despite the long-history of contemporary and palaeo-limnology in the catchment, there has never been a systematic catchment-scale investigation that attempts to elucidate the relative importance of the aforementioned drivers of change on biological proxies at the community level.

2.6 Justification for site and timescale of thesis

Reasons for choosing the Windermere catchment as a study site for this thesis are detailed below.

First, the Windermere Catchment Restoration Programme (WCRP) wanted this project to investigate baseline conditions, extent and causes of lake ecological change within the Windermere catchment in order to focus sustainable catchment mitigation measures, which consequently formed the aims of this thesis (*pers. Comm.* Michelle Donaghue, Lakes Manager, Environment Agency). The WCRP is a partnership of several organisations fore-fronted by the Environment Agency who have responsibility in restoring and conserving the international and nationally important water quality and ecology of Windermere and its catchment lakes. Implicitly, the aim of the WCRP is to achieve good ecological status in the larger lowland lakes which are under the remit of the WFD, but the health of upland lakes is recognised as integral, hence their inclusion in this project (WCRP, 2015b).

Second, increasing pressures from a range of anthropogenic stressors have jeopardised the delivery of ecosystem services from the Windermere catchment lakes (sections 2.3.3-2.4). Implicitly, the significance of the region in the conservation of natural habitats and species, and its designation as a National Park, which promotes public enjoyment, has led to conflicting demands on the region and its lakes (Pickering, 2001). This makes it an important study catchment to investigate the effects of multiple stressors on lake ecosystems and facilitate the aims of the WCRP.

Third, the heterogeneity of lake physical characteristics which have been well-studied in limnological monitoring makes this an ideal study catchment to attempt to evaluate how these traits could have influenced algal community change across broader spatial and longer temporal scales (Maberly and Elliott, 2012). Such a study is missing in catchment-scale palaeolimnological research (see section 1.3.1).

Finally, the timescale of 1800 to the present was chosen as an appropriate timescale to determine global to local drivers of change on lake ecology as it captures the pre- and post-1850 industrial revolution era that has been linked to lake ecosystem degradation both in the Windermere catchment and worldwide (Pennington, 1943; Steffen *et al.*, 2007). Although the Windermere catchment has a long history of human catchment disturbance (particularly since the mass deforestation of the 12th-13th centuries), palaeolimnological investigations recognised that the late 19th century onwards experienced the greatest lake ecological change, with loss of rare species, reductions in community diversity and proliferation of nutrient rich taxa (Pickering, 2001). In addition, setting reference conditions to periods in lake histories prior to any human-mediated catchment perturbations (which in the Windermere catchment would be the Neolithic era) is a major challenge of the WFD (Bennion and Battarbee, 2007). Therefore, by focussing on the period just before and after local and global human activity intensified, management efforts would likely be more sustainable and require less social, political and economic upheaval (Ison *et al.*, 2007). By elucidating more recent drivers of ecological community change in the lakes of the Windermere catchment it becomes easier to identify the activities that sustainable catchment mitigation should focus on.

The following chapter describes the fieldwork undertaken on the Windermere catchment described in this chapter, and introduces the individual sites in greater detail.

CHAPTER 3. METHODS I. FIELDWORK.

This methods chapter describes the fieldwork undertaken to collect and prepare sediment records for laboratory analyses detailed in chapter 4.

3.1 Fieldwork

Five fieldwork sessions were undertaken in November 2011, March 2012, November 2012, March 2013 and July 2013 to collect 27 lake sediment cores from 11 upland and lowland lakes in the Windermere catchment (Figure 3.1). All cores were retrieved from the deepest part of the lake (unless stated otherwise) identified by an echo sounder, and the location noted using a GPS. A 50cm Glew gravity corer (Glew, 1988) was used to retrieve cores from the upland tarns Stickle Tarn, Codale Tarn and Easedale Tarn where access was difficult and required transporting equipment long distances by foot. For Blelham Tarn, Esthwaite Water and Rydal Water where access was easier from the road, a 1m mini-Mackereth corer (Mackereth, 1969) (courtesy of Lancaster University) was used until it broke in March 2012, after which a 9cm diameter 1m length HON-Kayak gravity corer (Renberg, 1991) (courtesy of Loughborough University) was used to retrieve cores from the remaining sites (Blea Tarn, Little Langdale Tarn, Loughrigg Tarn, Grasmere and Elterwater inner, middle and outer basins). Immediately upon collection core lengths were measured and lithological character, colour changes and presence of macrofossils were noted. Those cores taken with the mini-Mackereth corer were covered with black plastic and kept in a cool (+4°C) environment to prevent pigment degradation (Leavitt and Hodgson, 2001). Within 2 days of collection they were sectioned in the laboratory into 0.5cm intervals, sealed in air-tight plastic bags and frozen (-20°C). Core sectioning for the HON-Kajak and Glew cores was performed in the field directly after retrieval and the samples were frozen (-20°C) on return to the laboratory.

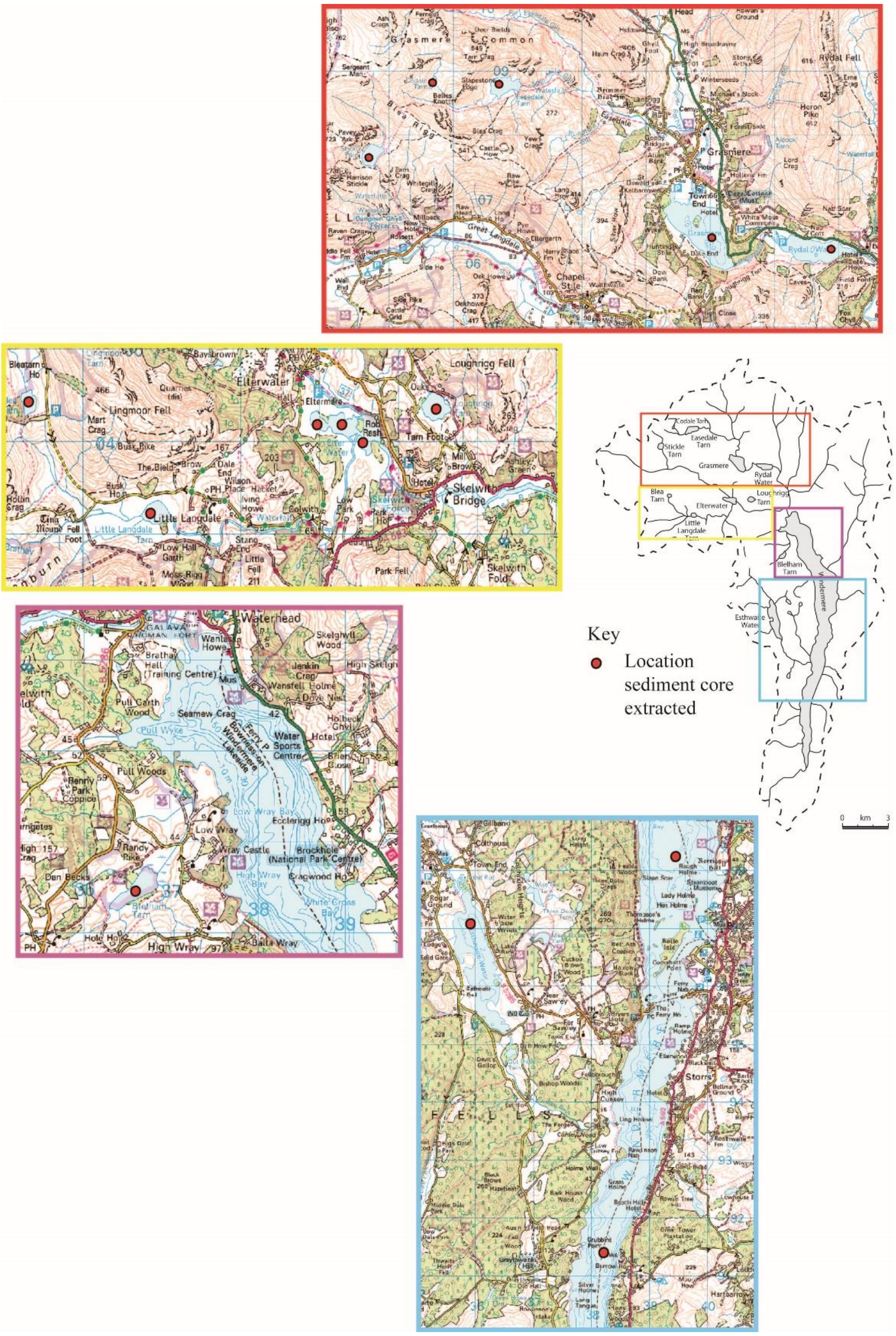


Figure 3.1 Map of Windermere catchment and coring locations from this study and core locations taken from the Windermere basins described in McGowan *et al*., (2012). Catchment map modified from McGowan *et al*., (2012), coring maps contains OS data © Crown copyright [and database right] (2014).

3.2 Individual study sites and sediment coring

For descriptions of Windermere north (WNB_{site}[2]) and south basins (WSB_{site}) and coring details see McGowan *et al.*, (2012). Catchment study sites and coring undertaken by the author are described in order of descending lake altitude.

3.2.1 Stickle Tarn (STI_{site}). Upland (469 m.a.s.l.)

Stickle Tarn (STI_{site}) (NY287 077) is a small, rapidly flushed, headwater upland corrie tarn and is the highest elevation lake in the catchment at 469 m.a.s.l. (Figure 3.2; Table 2.1). STI_{site} is recessed into the sheer rocky wall of Pavey Ark, one of the Langdale Pikes, with rocky scree slopes to the west and high moraines along the outer edge to the east (Haworth *et al.*, 2003). Bright Beck is the main inflow, a small stream which curves around the northern shores, and Stickle Ghyll is its main outflow (Haworth *et al.*, 2003). Apart from some footpaths and rough grazing of sheep, anthropogenic land use surrounding STI_{site} is minimal (Tipping *et al.*, 2002).

The diatom species within STI_{site} are characteristic of oligotrophic, circumneutral waters (Haworth *et al.*, 2003). However, in 1985 high concentrations of acidophilus species such as *Achnanthes marginulata* Grunow (1880) were recorded in STI_{site} sediments, but by 1999, circumneutral taxa such as *B. vitrea* dominated (Tipping *et al.*, 2002). TP concentrations (measured in this study) were recorded at 1.8 $\mu g/l^{-1}$ in November 2012 and 11.7 $\mu g/l^{-1}$ in July 2013 on one littoral water sample per occasion. In the 1980s a mean pH of 6.3 and mean alkalinity of $65\mu eq/l^{-1}$ was documented, with mean NH_4 from 1995-1997 $<3\mu eq/l^{-1}$ (Sutcliffe and Carrick, 1988; Tipping *et al.*, 2002).

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[2] Abbreviations of lake names will be followed by either $_{site}$ or $_{core}$ to attempt to distinguish between the lake itself and previous work ($_{site}$) to that undertaken in this thesis ($_{core}$). At certain points both terms were appropriate but only one adjunct was chosen.

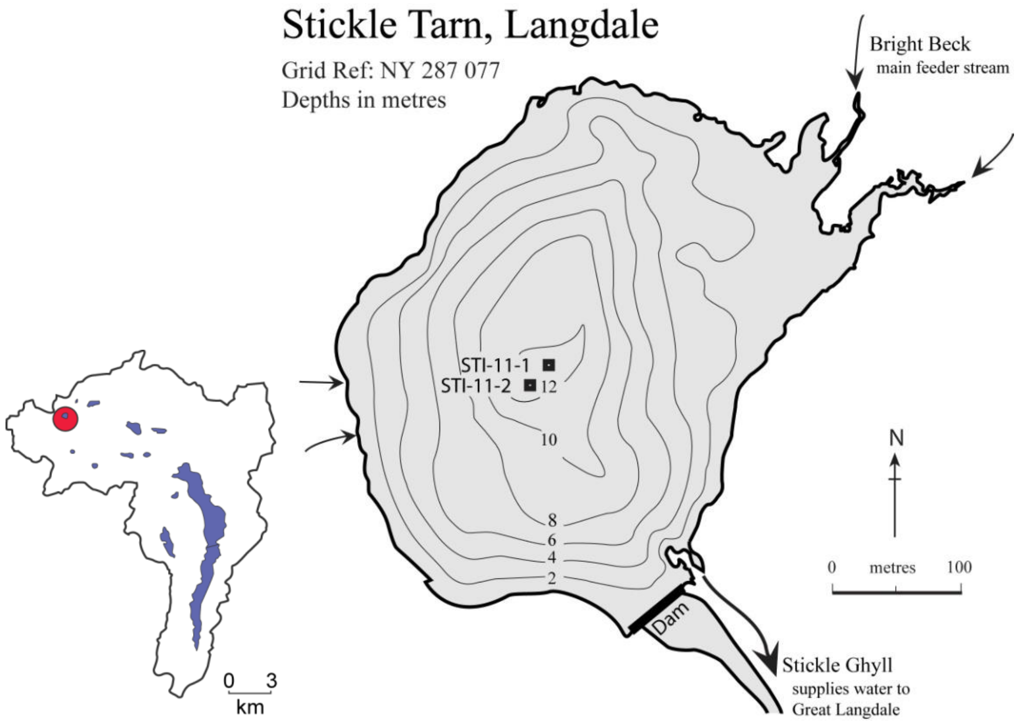


Figure 3.2 Location of Stickle Tarn in the Windermere catchment, UK (red dot) and bathymetric map with 2m depth intervals and coring locations.

Two cores, STI-11-1 and STI-11-2 were retrieved in November 2011, from the deepest location at STI$_{\text{site}}$ (Table 3.1). Lithological analyses (dry density (%LOI$_{105}$), OM content (%LOI$_{550}$), carbonate content (%LOI$_{925}$*1.36) and minerogenic content (100-%LOI$_{550}$+%LOI$_{925}$), which are described in section 4.1.2, were used to help determine which core should be chosen for further analyses. Sharp non-monotonic features in the %LOI$_{550}$ and %LOI$_{105}$ profiles of STI-11-2 compared to STI-11-1 was interpreted as disturbance to STI-11-2's sediment record, so STI-11-1 (STI$_{\text{core}}$) was used for further analyses.

Table 3.1 Stickle Tarn coring details. Grey shading indicates core used for sedimentary pigment, C and N isotope analyses and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Stickle Tarn	STI-11-1 (STI$_{\text{core}}$)	11/11/11	Glew	NY2891 /07645	13.1	17
	STI-11-2	11/11/11	Glew	NY28696 /07660	12.9	23.5

3.2.2 Codale Tarn (CT$_{site}$). Upland (467 m.a.s.l.)

Codale Tarn (CT$_{site}$) (NY297 088) is a very small, rapidly flushed, headwater upland cirque tarn, occupying a hillside shelf, the highest of three steps in the Easedale Valley (Figure 3.3; Table 2.1). CT$_{site}$ is in a peat and moraine covered valley, with rocky crags to the west and a steep shelf to the east where its outflow flows over exposed rock and drops down to Easedale Tarn 200m below (Haworth *et al*., 2003). The south of CT$_{site}$ is boggy and *Sphagnum* moss dominates (Haworth *et al*., 2003). Land use is minimal.

Submerged macrophytes within CT$_{site}$ are dominated by *Lobelia*, and the diatom flora consists of oligotrophic, low alkalinity taxa, predominantly *Navicula* and *Eunotia* spp. (Haworth *et al*., 2003). Similar to STI$_{site}$, fossil diatoms in CT$_{site}$ shifted from acid tolerant in the 1980s, to more circumnetural taxa in the late 1990s, indicating increasing pH (Tipping *et al*., 2002). Filamentous green algae were recorded in the early 1970s but relatively few desmids (David, 1972). The TP concentration of a littoral water sample was 10.5 µg/l^{-1} in July 2013. In the 1980s a mean pH of 5.6 and mean alkalinity of 7µeq/l^{-1} was documented, with mean NH$_4$ from 1995-1997 <2µeq/l^{-1} (Sutcliffe and Carrick, 1988; Tipping *et al*., 2002).

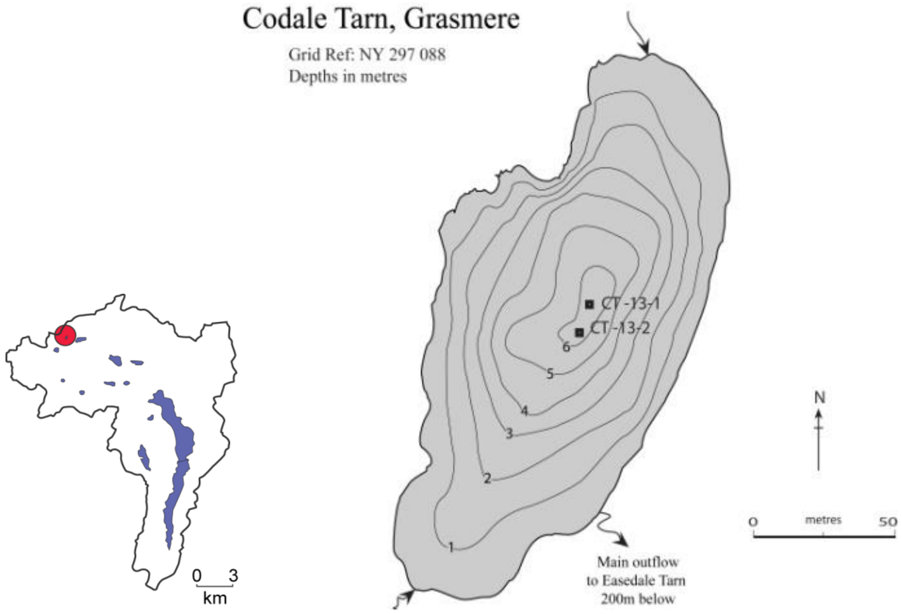


Figure 3.3 Location of Codale Tarn in the Windermere catchment, UK (red dot) and bathymetric map with 1m depth intervals and coring locations.

Two cores, CT-13-1 and CT-13-2 were retrieved in March 2013 (Table 3.2). Lithological analyses revealed sharper non-monotonic features in the %LOI$_{550}$ and %LOI$_{105}$ profiles of CT-13-2 compared with CT-13-1, which was interpreted as disturbance to CT-13-2's sediment record. Thus, CT-13-1 (CT$_{core}$) was chosen for further analyses.

Table 3.2 Codale Tarn coring details. Grey shading indicates core used for sedimentary pigment analyses and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Codale Tarn	CT-13-1 (CT$_{core}$)	16/03/13	Glew	NY28190 /05198	8.2	25.2
	CT-13-2	16/03/13	Glew	NY28194 /05191	6.3	25.8

3.2.3 Easedale Tarn (EAS$_{site}$). Upland (279 m.a.s.l.)

Easedale Tarn (EAS$_{site}$) (NY307 088) is an upland deep basin, with its main inlet receiving water from CT$_{site}$ and its shallower, irregular outlet flowing into Sourmilk Gill to the east (Figure 3.4; Table 2.1). Steep, rocky slopes surround EAS$_{site}$ to the north and west, whilst moraines with peaty pools are found to the south and east (Haworth *et al.*, 2003). The catchment is rocky with rough grassland, ferns and boggy areas throughout (Haworth *et al.*, 2003). Land uses include rough grazing and fell walking as EAS$_{site}$ lies on a popular trail from Grasmere.

EAS$_{site}$ is an oligotrophic, low alkalinity lake (Haworth *et al.*, 2003). Its high pH (~6.1) and depth accounts for the high abundance of planktonic diatoms documented in its sediment record, probably due to lower transparency (Tipping *et al.*, 2002). There are extensive areas of the submerged macrophyte *Potamogeton* spp., and large numbers of desmids. A thermocline at a depth of ~9m develops in summer (Haworth *et al.*, 2003). TP concentrations were recorded at 7 μg/l^{-1} in November 2012 and 11.3 μg/l^{-1} in July 2013 on one epilimnetic and one littoral water sample respectively. In the 1980s a mean pH of 6.1 and mean alkalinity of 7μeq/l^{-1} was documented, with mean NH_4 from 1995-1997 <2μeq/l^{-1} (Sutcliffe and Carrick, 1988; Tipping *et al.*, 2002).

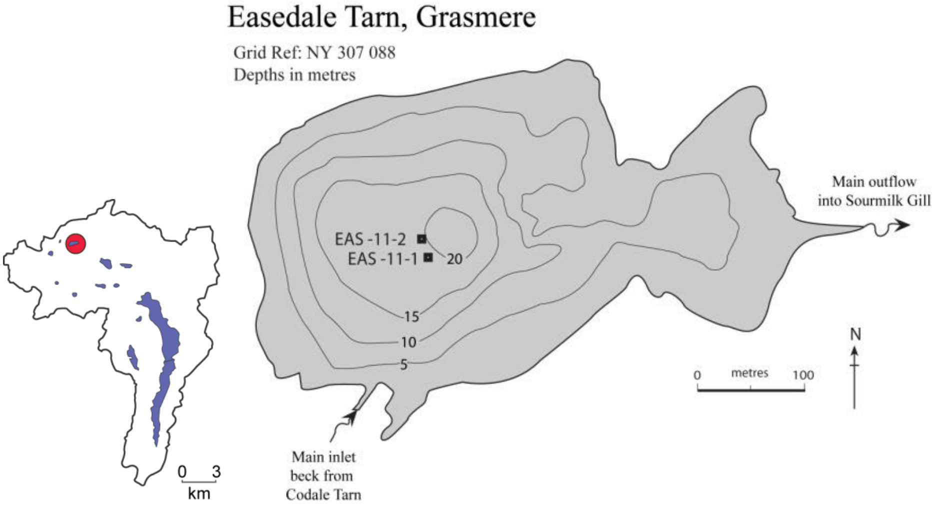


Figure 3.4 Location of Easedale Tarn in the Windermere catchment, UK (red dot) and bathymetric map with 5m depth intervals and coring locations.

Two cores, EAS-11-1 and EAS-11-2 were retrieved in November 2011 (Table 3.3). Lithological analyses revealed similar records so EAS-11-1 (EAS_{core}) was used for further analyses due to its longer length.

Table 3.3 Easedale Tarn coring details. Grey shading indicates core used for sedimentary pigment, C and N isotope analyses and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Easedale Tarn	EAS-11-1 (EAS_{core})	11/11/11	Glew	NY30717 /87959	19.5	27.5
	EAS-11-2	11/11/11	Glew	NY30726 /87979	19.7	21

3.2.4 Blea Tarn (BT_{site}). Upland (192 m.a.s.l.)

Blea Tarn (BT_{site}) (NY293 044) is a small, shallow, headwater upland basin which lies in a depression of glacial drift in a small hanging valley in the Langdale mountains (Figure 3.5; Table 2.1). Its largest inflow to the north flows through an area of bog and its outflow drains south to the River Brathay and Little Langdale Tarn (Haworth, 1969). The basin contours of BT_{site} undulate and drop steeply in the middle, making this a difficult site to core (Haworth *et al*., 2003). Its catchment consists of *Sphagnum* bog, moorland pasture and a small plantation of conifers (Haworth, 1969). Land use is minimal consisting of one farm and rough sheep grazing.

BT_{site} is an oligotrophic, low alkalinity lake whose diatom flora is typical of base-poor waters and acid *Sphagnum* mosses (Haworth, 1969). In mid-20th century sediments, shifts to acid-tolerant diatom taxa such as *Achnanthes* and *Pinnularia* spp. were recorded and related to catchment in-wash (Haworth, 1969). Submerged macrophytes are common and littoral grasses and sedges line its artificially straightened inflow (Haworth *et al*., 2003). Epilimnetic TP concentrations were recorded at 5.3 $\mu g/l^{-1}$ in November 2012 and 13.3 $\mu g/l^{-1}$ in July 2013 on one epilimnetic water sample per session. In the 1980s a mean pH of 6.9 and mean alkalinity of $78\mu eq/l^{-1}$ was measured (Sutcliffe and Carrick, 1988). Three samples taken in 2000 recorded mean total dissolved nitrogen (TDN) to be 28.1 $mmol/m^{-3}$ (Jones *et al*., 2004).

Two cores, BT-13-1 and BT-13-2 were retrieved in July 2013 (Table 3.4). Lithological analyses revealed similar records so BT-13-2 (BT_{core}) was used for further analyses due to its longer length.

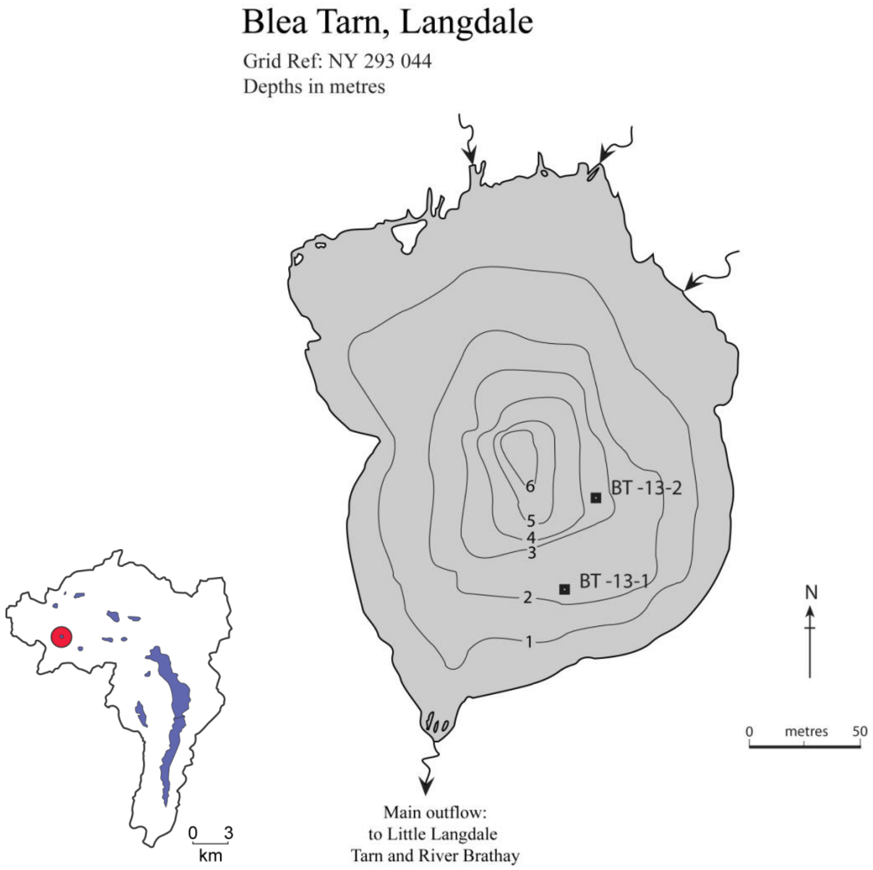


Figure 3.5 Location of Blea Tarn in the Windermere catchment, UK (red dot) and bathymetric map with 1m depth intervals and coring locations.

Table 3.4 Blea Tarn coring details. Grey shading indicates core used for sedimentary pigment analysis.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Blea Tarn	BT-13-1	06/07/13	HON-Kayak	NY293/ 043 (GPS broken)	2	33
	BT-13-2 (BT_{core})	06/07/13	HON-Kayak	NY293/ 043 (GPS broken)	3.4	43.5

3.2.5 Little Langdale Tarn (LLT_{site}). Upland (102 m.a.s.l.)

Little Langdale Tarn (LLT_{site}) (NY309 032) is a small, shallow, upland basin with a very large catchment prone to flooding, consisting of rocky areas, grassland and bog (Figure 3.6; Table 2.1). Its inflows are Greenburn Beck and the River Brathay which were artificially straightened in the 1800s to improve field drainage, and between ~1840 to the 1920s, Greenburn Beck was dammed to supply water to Greenburn copper mine (Haworth *et al*., 2003). The high sediment accumulation rate and steep basin slopes of LLT_{site} make this a difficult coring location. An extensive area of *Phragmites* lines the south of LLT_{site} and to the northwest exposed rock, with fen and willow also bordering the tarn (Haworth *et al*., 2003). Land use is minimal apart from some rough grazing.

LLT_{site} is an oligo-mesotrophic tarn, which has experienced acidification related to its peaty catchment, with periods of high concentrations of Al (Hürrig, 1999). The diatom community composes of acid-tolerant species from multiple habitats (Haworth *et al*., 2003). Epilimnetic TP concentrations were recorded at 9.4 $\mu g/l^{-1}$ in November 2012 and 14.6 $\mu g/l^{-1}$ in July 2013. In the 1980s a mean pH of 6.6 and mean alkalinity of 93$\mu eq/l^{-1}$ was measured (Sutcliffe and Carrick, 1988).

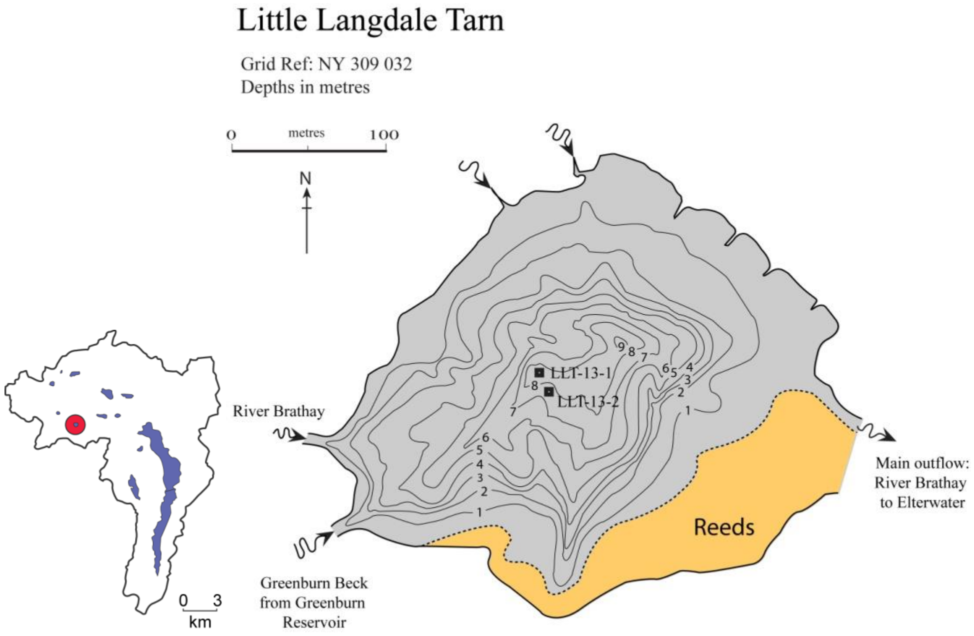


Figure 3.6 Location of Little Langdale Tarn in the Windermere catchment, UK (red dot) and bathymetric map with 1m depth intervals and coring locations.

Two cores, LLT-13-1 and LLT-13-2 were retrieved close to the deepest location in July 2013 (Table 3.5). Lithological analyses revealed similar records so LLT-13-1 (LLT$_{core}$) was used for further analyses due to its longer length.

Table 3.5 Little Langdale Tarn coring details. Grey shading indicates core used for sedimentary pigment analysis

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Little Langdale Tarn	LLT-13-1 (LLT$_{core}$)	07/07/13	HON-Kayak	NY30864 /03231	8	27.5
	LLT-13-2	07/07/13	HON-Kayak	NY30866 /03223	7.8	26.5

3.2.6 Loughrigg Tarn (LOU$_{site}$). Lowland (94 m.a.s.l.)

Loughrigg Tarn (LOU$_{site}$) (NY345 043) is a lowland lake in a shallow col with a long WRT, excavated by a glacier moving south from Grasmere (Figure 3.7; Table 2.1). LOU$_{site}$ is surrounded by fells to the north, but in close proximity to the lake the catchment vegetation is mainly grassland, a large species rich wetland area to the west and small pockets of deciduous woodland including oak, birch and hazel (Haworth *et al*., 2003). The small stream inflows have been channelled through fields to the north and the outflow leaves LOU$_{site}$ to the south via Tarn Foot Farm (Haworth *et al*., 2003). Land use around LOU$_{site}$ is sheep and cattle grazing and a caravan site.

LOU$_{site}$ is a eutrophic, high alkalinity basin with records of large-celled and dense phytoplankton biomasses (Gorham *et al*., 1974). The algal flora is mainly diatoms typical of nutrient-rich high alkalinity waters, and some green algae, flagellates and cyanobacteria in summer months (Haworth *et al*., 2003). Epilimnetic TP was 18.4 $\mu g/l^{-1}$ in November 2012 and 23.5 $\mu g/l^{-1}$ in July 2013. In the 1980s a mean pH of 7.5 and mean alkalinity of 337$\mu eq/l^{-1}$ was measured (Sutcliffe and Carrick, 1988).

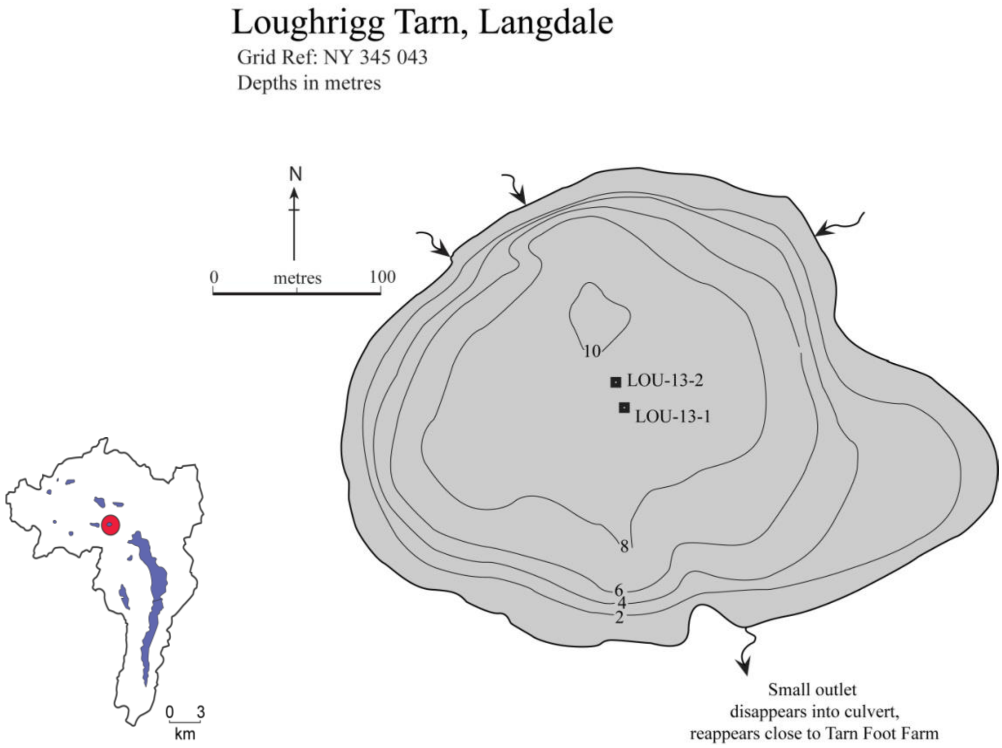


Figure 3.7 Location of Loughrigg Tarn in the Windermere catchment, UK (red dot) and bathymetric map with 2m depth intervals and coring locations.

Two cores, LOU-13-1 and LOU-13-2 were retrieved close to the deepest location in July 2013 (Table 3.6). Lithological analyses revealed similar records so LOU-13-1 (LOU$_{core}$) was used for further analyses due to its longer length.

Table 3.6 Loughrigg Tarn coring details. Grey shading indicates core used for sedimentary pigment analysis and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Loughrigg Tarn	LOU-13-1 (LOU$_{core}$)	07/07/13	HON-Kayak	NY34482 /04353	8.4	41.5
	LOU-13-2	07/07/13	HON-Kayak	NY34483 /04386	8.6	37

3.2.7 Esthwaite Water (EST$_{site}$). Lowland (65 m.a.s.l.)

Esthwaite Water (EST$_{site}$) (SD360 965) is a shallow lowland basin, with a long WRT, and lies in a sheltered fertile valley (Figure 3.8; Table 2.1). Its main inflow Black Beck drains through the village of Hawkshead, with its outflow Cunsey Beck draining into Windermere’s south basin. North Fen National Nature Reserve at EST$_{site}$ supports a severely reduced community of the nationally important aquatic macrophyte slender naiad *Najas flexilis* (WCRP, 2014). Steep fells, the urban settlement of Hawkshead popular with tourists and lowland improved grassland and grazing deliver nutrient-rich runoff from the small catchment to EST$_{site}$ (Dong *et al*., 2012).

EST$_{site}$ is a eutrophic, highly productive basin where P concentrations increased in the 1970s and high concentrations were sustained throughout the 1980s and 1990s on account of nutrient loading from agricultural, sewage and fish farm (rainbow trout) waste (George *et al.*, 2000; Dong *et al.*, 2012). In 2008, its mean TP was 28μg/l which has been ascribed to high internal-P loads (Dong *et al*., 2012). EST$_{site}$ becomes thermally stratified from end of April to mid-October, with its hypolimnion becoming anoxic (Maberly *et al*., 1994). Its phytoplankton succession is typical of thermally stratified temperate lakes, with spring diatom blooms dominated by *A. formosa* and *Aulacoseira subarctica* (Müller) Haworth, and summer blooms dominated by the dinoflagellate *Ceratium* and cyanobacterial taxa *Aphanizomenon* and *Microcystis* (George *et al*., 2000). In recent decades, declines in its submerged macrophyte community was attributed to nutrient enrichment (Bennion *et al*., 2000). The mean Chl. *a* from 1964 to 1989 was 18.4 $\mu g/l^{-1}$ owing to its high nutrient content (Talling, 1993).

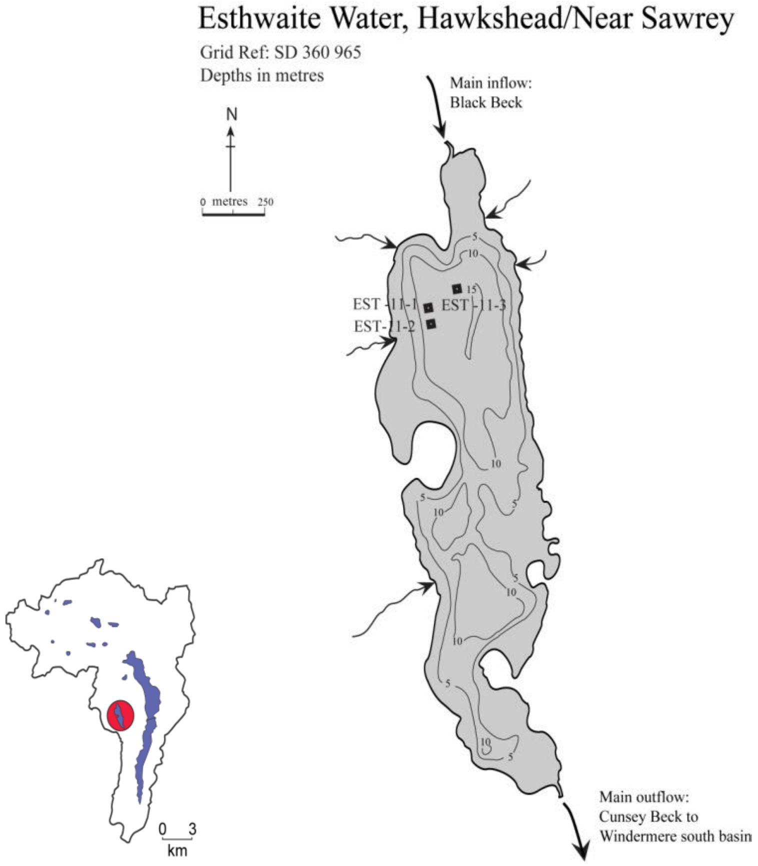


Figure 3.8 Location of Esthwaite Water in the Windermere catchment, UK (red dot) and bathymetric map with 5m depth intervals and coring locations.

Three cores, EST-11-1, EST-11-2 and EST-11-3 were retrieved in November 2011, close to the deepest part of the lake but taking care to avoid past coring locations (Table 3.7). Lithological analyses revealed similar records so EST-11-3 (EST$_{core}$) was used for further analyses due to its longer length.

Table 3.7 Esthwaite Water coring details. Grey shading indicates core used for sedimentary pigment, C and N isotope analyses and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Esthwaite Water	EST-11-1	11/11/11	Mackereth	SD35841 /96988	12.3	80
	EST-11-2	11/11/11	Mackereth	SD35823 /96963	12.4	66
	EST-11-3 (EST$_{core}$)	11/11/11	Mackereth	SD35918 /97082	14.9	84.5

3.2.8 Grasmere (GRA_{site}). Lowland (62 m.a.s.l.)

Grasmere (GRA_{site}) (NY335 074) is a deep, rapidly-flushed, moraine-dammed lowland lake with a larger deeper basin (max. depth=21.5m) to the east and a smaller shallower (max. depth=10.2m) basin to the west, separated by a small island (Figure 3.9; Table 2.1). It lies within an Environmentally Sensitive Area, a designation which aims to protect the wildlife, landscape and historic value through sustainable agriculture (Reynolds *et al*., 2012). GRA_{site}'s main inflow, the River Rothay, drains through Grasmere village and continues to outflow to Rydal Water. Its mountainous catchment and thin acidic soils support open fell and bog, with improved pasture for sheep grazing in the valley bottom and some scattered woodland (Reynolds and Lund, 1988).

GRA_{site} is a meso-eutrophic basin attributed to the high NH_4 and P delivery from sewage effluent (Reynolds and Lund, 1988). Between 1994 and 1995, 74% of GRA_{site}'s P load (total = 1668 kg P yr^{-1}) came from the River Rothay WwTW (Reynolds *et al*., 2012). The lake was historically oligotrophic due to its base-poor geology, high rainfall and resultant chemically dilute inflows. By the mid-1850s, *A. formosa* became established corresponding to increased resident and tourist populations (Barker *et al*., 2005). The phytoplankton flora are typical of meso-eutrophic sites particularly under periods of low flushing (Reynolds *et al*., 2012).

Two cores, GRA-13-1 and GRA-13-2 were retrieved close to the deepest location of GRA_{site} and GRA-13-3 was taken from the western basin in July 2013 (Table 3.8). Lithological analyses revealed similar records for GRA-13-1 and GRA-13-2 so GRA-13-1 (GRA_{core}) was used for further analyses due to its longer length. GRA-13-3 was taken to compare sedimentary algal pigments of sediments closer to the inflow that originally recieved sewage effluent before its re-location to the sediments of GRA_{core}, but time constraints prevented this investigation.

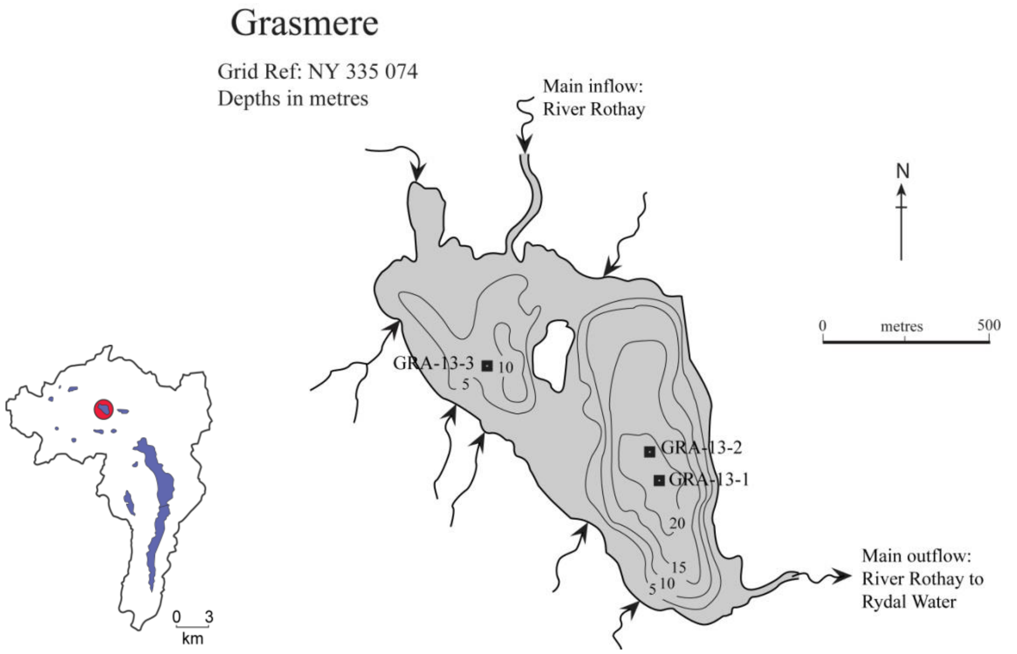


Figure 3.9 Location of Grasmere in the Windermere catchment, UK (red dot) and bathymetric map with 5m depth intervals and coring locations.

Table 3.8 Grasmere coring details. Grey shading indicates core used for sedimentary pigment analysis and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Grasmere	GRA-13-1 (GRA_{core})	08/07/13	HON-Kayak	NY34030 /06398	21.3	50
	GRA-13-2	08/07/13	HON-Kayak	NY34031 /06407	21.6	33
	GRA-13-3	08/07/13	HON-Kayak	NY33629 /06697	9.7	22

3.2.9 Elterwater (ELTIN$_{site}$/ELTMID$_{site}$/ELTOUT$_{site}$). Lowland (55 m.a.s.l.)

Elterwater (NY335 041) is a small, shallow lowland lake, 1km southeast of Elterwater village and comprises three chemically distinct inter-connected basins: ELTIN$_{site}$, ELTMID$_{site}$ and ELTOUT$_{site}$ (Figure 3.10; Table 2.1). ELTIN$_{site}$ is classed as hypereutrophic due to low hydrological renewal and historical delivery of WwTW effluent from 1973 until 1991 which accounted for 45% of its hydraulic load (Haworth *et al*., 2003). ELTMID$_{site}$ is classed as meso-eutrophic on account of minimal flushing which occurs only during flooding and attendant overflowing from ELTIN$_{site}$ and ELTOUT$_{site}$ (Goldsmith *et al*., 2003). ELTOUT$_{site}$ receives 98% of the total hydraulic load from Great and Little Langdale Becks, and as such has a high siltation rate and is classed as oligo-mesotrophic (Zinger-Gize *et al*., 1999). The catchment supports a SSSI on account of its diverse successional habitats including aquatic macrophytes such as the rare six-stamened waterwort *Elatine hexandra* (Lapierre), fen to marshy grasslands, willow and alder carr to oak woodland (Haworth *et al*., 2003). However, in the last decade the SSSI has been classed as in a state of decline (APEM, 2012). There is improved pasture and sheep grazing close to the lake.

ELTIN$_{site}$ maintains large blooms of small green algae in summer, whereas ELTMID$_{site}$ supports diatoms and cyanobacteria (Haworth *et al*., 2003). ELTOUT$_{site}$ has lower phytoplankton biomass due to greater flushing which removes silica (Si) for diatoms and nutrients. All basins have abundant cryptophyte and chrysophyte blooms in autumn/winter in comparison to other groups, typical of temperate dimictic lakes (Hutchinson, 1967). The highest concentrations of TP in 1974 and 1975 in ELTIN$_{site}$ reached 206 $\mu g/l^{-1}$ and 176 $\mu g/l^{-1}$ respectively, whereas in ELTMID$_{site}$ values reached 94 $\mu g/l^{-1}$ and 84 $\mu g/l^{-1}$, and at ELTOUT$_{site}$, 21 $\mu g/l^{-1}$ and 27 $\mu g/l^{-1}$ (Lund, 1981). In 1995, Elterwater had a mean TP concentration of 200 $\mu g/l^{-1}$ (Carvalho and Moss, 1995).

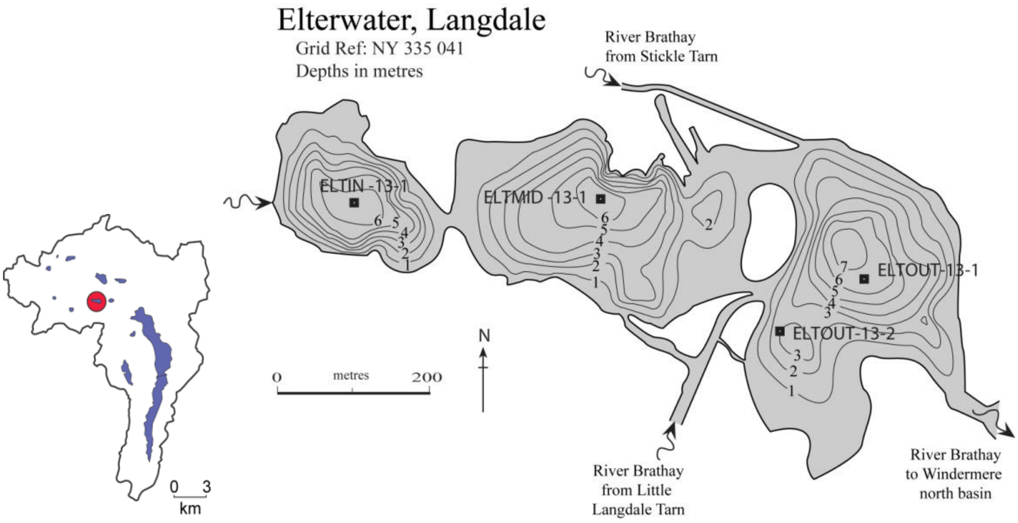


Figure 3.10 Location of Elterwater in the Windermere catchment, UK (red dot) and bathymetric map with 1m depth intervals and coring locations.

One core each from ELTIN$_{site}$ (ELTIN-13-1 (ELTIN$_{core}$)) and ELTMID$_{site}$ (ELTMID-13-1 (ELTMID$_{core}$)) was retrieved at the basin's deepest locations and two were retrieved from ELTOUT$_{site}$ (ELTOUT-13-1, ELTOUT13-2) in July 2013 (Table 3.9). ELTOUT-13-2 was retrieved away from the lake's inflow and used for further analyses (ELTOUT$_{core}$), as large clumps of terrestrial leaf litter and vegetation were observed in ELTOUT-13-1.

Table 3.9 Elterwater coring details. Grey shading indicates cores used for sedimentary pigment analysis and ELTIN$_{core}$ used for ^{210}Pb dating additionally.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Elterwater	ELTIN-13-1 (ELTIN$_{core}$)	09/07/13	HON-Kayak	NY32973 /04178	7	35
	ELTMID-13-1 (ELTMID$_{core}$)	09/07/13	HON-Kayak	NY33291 /04184	7.4	30
	ELTOUT-13-1	09/07/13	HON-Kayak	NY33605 /04104	6.3	33
	ELTOUT-13-2 (ELTOUT$_{core}$)	09/07/13	HON-Kayak	NY33553 /03978	2.9	40

3.2.10 Rydal Water (RYD$_{site}$). Lowland (53 m.a.s.l.)

Rydal Water (RYD$_{site}$) (NY356 061) is a small, deeply excavated lowland lake and resides directly downstream of GRA$_{site}$ (Figure 3.11; Table 2.1). It has a very short WRT. It consists of a deeper basin to the west of Heron Island and a basin half as shallow to the east (Haworth *et al*., 2003). RYD$_{site}$ lies in the Rothay valley, with a mountainous upland catchment consisting of improved grasslands and popular walking trails close to the shore and the hamlet of Rydal (Haworth *et al*., 2003). Reed beds fringe the lake and the inflow supports a diverse fen habitat including willow carr and alder (Haworth *et al*., 2003). Its sediments are organic-rich ascribed to the entrapment of mineral material upstream at GRA$_{site}$ and its fen habitat (Haworth *et al*., 2003).

RYD$_{site}$ like GRA$_{site}$ is meso-eutrophic with very similar phytoplankton assemblages (Haworth *et al*., 2003). Because it is extremely well-flushed, small cryptophytes, chrsophytes and diatoms (dominated by *A. formosa* since the enrichment of GRA$_{site}$ upstream) but very few cyanobacteria are recorded (Haworth *et al*., 2003). In the 1980s a mean pH of 7.5 and mean alkalinity of 337μeq/l^{-1} was measured (Sutcliffe and Carrick, 1988). In the early 2000s mean TP was 15.5 mg/m^{-3} (Ings *et al*., 2010). Seven years prior to the establishment of the River Rothay WwTW upstream in 1971, live cells of *A. formosa* collected from the top 5m of the water column averaged 6 cells ml^{-1}, whereas 7 years after 1053 cells ml^{-1} were recorded on average (Lund, 1981).

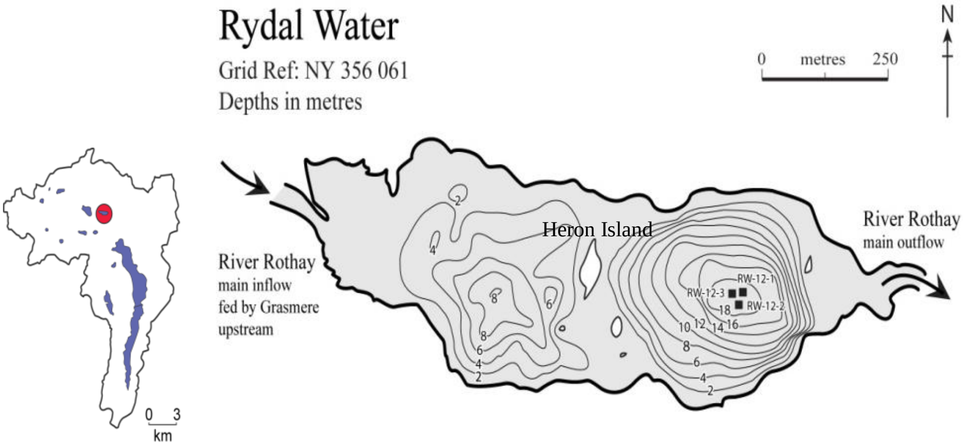


Figure 3.11 Location of Rydal Water in the Windermere catchment, UK (red dot) and bathymetric map with 2m depth intervals and coring locations.

Three cores, RYD-12-1, RYD-12-2 and RYD-12-3 were retrieved in March 2012 from the deepest part of the lake (Table 3.10). Lithological analyses revealed similar records so RYD-12-3 (RYD$_{core}$) was used for further analyses due to its longer length.

Table 3.10 Rydal Water coring details. Grey shading indicates core used for sedimentary pigment, C and N isotope analyses and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Rydal Water	RYD-12-1	27/03/12	Mackereth	NY35851 /06154	18.7	83
	RYD-12-2	27/03/12	Mackereth	NY35861 /06163	19.3	84
	RYD-12-3 (RYD$_{core}$)	27/03/12	Mackereth	NY35894 /06218	18.8	85

3.2.11 Blelham Tarn (BLE_{site}). Lowland (42 m.a.s.l.)

Blelham Tarn (BLE_{site}) (NY365 004) is a small, shallow (max depth=14.5m), monomictic and rapidly flushed lowland lake (Figure 3.12; Table 2.1). Its main inflow Ford Wood Beck drains the hamlet of Outgate and its main outflow Blelham Beck feeds into Windermere's north basin. Its catchment supports improved and unimproved pasture, scattered woodland and an area of carr/bog including wet heath, fen and a *Phragmites* swamp designated a SSSI to the southwest (Haworth, 1976; Haworth, 1984; George *et al.*, 2000).

BLE_{site} is a eutrophic, productive basin on account of a small sewage outlet at Outgate and its agricultural catchment. These nutrient inputs corresponded to increased sedimentary cyanobacterial pigment concentrations in the sediments of the tarn (Moorhouse *et al.*, 2014). BLE_{site} undergoes thermal stratification from mid-May to mid-October, and hypolimnetic anoxia from mid-July until mixing (Foley *et al.*, 2012). Like EST_{site}, earlier spring and summer blooms of algae similar to Windermere support abundant cladocera and copepod populations (Talling, 2003). Diatoms typical of nutrient-rich waters such as *A. formosa* and *Stephanodiscus* spp. and heterocystous cyanobacteria such as *Oscillatoria*, *Anabaena* and *Aphanizomenon* spp. have been recorded (Elliott and Thackeray, 2004). The mean Chl. *a* from 1964 to 1989 was $13.6\mu g/l^{-1}$ owing to its high nutrient content (Talling, 1993).

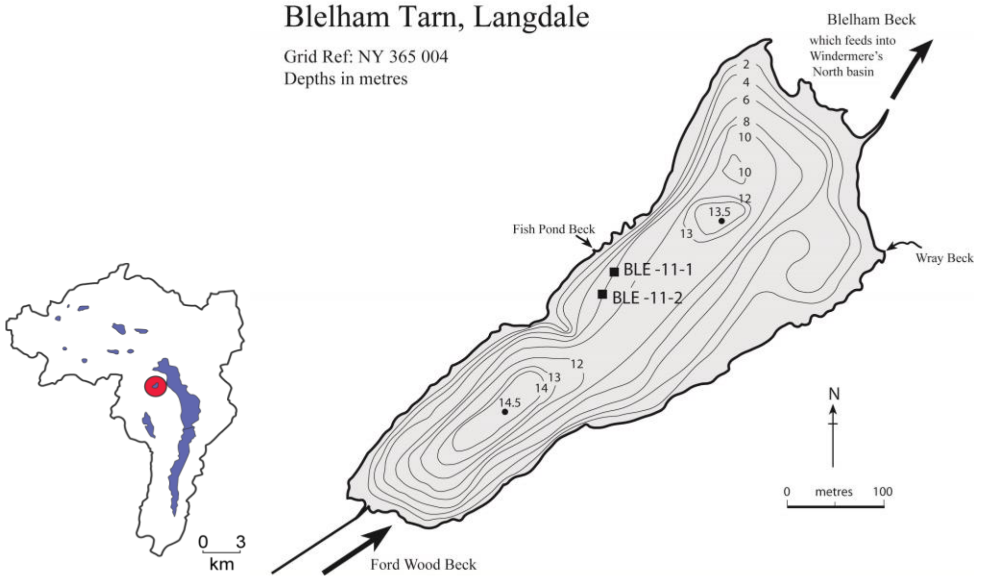


Figure 3.12 Location of Blelham Tarn in the Windermere catchment, UK (red dot) and bathymetric map with 2m depth intervals and coring locations.

Two cores, BLE-11-1 and BLE-11-2 were retrieved in November 2011, avoiding areas previously cored and the experimental "Lund tubes" (Lack and Lund, 1974; Haworth, 1976) (Table 3.11). Lithological analyses of both cores showed similar records so BLE-11-1 (BLE_{core}) was chosen for further analyses.

Table 3.11 Blelham Tarn coring details. Grey shading indicates core used for sedimentary pigment, C and N isotope analyses and ^{210}Pb dating.

Site	**Core code**	**Date of coring**	**Corer used**	**BNG coordinates of core location**	**Depth core retrieved (m)**	**Length of core after extrusion (cm)**
Blelham Tarn	BLE-11-1 (BLE_{core})	10/11/11	Mackereth	NY36599 /00456	11	77.5
	BLE-11-2	10/11/11	Mackereth	NY36545/ 00389	11.7	84.5

The laboratory analyses undertaken on the sediment cores shaded in grey in Tables 3.1-3.11 are detailed in the following chapter.

CHAPTER 4. METHODS II. LABORATORY AND COLLECTION OF SEDIMENTARY AND ENVIRONMENTAL RECORDS.

This methods chapter describes the laboratory, historical and instrumental data collection used and its preparation for further statistical investigation as detailed in Chapter 5.

4.1 Laboratory analyses

The large numbers of cores collected meant different cores underwent different analyses, but in all cases at least one core from each site was sampled for algal pigments; the main proxy of this thesis and nine cores were dated (Table 4.1). All analyses for WNB_{core} and WSB_{core} had been previously undertaken and are described in McGowan *et al.*, (2012). OM and sedimentary algal pigment analyses were undertaken at the University of Nottingham (UoN) by the author. C and N mass and isotope analyses were undertaken at the Stable Isotope Mass Spectrometer facility at the Lancaster Environment Centre, Lancaster University, UK (LEC) for BLE_{core} and RYD_{core}, and to the Limnology Laboratory, School of Biology, University of Regina, Canada (UOR) for EST_{core}, EAS_{core}, STI_{core}. ^{210}Pb dating was undertaken at the Environmental Radiometric Facility at University College London, UK (UCL) in 2012 for BLE_{core}, EAS_{core}, EST_{core}, STI_{core} and RYD_{core}, whereas cores $ELTIN_{core}$, GRA_{core}, LOU_{core} and CT_{core} were sent to the Aquatic Research Centre, University of Brighton, UK (UoB) in 2013.

Given that resources were limited, cores BT_{core}, LLT_{core} $ELTMID_{core}$ and $ELTOUT_{core}$, were not chosen for ^{210}Pb analysis for the following reasons. First, BT_{core} and LLT_{core} had high percentage loss-on-ignition (%LOI) values and were macrofossil-rich indicating high inputs of terrestrial vegetation. Although this points to catchment disturbance and provides an insight into lake ecological drivers, it may have masked the in-lake algal response of interest for this study. Second, it was felt that a sufficient number of upland tarns had been investigated as part of this thesis to provide an adequate understanding of algal community response to the environmental pressures and physical characteristics of these sites. $\mathrm{ELTMID}_{\mathrm{core}}$ and $\mathrm{ELTOUT}_{\mathrm{core}}$ were not chosen because it was reasoned that the results of the most eutrophic basin, $\mathrm{ELTIN}_{\mathrm{site,}}$ alone would be sufficient to achieve the stated aims of this research.

Table 4.1 Inventory of cores and laboratory analyses. X = completed analyses for this thesis.

Core		**Laboratory analyses performed**			
Full core inventory	Core and its abbreviation investigated in this thesis	Loss-on-Ignition	HPLC	Stable and bulk C/N	Lead-210 dating
BLE-11-1	$\mathrm{BLE}_{\mathrm{core}}$	X	X	X	X
BLE-11-2		X			
BT-13-1		X			
BT-13-2	$\mathrm{BT}_{\mathrm{core}}$	X	X		
CT-12-1	$\mathrm{CT}_{\mathrm{core}}$	X	X		X
CT-12-2		X			
EAS-11-1	$\mathrm{EAS}_{\mathrm{core}}$	X	X	X	X
EAS-11-2		X			
ELTIN-13-1	$\mathrm{ELTIN}_{\mathrm{core}}$	X	X		X
ELTMID-13-1	$\mathrm{ELTMID}_{\mathrm{core}}$	X	X		
ELTOUT-13-1	$\mathrm{ELTOUT}_{\mathrm{core}}$	X	X		
EST-11-1		X			
EST-11-2		X			
EST-11-3	$\mathrm{EST}_{\mathrm{core}}$	X	X	X	X
GRA-13-1	$\mathrm{GRA}_{\mathrm{core}}$	X	X		X
GRA-13-2		X			
GRA-13-3		X			
LLT-13-1		X			
LLT-13-2	$\mathrm{LLT}_{\mathrm{core}}$	X	X		
LOU-13-1	$\mathrm{LOU}_{\mathrm{core}}$	X	X		X
LOU-13-2		X			
RYD-12-1		X			
RYD-12-2		X		X	
RYD-12-3	$\mathrm{RYD}_{\mathrm{core}}$	X	X		X
STI-11-1	$\mathrm{STI}_{\mathrm{core}}$	X	X	X	X
STI-11-2		X			

4.1.1 Sediment chemistry: introduction to the content and sources of sedimentary organic matter

Sediment composition is controlled by primary production, degradation and in-wash, all of which can be used to infer past environmental change (Shuman, 2003). Lacustrine sedimentary OM comprises the detritus of micro-organisms and plant material from the lake and its catchment and therefore provides a record of community changes in lake and catchment flora (Meyers and Teranes, 2001). Consequently, differences in the biochemical composition of autocthonous and allocthonous sources of sedimentary OM can aid the identification of changing OM sources through time. In addition, redox reactions performed by microbial communities are important in the decomposition of sedimentary OM and play a key role in the cycling of plant-derived nutrients such as C and N (Meyers and Ishiwatari, 1993). Therefore, investigating OM content alongside $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ isotopes, and the use of C/N ratios of bulk sediments can reveal depositional alteration of OM, which in turn indicates modifications to the lake environment, such as climatic alterations of water column mixing and changes to OM source (Meyers and Ishiwatari, 1993). For instance, microbial denitrification of sinking algal matter in productive lakes can increase the C/N ratio, however, it is rare that such processes alter the elemental composition of sedimentary OM and the large differences in C/N ratios of higher plants and algae remain (Meyers and Teranes, 2001). Thus, investigating the extent and sources of lacustrine OM are a useful tool to understand changes to the productivity of a lake and its catchment and are discussed in sections 4.1.2 and 4.1.3.

4.1.2 Loss-on-ignition as a proxy for organic matter content

The percentage loss-on-ignition (%LOI_{550}) gives a crude measure of the OM content of the sediment (Dean, 1974). It can therefore indicate the extent of past primary production both of a lake and its catchment. However, it cannot distinguish whether the OM is autochthonous or allocthonous without additional analyses. By undertaking sequential weight measurements after combustion at different temperatures, the dry density, water content, OM content and carbonate content can be calculated, determining overall sediment composition and aiding the interpretation of OM source (Heiri *et al*., 2001).

%LOI_{550} has been used in multiple studies to infer historical changes to OM deposition from both natural and anthropogenic drivers of environmental change. In remote lakes, historical increases in temperature stimulated autochthonous production and so, OM deposition (Nesje and Dahl, 2001). However, in anthropogenically disturbed catchments, nutrient fertilisation from point and diffuse sources stimulated phytoplankton biomass and attendant OM deposition increased (Dong *et al.*, 2011). The residue-on ignition (100-%LOI$_{550}$+%LOI$_{925}$), a proxy for minerogenic in-wash, can also be used in disturbed catchments to interpret whether dilution of OM content occurred from enhanced catchment erosion via agricultural activity (Moorhouse *et al.*, 2014). Thus, %LOI plays an important role in determining how and why sediment composition changes over time.

Sequential weight %LOI is based on the principle of differential thermal analysis, where OM ignites at 200°C and depletes at 550°C, whereas carbonate minerals are destroyed at higher temperatures above 800°C (Santisteban *et al.*, 2004). However, lattice water in clays can inflate %LOI values, thus direct measurement of total organic carbon (TOC) is preferred (Dean, 1974; Heiri *et al.*, 2001; Meyers and Teranes, 2001). Despite these shortcomings, general trends in %LOI are well correlated to organic carbon (OC) formed by decomposition of plant and algal material and which composes a large % of OM (~58%) (Santisteban *et al.*, 2004). Thus, %LOI measurements were helpful to this project because sedimentary pigments were expressed as relative pigment mass to the OM-specific concentration, which takes into account algal abundance changes relative to the magnitude of OM changes, minimizing dilution effects from minerogenic inwash (see 4.1.4) (Leavitt, 1993). In addition, dry mass density measurements (%LOI$_{105}$) were required to calculate dry mass accumulation rates for ^{210}Pb constant rate of supply (CRS) modelling (see 4.1.5), and interpretation of stable and bulk C and N isotopes was aided by %LOI measurements (see chapter 9).

1cm^3 of wet sediment was analysed at 0.5cm resolution from every sediment core retrieved and sequential %LOI was performed following the method described in Heiri *et al.*, (2001). Bulk sediment was analysed for dry density (%LOI$_{105}$), OM content (%LOI$_{550}$), carbonate content (%LOI$_{925}$*1.36) and minerogenic content (100-%LOI$_{550}$+%LOI$_{925}$).

4.1.3 Relative mass of C and N and the C/N ratio as a tool to understand sources of organic matter

Measuring the change in % mass of C relative to N in lacustrine sediment reveals changes in organic sedimentation because C/N ratios can indicate whether sedimentary OM is autochthonous or allochthonous (e.g. derived from algae or vascular plants) (Meyers and Teranes, 2001). The presence or absence of the polysaccharide cellulose, the main component of plant cell walls and other vegetative fibres, is a major control on the C/N ratio (Meyers and Ishiwatari, 1993). Typically, non-vascular, protein-rich, cellulose-poor aquatic plants and algae have C/N ratios between 4 and 10, and vascular, cellulose-rich, protein-poor terrestrial vegetation have much higher ratios of 20 and above (Figure 4.1) (Meyers and Teranes, 2001). C/N ratios in most lakes are between 10-20 which implies a mixture of algal and vascular plant material.

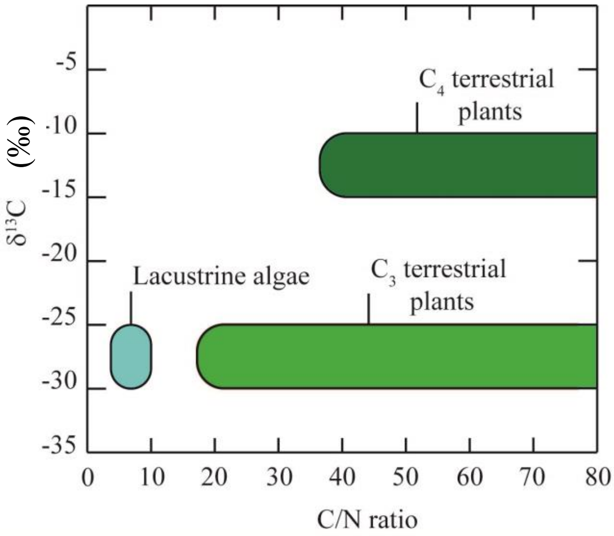


Figure 4.1 The $\delta^{13}C_{org}$ and atomic C/N ratios of organic matter derived from lacustrine algae, C_3 terrestrial plants and C_4 terrestrial plants that use atmospheric CO_2 as their carbon source for photosynthesis. Modified from Meyers and Teranes (2001).

Degradation of OM can alter the elemental composition and hence C/N ratios of sedimentary OM. For example, algal material can undergo selective degradation of N-rich proteins through microbial denitrification during sinking and early diagenesis (Meyers and Teranes, 2001). However, these processes do not commonly alter the C/N compositions of OM on a scale great enough to eliminate the differences between algal and vascular plant C/N ratios (Meyers and Teranes, 2001). Therefore, C/N ratios are an effective means of distinguishing between autochthonous- and allochthonous-derived OM.

I. Carbon isotope ratios

The ratios of stable C isotopes in sediment can indicate changes in lake productivity, the origins of OM and changes in nutrient source. Phytoplankton preferentially uptake ^{12}C over ^{13}C to produce isotopically lighter organic material (around -20‰) to that of its DIC source (Meyers and Teranes, 2001). As the removal and sedimentation of ^{12}C algal material from the DIC reservoir continues, the ^{13}C pool increases, leading to a subsequent increase in OM with higher $\delta^{13}C_{org}$ values (Verburg, 2007). Thus, increasing $\delta^{13}C_{org}$ values of sediment often indicate increasing algal productivity (e.g. Schelske and Hodell, 1995; O'Reilly *et al.*, 2003). $\delta^{13}C_{org}$ values can be used to distinguish between algae and higher plants which use the C_3 pathway for C uptake, and higher plants which use the C_4 pathway (Figure 4.1) (Meyers and Teranes, 2001). The C/N ratios then help distinguish between C_3 plants and C_3 algae as their $\delta^{13}C_{org}$ values overlap (Meyers and Teranes, 2001).

Caveats to the use of $\delta^{13}C_{org}$ as a lake productivity proxy exist, however, including the Suess effect, which is the dilution of heavy atmospheric C isotopes (^{14}C and ^{13}C) by CO_2 released from combustion of fossil fuels and deforestation, as CO_2 in fossil fuels is depleted in ^{13}C and has no ^{14}C (Verburg, 2007). Because CO_2 is exchanged between air and water, the Suess effect needs to be considered when interpreting the $\delta^{13}C_{org}$ in aquatic systems (Verburg, 2007).

Other factors which may influence the $\delta^{13}C_{org}$ composition of lacustrine sediments include aqueous CO_2 distributions, primary producer composition and the environment of a lake’s catchment (e.g. Cifuentes *et al.*, 1988; Rau *et al.*, 1989; Hollander and McKenzie, 1991; Bernasconi *et al.*, 1997). In certain cases when primary productivity is high, CO_2 ($\delta^{13}C$= -7‰) is diminished and algae switch to HCO_3^- ($\delta^{13}C$= 1‰) as their C source, leading to a less negative

$\delta^{13}C_{org}$ value (Meyers and Teranes, 2001). Different algal groups have also been shown to utilise different isotopic fractions of C, principally when CO_2 becomes depleted, and thus algal community composition may alter $\delta^{13}C_{org}$ values (Hollander and McKenzie, 1991; Lehmann *et al.*, 2004).

Another notable influence is the effect of catchment vegetation, for example a shift from C_4 grasses to C_3 woody plants, which can lower the $\delta^{13}C_{org}$ value of lacustrine OM when terrestrial inputs are significant (Qui *et al.*, 1993). Furthermore, Rau (1978) showed that extensive respiration of OM in Findlay Lake, Washington state and its surrounding catchment produced isotopically-light dissolved CO_2, which was then utilised by the algae and led to depleted $\delta^{13}C_{org}$ values as low as -47‰. This was expanded by Maberly *et al.*, (2013) who found lakes within productive catchments (measured by Net Primary Productivity (NPP)) of the English Lake District received large excesses of CO_2 derived from the decomposition of terrestrial C that were delivered to the lakes through hydrological pathways. This led to a depleted $\delta^{13}C$ value in the DIC of lake water and epilithic diatoms, which were strongly correlated with measures of lake productivity including Chl. *a* (Maberly *et al.*, 2013). Thus, catchment land use may influence the isotopic C fraction utilised by algae and so, more negative $\delta^{13}C_{org}$ values indicate increased productivity at these sites. This example from the English Lake District may be relevant to consider when interpreting the $\delta^{13}C_{org}$ values in this thesis.

II. Nitrogen isotope ratios

Identifying the $\delta^{15}N_{org}$ isotope composition of lacustrine sediments can help reveal sources of OM, productivity rates and in particular the availability of N to aquatic photosynthesisers (Meyers and Teranes, 2001). Application of $\delta^{15}N_{org}$ is based on the different $^{14}N/^{15}N$ ratio of terrestrial plants to algae and can also be used to decipher the sources of sedimentary OM. Algae utilise NO_3 from dissolved inorganic nitrogen (DIN) which has a higher $\delta^{15}N$ value (7-10‰) than that of atmospheric N_2 gas (0‰) used by terrestrial photosynthesisers (Peters *et al*., 1978). Thus, the $\delta^{15}N_{org}$ to some extent can be used to distinguish between autochthonous and allocthonous OM.

However, a number of caveats to the use of $\delta^{15}N_{org}$ as a proxy of past productivity and OM source must be noted. Algae preferentially exploit ^{14}N from DIN resulting in OM with a lower $\delta^{15}N_{org}$ value than the total NO_3 (Meyers and Teranes, 2001). The subsequent increase of ^{15}N in the DIN reservoir then results in OM with an increasing $\delta^{15}N_{org}$ value (e.g. Fogel and Cifuentes, 1993). Additionally, P not N is often the limiting nutrient in aquatic ecosystems, which can result in an unaltered $\delta^{15}N_{org}$ value if P is depleted before a significant amount of NO_3 has been consumed (Altabet and François, 1993; 1994).

The algal assemblage can also influence the $\delta^{15}N_{org}$ value of lacustrine OM. N_2-fixing cyanobacteria consume atmospheric N_2 and so, an assemblage rich in this group would lead to a lower sedimentary $\delta^{15}N_{org}$ (Fogel and Cifuentes, 1993). Contrastingly, heterotrophs increase the $\delta^{15}N_{org}$ of OM as each trophic transfer increases its value by 3-4‰ (DeNiro and Epstein, 1981; Minagawa and Wade, 1984; Peterson and Fry, 1987). Likewise, microbial denitrification, which prefentially uses lighter N isotopes in the reduction of NO_3 to N_2, can further enrich the residual ^{15}N in DIN, more pronounced in anoxic waters (Meyers and Teranes, 2001).

Anthropogenic disruption of the N biogeochemical cycle has further influenced the N isotope composition of lacustrine OM. Agricultural runoff and urban sewage has a heavy isotopic value ($\delta^{15}N_{org}$= 10-25‰) which mimics high primary production (Teranes and Bernasconi, 2000). In contrast, the prevalence of atmospheric N deposition from the 1950s correlates to depletions of 2‰ in sediment $\delta^{15}N_{org}$ in pristine arctic lakes (Wolfe *et al*., 2006). Coupled with other sedimentary biochemical proxies however, $\delta^{15}N_{org}$ values can help elucidate past productivity rates, OM sources and the anthropogenic forces that alter these in lake ecosystems.

III. Use of C and N mass, ratios, and isotopic composition in palaeolimnology

The application of %C, %N, C/N ratios, $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ used in conjunction and alongside other biogeochemical proxies (e.g. algal pigments), has been successfully undertaken in many palaeolimnological investigations. In Lough Neagh, Northern Ireland, post-1955 sedimentary deposits were characterised by increased %C, %N, $\delta^{15}N_{org}$, cyanobacterial pigments and decreased $\delta^{13}C_{org}$ values (Bunting *et al.*, 2007). Regression analysis revealed strong correlation of these proxies to N influx of agricultural waste, with this source ultimately being attributed to the eutrophication of this P-rich lake (Bunting *et al.*, 2007). In contrast, a set of Canadian sub-alpine lakes responded to DOM influxes produced by shifts from arid to wet episodes (Bunting *et al.*, 2010). Increases in sedimentary %LOI, %C, %N and algal abundances were negatively correlated to $\delta^{15}N_{org}$ values, reflecting the influx of depleted $\delta^{15}N_{org}$ of terrestrially-derived DOM in lakes below the tree-line (Hood *et al.*, 2005; Bunting *et al.*, 2010). The C/N ratios and $\delta^{13}C_{org}$ did not clearly identify the origins of the sedimentary OM however, due to low C/N ratios and $\delta^{13}C_{org}$ values in all lakes (Bunting *et al.*, 2010). This highlights the importance of understanding the limitations of such proxies, and the complex processes which can alter there sediment values. However, as the studies cited above highlight, these geochemical proxies are extremely useful when unpicking historical changes in primary production if used alongside other methods such as algal pigments, and therefore support their selection for use in this thesis.

IV. C and N mass and isotopic laboratory preparation and analyses

Approximately 25mg of wet sediment was taken from each 0.5cm interval of the following cores: BLE_{core}, EST_{core}, EAS_{core}, STI_{core}, RYD_{core}, and freeze-dried. This material was then packaged into air-tight bags and sent to the appropriate laboratories.

Both laboratories followed similar methodologies whereby approximately 1200µg of homogenised dry bulk sediment for each core interval was placed in a tin capsule. Sediment was not treated with HCl because carbonate content was less than 3% dry mass. This sediment then underwent combustion. At LEC, combustion was performed at 920°C in a Vario Pyrocube analyser linked to an Isoprime-100 continuous flow mass spectrometer. At UOR, combustion was performed at 1020°C in a Thermo Scientific Delta V isotope ratio mass spectrometer equipped with a continuous flow interface (ConFlo IV) and a Costech ECS 4010 elemental analyser. The high temperature combustion in the elemental analyser oxidises the C and N constituents of the sediment into simple N-based gases and CO_2 which are measured by the mass spectrometer. Relative (% dry mass) contents of C and N were measured. Atomic ratios of C/N were calculated by multiplying the C/N mass ratio by 1.167 (the ratio of atomic weights for C and N). Atomic C/N values were used because they reflect biochemical stoichiometry (Meyers and Teranes, 2001). $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ stable isotope ratios were expressed per mil (‰) and calculated relative to known international standards of Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}C_{org}$ and atmospheric N_2 gas for $\delta^{15}N_{org}$ respectively. $\delta^{13}C_{org}$ values were not corrected for the Suess effect to avoid ambiguity of interpretation. Typical analytical errors at both laboratories were < 0.2‰ for $\delta^{13}C_{org}$ and <0.4‰ for $\delta^{15}N_{org}$.

4.1.4 Sedimentary algal pigments: preparation and analysis using HPLC

Reversed-phase high performance liquid chromatography (HPLC) is an analytical technique that allows for the rapid isolation and separation of biochemical markers that include sedimentary algal pigments. The method outlined below was chosen because it is able to rapidly and effectively identify and quantify photosynthetic pigments, and is therefore able to address a fundamental requirement of this large-scale, multi-core project. The HPLC laboratory at the School of Geography, UoN, UK was used to carry out this analysis.

The fundamental principles of reversed-phase HPLC involve the separation of pigments according to their differential polarities. Pigment mixtures are forced under high pressure through a column of packing material (stationary phase) which consists of small particles (5µm) coated in a non-polar (e.g. C8, C18) monomer or polymer, by a polar solvent stream (mobile phase) (Leavitt and Hodgson, 2001; McGowan, 2013). Pigments which are polar (water- rather than lipid-soluble), such as fucoxanthin, elute from the column early as they have less affinity for the non-polar stationary phase but greater affinity for the mobile phase (McGowan, 2013). The mobile phase often comprises two or three solvents with different polarities which are mixed to create a stream of successive polarity gradients which for reversed-phase HPLC is from polar to non-polar, further aiding pigment separation (Leavitt and Hodgson, 2001). The mobile phase and the mass of a pigment determines how long it is retained on the column (the retention time) and so, the pigment elution order (Figure 4.2) (McGowan, 2013).

There are many methods that use different combinations of solvents and gradients and the choice often depends on the origin of the pigment samples and the level to which the researcher wants to identify compounds present in the samples. A modified approach of Chen *et al.*, (2001) was chosen for this study because it separates the main indicators carotenoids and Chls and their degradation products regularly found in lake sediments. Although results and statistical analyses described later in this thesis focus on key stable carotenoid and Chl markers, their degradation products provide an insight into possible depositional losses (Leavitt and Hodgson, 2001).

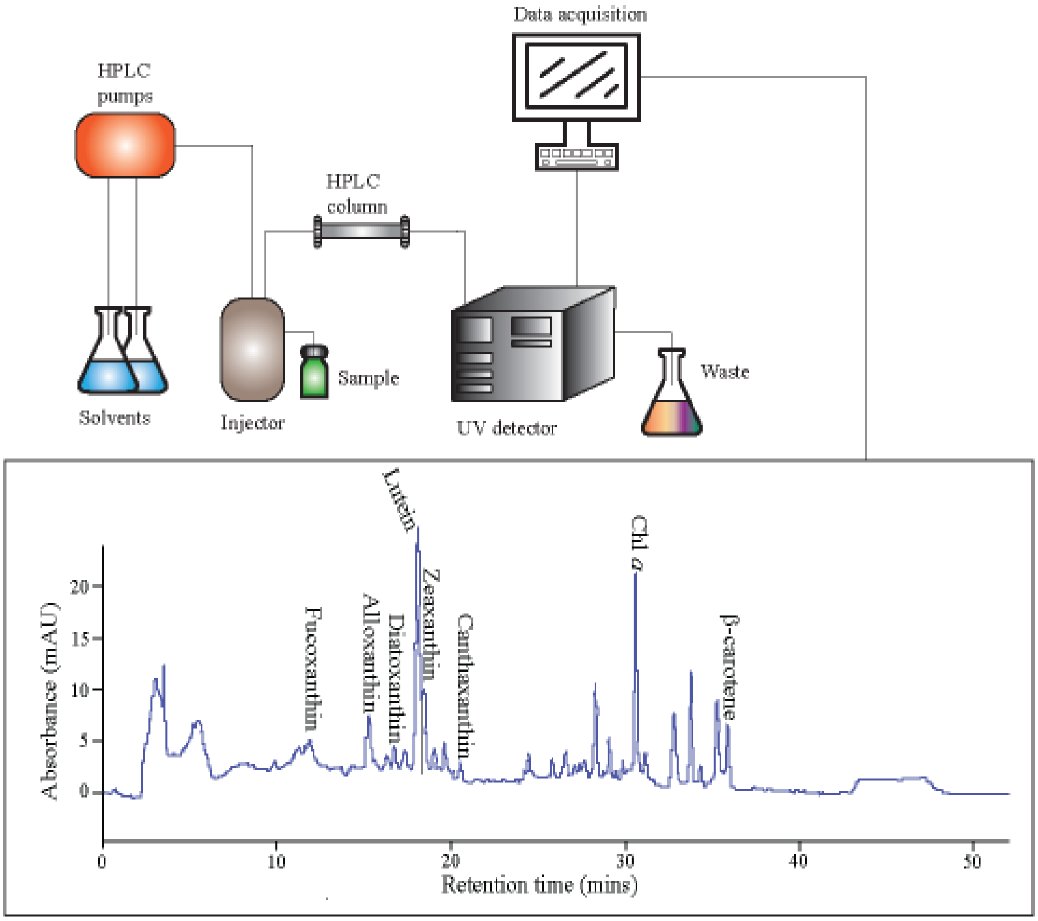


Figure 4.2 Schematic of HPLC instrumental system and chromatogram output used for pigment analysis at UoN. Modified from Czaplicki (2013).

Once 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 (Figure 4.3) (McGowan, 2013). Identification of the pigment is performed by comparison of position and retention time on the chromatogram, the shape of the spectrum and the wavelength of maximum absorbance (e.g. 475nm and 508 for myxoxanthophyll) with known commercial pigment standards (DHI Denmark) that have been analyzed using the same separation conditions (Figure 4.3) (McGowan, 2013). These commercial standards are also used to calibrate the machine to convert peak areas to pigment molar mass.

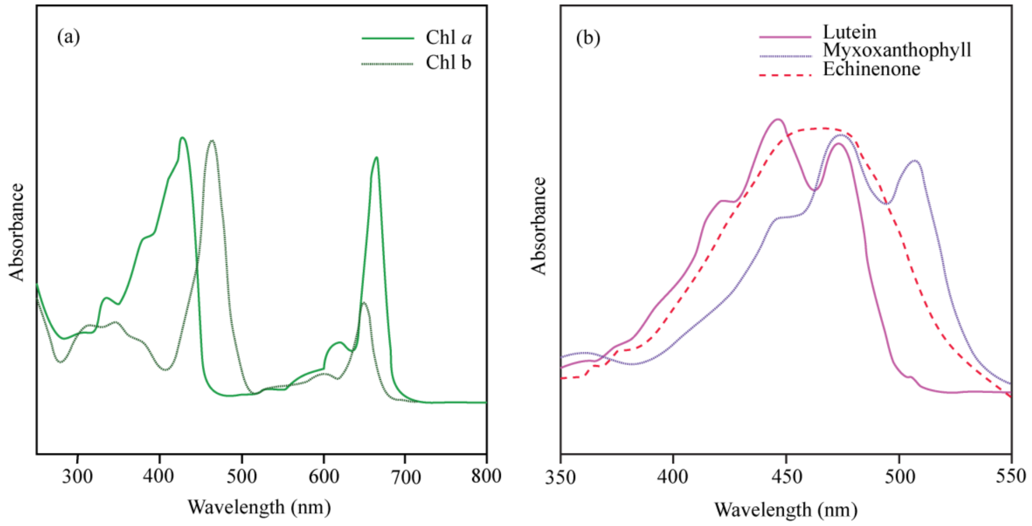


Figure 4.3 Examples of pigment absorption spectra at multiple wavelengths as produced by PDA detection. Modified from McGowan (2013).

V. Method for HPLC

Aliquots of sediment were taken from every 0.5cm core interval from all selected cores and frozen at -20°C (Table 4.1). Although not undertaken by the author, the following procedures were exactly the same for $\mathrm{WNB_{core}}$ and $\mathrm{WSB_{core}}$, described in McGowan *et al*., (2012). The frozen subsamples were freeze-dried (lyophilized) in an inert vacuum chamber (covered in black plastic to eliminate light) a few days prior to HPLC analysis. Lyophilization removes water to allow for effective and reproducible extraction (Leavitt and Hodgson, 2001). Subsequently, a subsample of freeze-dried material (~0.2g) was weighed and transferred into a labeled vial before undergoing extraction which involved the addition of 5ml solution of acetone, methanol and HPLC-grade de-ionised water (80:15:5). The extract was left overnight at -10°C following Leavitt and Hodgson (2001). After 12 hours, the supernatant was decanted into a 50ml beaker followed by two successive solvent rinses. The extracts were filtered using a 0.22 µm PTFE syringe filter to remove the sediment. Samples were then evaporated to dryness under a stream of N_2 gas. Once dry, the samples were kept for no more than 2-3 days in a freezer under N_2 gas before being re-dissolved in injection solution chemically similar to the mobile phase to reduce error associated with over- or under-injection (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) (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 amount was judged by visual inspection. Samples were then transferred into HPLC vials.

VI. Separation of pigments in HPLC

The HPLC system comprised an Agilent 1200 series quaternary pump, autosampler, and PDA detector which detects UV and visible spectra data every 2 seconds. Each 52-minute run started and ended with a “green” standard (a pigment extract from grass containing known Chls and carotenoid pigments, prepared in the same way as the lake samples) which identified whether there was any drift in retention times and so aided pigment identification. The separation method used was an adaptation of Chen *et al.*, (2001) which consisted of a mobile phase composed of solvent A (80:20 methanol: 0.5m ammonium acetate), solvent B (90:10 acetonitrile: de-ionised water), and solvent C (ethyl acetate) and a stationary phase consisting of an ODS Hypersil column (250 x 4.6 mm; 5 μm particle size). Solvents were de-gassed prior to use. The solvent gradient stream is described in Table 4.2.

Table 4.2 Solvent separation gradients. Modified from Chen *et al.*, (2001).

Time (mins)	**% Solvent A**	**% Solvent B**	**%Solvent C**	**Flow (ml/min^{-1})**
0	100	0	0	1
4	0	100	0	1
38	0	25	75	1
39	0	25	75	1
43	100	0	0	1
52	100	0	0	1

VII. Identification and quantification of sedimentary pigments

The resulting chromatograms from the HPLC runs were used to identify pigments via comparison with known retention times and absorbance spectra of pigment standards (McGowan, 2013). 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 allocthonous minerogenic material and pigment degradation from the mineralization of labile bulk OM (Equation 1) (McGowan, 2013). Pigment standard calibration curves were developed by injecting known quantities of commercial pigment standards stock solution into the HPLC to obtain the relationship between pigment mass and peak area. A linear regression of pigment peak area against pigment mass (as volume x concentration) was then undertaken to give the calibration constant (slope).

Concentration of pigment (nmole pigment g^{-1} organic weight sediment) =
((pigment peak area/calibration constant)*(TV*IV)) / ((EM)*(%LOI_{550}/100))
Equation 1

Where: TV = Total solution and pigment volume (µl); IV = Injection solution volume (µl); EM = Extraction weight of sediment (g); %LOI_{550} = Organic matter content (as a % of dry mass).

Pigment preservation condition was calculated by the ratio of Chl. *a* to pheophytin *a* (Leavitt and Hodgson, 2001). The UV radiation (UVR) or water clarity index was calculated for those lakes where the UVR-absorbing compound (described in Leavitt *et al*., 1997) was found, by dividing by the sum of four abundant carotenoids (alloxanthin, diatoxanthin and lutein-zeaxanthin) and multiplying by 100.

4.1.5 Sediment chronologies. ^{210}Pb dating

Accurate sediment chronologies are crucial in palaeolimnology to help decipher the timings and so, causal mechanisms of lake ecosystem change. In addition, accurate chronologies enable sedimentation rates to be calculated which provide important insights into catchment and in-lake sedimentation processes. ^{210}Pb (half-life is 22.3 years) is one of the most widely used natural radioactive isotopes for dating recent sediments (0-150 years), and has been shown to accurately determine timings of accelerated soil erosion or lake eutrophication with the use of appropriate models (Appleby, 2001).

^{210}Pb is one of the daughter products of the ^{238}U decay series (Figure 4.4), and it is the disequilibrium between its parent radium-226 (^{226}Ra) through the diffusion of the immediate gaseous isotope radon-222 (^{222}Rn) that permits its application (Noller, 2000).

$4.51\text{x}10^7$yrs 1602 yrs 3.82 days 22.26 yrs 138.4 days

^{238}U-----^{226}Ra-----^{222}Rn-----^{210}Pb-----^{210}Po-----^{206}Pb

Figure 4.4 ^{238}U decay series and the half-lives of its daughter products involved in ^{210}Pb production. Modified from Appleby (2001).

Part of the ^{226}Ra found in soils decays and releases ^{222}Rn to the atmosphere, which decays in 3.8 days. ^{222}Rn decay releases four daughter products including unsupported ^{210}Pb, all of which are then scavenged by rain water (wet deposition) or to aerosols (dry deposition) and following removal from the atmosphere, adsorbed by OM, ending up in lake sediments via precipitation or catchment runoff (Figure 4.5) (Noller, 2000). The unsupported ^{210}Pb differs from supported ^{210}Pb which is derived from the in-situ decay of ^{226}Ra at depth (Noller, 2000). Chronologies are developed by comparing the unsupported ^{210}Pb, whose activity then becomes a function of its half-life from the upper, newly-deposited sediments, with the activity at lower depths (Noller, 2000).

Unsupported ^{210}Pb cannot be measured directly or indirectly so is calculated by subtracting the supported ^{210}Pb from the total ^{210}Pb activity (Equation 2) (Appleby, 2008). Supported ^{210}Pb is measured indirectly using alpha or gamma spectrometry, by assuming equilibrium to ^{226}Ra activity (Harle and Heijinis, 2014). Total ^{210}Pb is measured either directly or indirectly, via the progeny ^{210}Po, which is assumed to be in equilibrium with ^{210}Pb (Harle and Heijinis, 2014).

$$C_{uns}(t)=C_{uns}(0)e^{-\lambda t} \qquad \text{Equation 2}$$

Where $C_{uns}(t)$=present unsupported activity, $C_{uns}(0)$=estimated initial concentration, λ=decay rate constant, t=age of sediment.

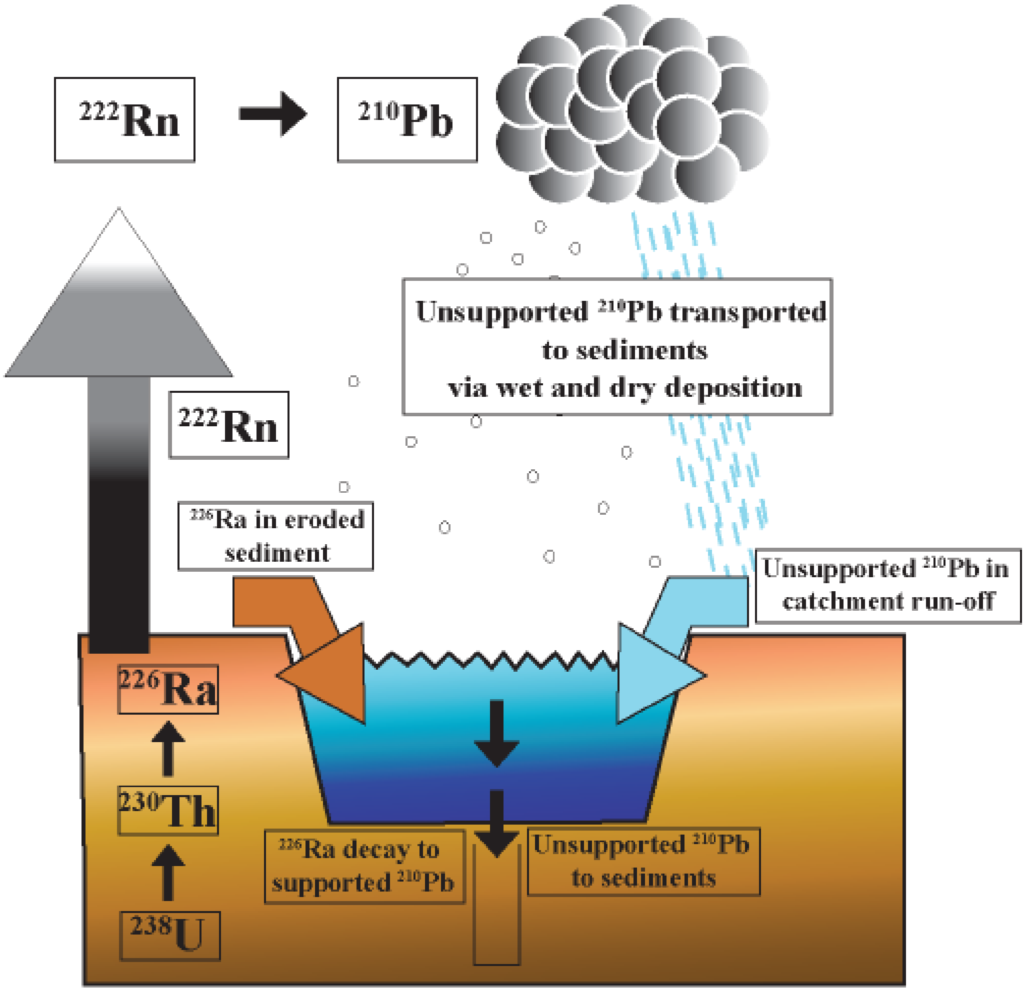


Figure 4.5 ^{238}U decay cycle and pathways ^{210}Pb reaches lacustrine sediments. Modified from Oldfield and Appleby (1984).

Variation in erosion and sedimentation from climatic and anthropogenic activity in recent years alters the flux of unsupported ^{210}Pb to lacustrine sediment (Appleby, 2001). To account for this, the Constant Rate of Supply (CRS) model was developed, which assumes non-uniform sedimentation but uniform ^{210}Pb flux from the atmosphere (Robbins, 1978; Oldfield and Appleby, 1984). It can be calculated with Equations 3 and 4 (Appleby and Oldfield, 1978) and has been validated at sites including BLE$_{site}$ by the reciprocal relationship between changing mean sedimentation rates and surface ^{210}Pb flux (Appleby and Oldfield, 1983). The CRS model takes into account discrepancies between atmospheric ^{210}Pb flux and the sediment ^{210}Pb profile, such as those produced by catchment inputs, water column losses via outflows and sediment focussing which is greater in drainage lakes compared to seepage

(Binford *et al.*, 1993; Appleby, 2001). It can be used to model accumulation rates of sediment too (Appleby and Oldfield, 1978).

CRS model: The initial concentration of ^{210}Pb=$C_{uns}(t)$ at a given time (t) must correspond to:

$$C_{uns}(t)\ r(t)=\text{constant} \qquad \text{Equation 3}$$

Where r(t)=dry mass accumulation rate (g cm^{-2} yr^{-1}) at time (t). Age (t) at depth x can then be calculated by:

$$t=\frac{1}{\lambda}\,\text{In}\,\frac{Ao}{Ax} \qquad \text{Equation 4}$$

Where λ is the decay rate constant, Ao is the total unsupported ^{210}Pb activity in the sediment column and Ax is the total unsupported activity in the sediment column beneath depth x.

To validate chronologies derived from the ^{210}Pb models, artificial radionuclide activity can be measured. The atmospheric fallout of caesium-137 (^{137}Cs) and americium-241 (^{241}Am) from the decay of plutonium-214 (^{214}Pu) released from nuclear weapons testing between 1953-1963 and the Chernobyl disaster of 1986, can be used as stratigraphic markers through the detection of activity peaks in the sediments to which they adhere (Appleby, 2001). A sharp increase in radionuclide fallout activity was found to correspond to 1963 prior to the Nuclear Test Ban Treaty (1963) in most sediments; however the Chernobyl disaster of 1986 released radionuclides detected at an order of magnitude greater than weapons testing in some parts of the UK (Appleby, 2001). These peak dates of 1963 and 1986 can be compared with the ^{210}Pb chronology to not only help validate the model but understand possible variation in atmospheric and sediment flux to the lake bottom.

Limitations to ^{210}Pb dating revolve around variation in its atmospheric deposition and storage in lake sediment systems. Variations in rainfall can lead to different delivery of atmospheric ^{210}Pb and other radioisotopes to a lake (Appleby, 2001), but even in regions where wet deposition is similar, factors such as forest canopy and topography have been shown to increase deposition (Branford *et al.*, 1998; Yamamoto *et al.*, 1998). Further, lower WRTs have been shown to increase removal of isotopes before they reach the sediment (Appleby, 2001). Once deposited in the sediments, redistribution of radionuclides within the sediment column can occur through slumping, slides, physical or biological mixing at the sediment-water interface, and chemical advection or diffusion within pore waters, in particular ^{137}Cs due to its higher solubility than ^{210}Pb (Appleby, 2001). Thus, sediment composition can decide the extent to which these processes occur, for instance, greater mobility of ^{137}Cs is found in organic-rich sediments (Appleby, 2004). Further, adsorption of ^{137}Cs is greatest with small particles, clay minerals, higher pH and low oxygen, thus the size, mineralogy and chemistry of the sediments can affect ^{137}Cs mobility (Foster *et al.*, 2006). The result of the aforementioned processes is a flattening of ^{210}Pb profiles versus depth, and disturbance to ^{137}Cs and ^{241}Am peaks, often resulting in a ‘tail’ of ^{137}Cs to sediments dated prior to the 1950s (Appleby, 2001). Despite these caveats, the CRS model has been validated for use in developing accurate chronologies, and is often supported by the ^{137}Cs and ^{241}Am profiles, with the 1963 peak in ^{137}Cs well-fixed in many sediment cores (Appleby and Oldfield, 1983; Appleby, 2001; Smol, 2002).

VIII. ^{210}Pb dating laboratory analyses

Subsamples of wet sediment from each 0.5cm interval were freeze-dried to enable dry-mass accumulation rates to be calculated and packaged in air-tight bags before being sent to the appropriate research laboratory. Dried sediment samples sent to UCL were analysed for ^{210}Pb, ^{226}Ra via its daughter isotope ^{214}Pb, ^{137}Cs and ^{241}Am by direct gamma assay using a ORTEC HPGe GWL series, well-type coaxial, low background, intrinsic germanium detector at selected 0.5cm sediment intervals. At UoB the activities of ^{137}Cs, ^{210}Pb and ^{214}Pb were analysed using a well-type, ultra-low background HPGe gamma ray spectrometer at selected 0.5cm sediment intervals. Gamma spectrometry used at both facilities measures ^{210}Pb activity via its gamma emissions at 46.5 keV. ^{226}Ra was used to determine the ^{210}Pb supported activity profile, measured by the 295 keV and 352 keV gamma rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow for radioactive equilibrium. ^{137}Cs and ^{241}Am emissions were measured at 662 keV and 59.5 keV (Appleby *et al.*, 1986). Calibration of the detectors is undertaken at both facilities using known activity sources such as bentonite clay spiked with a mixed gamma-emitting radionuclide standard, QCYK8163 and sediment samples such as IAEA marine sediment certified reference material (IAEA 135) as used at UoB. Corrections were made for the low-gamma self-absorption of the samples (Appleby and Oldfield, 1992).

Detection limits were dependent on radionuclide gamma energy, count time, and sample mass. Longer count times were used for LOU$_{core}$, CT$_{core}$, GRA$_{core}$ and particularly for ELTIN$_{core}$ which exceeded 400,000 seconds due to the low dry sample mass. This was due to the high water content of this core and the floccy nature of the sediment, potentially an attribute of a high proportion of algal particulate matter.

IX. Developing suitable age-depth models using ^{210}Pb records

The CRS model was used to determine the chronologies of BLE$_{core}$, CT$_{core}$, EAS$_{core}$, EST$_{core}$, LOU$_{core}$, RYD$_{core}$ and STI$_{core}$ due to the non-monotonic features of the ^{210}Pb profiles (Appleby, 2001). This was calculated using equations 3 and 4, and validated using the ^{137}Cs and ^{241}Am profiles. However, the very low detection of ^{210}Pb activity for ELTIN$_{core}$ meant that an accurate chronology could not be developed using these data. For GRA$_{core}$ the low detection of ^{210}Pb resulted in an age-depth model which suggested the sediments were younger when compared with ^{137}Cs maxima and previous palaeolimnological work undertaken by Barker *et al.*, (2005). Thus it was deemed appropriate to use the ^{137}Cs profiles that had two distinct ^{137}Cs maxima indicating the 1986 Chernobyl accident and 1963 weapons testing. Where activity peaks reached zero this was determined to be 1940 prior to nuclear weapons testing which began in 1945 (Ritchie and McHenry, 1990). The chronology was thus interpolated between these three dates. These chronologies were validated by comparing palaeolimnological proxy change and timings from this study to previous work undertaken by Barker *et al.*, (2005) at GRA_{site} and Lund (1981) at ELT_{site}.

The decay rate and reduced accuracy of counting ^{210}Pb at low activities means that before c.150 years (which for this project is from 1861-63, depending on core collection date), extrapolation of sediment chronologies to 1800 had to be performed. This was done by extrapolating the age-depth models backwards using the deepest calculated sedimentation rate (i.e. as calculated using the two deepest ^{210}Pb dates) until the depths corresponding to 1800.

Sediment accumulation rates (r) (g cm^{-2} yr^{-1}) were calculated for each core using Equation 5, with the cumulative dry mass (g cm^{-2}) calculated by the UCL and UoB laboratories. For GRA_{core} and $\text{ELTIN}_{\text{core}}$ the sediment accumulation rate (g cm^{-3} yr^{-1}) was determined by dividing dry bulk density (g cm^{-3}) by years per cm (yrs cm^{-1}).

$$r = \lambda M \qquad \text{Equation 5}$$

Where λ is the decay rate constant of ^{210}Pb and M is the slope of the line of cumulative dry mass (g cm^{-2}) vs. In(Ao/Ax) from Equation 4.

4.2 Historical and instrumental data collection of local and regional environmental records

In order to understand the causal mechanisms of sedimentary algal pigment changes, they were compared with other available environmental data. Although there are often discrepancies between the time-series of monitored vs. palaeo-records, the points at which they overlap provide important insights (Battarbee *et al.*, 2012). To improve this overlap it is important to use high quality monitoring data that have been collected at an appropriate temporal resolution to fit the palaeo-records (Battarbee *et al.*, 2012). As such, only the best available data from the Windermere catchment were selected for use in this study.

4.2.1 Metereological data collection

Regional climate datasets were acquired and used for this project because they were annually resolved and started in the 19th century, and were therefore comparable with sediment records over the period of interest. Although more local datasets exist they do not extend so far back in time. Furthermore, Battarbee *et al*., (2002a) found that sediment proxies (including diatoms, pigments and cladoceran assemblages, C, N composition of OM) did not correlate to changes in local seasonal and annual temperature changes over the last 200 years, but did over coarser time periods and across a continental-scale. Thus, freely accessible regional instrumental climate records were deemed the most applicable for investigating the centennial, regional-scale relationship between climate and sedimentary algal communities of interest in this study.

Climate data collated included annual precipitation data from the Central Lake District (1788-2000) (Barker *et al*., 2004), annual NAO index data (1865-2011) (Hurrell, 1995; Jones *et al.*, 1997) and national annual temperature data from the Central England Temperature record (CET; 1689-2011) (Parker *et al*., 1992). Annual UK atmospheric SO_2 and NO_x emissions per million/tonne (1970-2010) were used as proxies for atmospheric deposition, and were obtained from the Environmental Statistics Service of DEFRA (2012), as deposition data was not readily available.

4.2.2 Historical catchment land use and human population data collection

Agricultural livestock, land use and human population data from the Windermere catchment were collated from open access sources (described in McGowan *et al*., (2012)). The data were only available by parish or other administrative district boundaries and not individual lake catchments. Thus, comparison between 1:25,000 Ordnance Survey topographic maps and the parish/urban district boundary maps from Vision of Britain (VOB, 2011) was undertaken to approximate the best fit between a lake’s catchment and its administrative district (Table 4.3). The agricultural and population data were therefore attributed to each lake according to the administrative boundaries in which the lake was found.

Publicly available agricultural livestock and land-cover data were only available from 1866-1988, at decadal resolution and obtained from the Ministry of Agriculture, Fisheries and Food (MAFF) census stored in the National Archives (MAF/68). Agricultural livestock was converted to numbers per hectare from total numbers to allow for comparison of intensification changes within an area. Land use data, recorded in hectares, were converted into % cover to eliminate the effect of boundary size so comparison is between % changes in catchment land use only. National-scale P and N fertiliser application data were available annually for the years 1974-2010, and were sourced from DEFRA (2011).

Table 4.3 The Parish and Urban Districts in which each lake and its catchment was historically found from beginning of agricultural (1866) and population (1801) censuses to present (VOB, 2011).

Lake and its catchment	Parish-level (P) and/or Urban District (UD) in which lake and its catchment found
BLE_{site}	Claife P, Hawkshead and Monk Coniston with Skelwith P Hawkshead P.
BT_{site}	Lakes UD, Langdales P.
CT_{site}	Grasmere P/UD, Lakes UD.
EAS_{site}	Grasmere P/UD, Lakes UD.
EST_{site}	Claife P, Hawkshead P.
$ELTIN_{site}$/$ELTMID_{site}$/$ELTOUT_{site}$	Grasmere P/UD, Lakes UD, Langdales P, Rydal and Loughrigg P, Skelwith P.
GRA_{site}	Grasmere P/UD, Rydal and Loughrigg P.
LLT_{site}	Lakes UD, Langdales P.
LOU_{site}	Lakes UD, Rydal and Loughrigg P.
RYD_{site}	Lakes UD, Rydal and Loughrigg P.
STI_{site}	Grasmere P/UD, Langdales P.
WNB_{site}	Ambleside P, Claife P, Grasmere P/UD, Lakes UD, Langdales P, Rydal and Loughrigg P, Skelwith P, Troutbeck P.
WSB_{site}	Applethwaite P, Bowness-on-Windermere P, Hawkshead P, Satterthwaite P, Undermillbeck P, Windermere P.

Human population data for each district were obtained from the national population census of England and Wales, 1801-2001. The data, which were collected every ten years, were compiled into total resident population per hectare from three separate sources: Histpop (2011) for years 1801-1921, Vision of Britain (2011) for 1881-1961 and the Census Dissemination Unit (2011) for 1971-2001. Human population was used as a proxy for sewerage pressure, with greater numbers in a given area suggesting increased human waste production and potential increased pressure on the surrounding water bodies.

4.2.3 Local council records

Information on the timing of WwTW installations or adaptations and hydromorphological alterations within the Windermere catchment was required to assess their relationship to sedimentary algal pigment changes. These data were acquired from the following published work: McGowan *et al.*, (2012), Dong *et al.*, (2011), Barker *et al.*, (2005), Zinger-Gize *et al.*, (1999), Hürrig, (1999), Jones (1972), Haworth (1984), Haworth *et al.*, (2003), and the Kendal and Barrow County Archival Records Offices. Data sources from these offices included the Grasmere Urban District minutes (1920-1934) and the North Lonsdale Rural District Council Sewerage and Water Supplies folders (1900-2005), which contained stakeholder letters, council minutes, and planning permits. These qualitative records also provided a broader insight into regional industrial and urban changes, thus fleshing out the gaps of the quantitative monitoring data during interpretation of historical algal community change.

4.3 Summary

The main focus of this project is the sedimentary algal pigment records which have previously been shown by McGowan *et al.*, (2012) to be useful proxies for algal community change in Lake Windermere, and thus deemed ideal to investigate the aims of this thesis (section 1.6). Methods to analyse sedimentary %LOI, %C, %N, C/N ratios, $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ were described, as were ^{210}Pb, ^{137}Cs and ^{241}Am radioisotope dating. The rationale for the use of these analyses in this project was addressed. Further, the method used to collate local council records and historical instrumental data to a form which could be used for statistical investigation into past climate, nutrient and hydromorphological drivers of algal community change was also explained (further details in section 5.7).

Methodological issues which were addressed primarily related to sediment core choice for analyses and creating chronologies from cores with low sample size and ^{210}Pb detection counts. First, cores were chosen for ^{210}Pb dating and C and N analyses on the basis of their quality, the management interest of the site from which they were retrieved (e.g. the hypereutrophic ELTIN$_{site}$ over the oligotrophic ELTOUT$_{site}$) and the need to ensure an even distribution of physical characteristics of these sites in order to address the role landscape characteristics play on algal community response (Table 2.1). Second, workable chronologies on cores with low ^{210}Pb counts was established using the available radioisotope (^{137}Cs) data and past work. The large amounts of sedimentary proxy data produced by this laboratory work then had to be synthesised and statistically analysed in order to address the aims of this thesis and are detailed in the following chapter.

CHAPTER 5. METHODS III: STATISTICAL ANALYSES

This methods chapter describes the statistical analyses undertaken on the sedimentary algal pigment and historical environmental data described in chapter 4. These analyses were performed in order to address the aims outlined in section 1.6. All analyses were undertaken by the author.

5.1 Selection of sedimentary algal pigments for statistical analyses

Sedimentary algal pigments selected for statistical analysis were chosen on account of their low lability, presence in all sediment cores from each site and ability to represent the main freshwater algal groups found in Windermere and its catchment (Table 5.1) (Reynolds and Irish, 2000). Three cyanobacterial pigments were chosen in order to capture the different cellular organisations (unicellular, colonial and filamentous) that make up this diverse algal group. The notoriety of cyanobacteria as harmful bloom-forming species which dominate communities across a wide range of nutrient and temperature gradients provided the motivation to investigate changes in their abundance across the Windermere catchment (Taranu *et al.*, 2012).

Table 5.1 Sedimentary algal pigments chosen for numerical analyses and affinity to single, dominant algal group. Stability estimate ranges from 1 (most stable) to 4 (least stable). - is unknown. Modified from Leavitt and Hodgson (2001).

Pigment	Affinity (algal group of process)	Stability
Alloxanthin	Cryptophytes	1
Aphanizophyll	Filamentous/N_2-fixing cyanobacteria	-
β-carotene	Most algae and plants	1
Canthaxanthin	Colonial cyanobacteria	1
Diatoxanthin	Diatoms, dinoflagellates, chrysophytes	2
Lutein	Green algae, euglenophytes, higher plants	1
Zeaxanthin	Cyanobacteria, prochlorophytes, rhodophytes, chlorophytes	1

5.2 Transformation of seven stable pigments for further analyses

Standardising data allows for the comparison of datasets with different units or scales of measurements. One method of standardisation results in "z-scores" which possess a mean of 0 and a standard deviation of 1, thus enabling the direct comparison between different pigments within and among datasets. This approach was used to address the issue of differential preservation or difference in measured concentrations of the seven algal pigments between sites. Moreover, having the species data on the same scale permitted ordination methods such as principal components analysis (PCA) to more accurately predict which axis and where on the axis the response variable (species data) was predicted to fall (Lepš and Šmilauer, 2003).

The seven stable pigment concentrations outlined in Table 5.1. were centralised and standardised in the statistical software programme R, using the scale() function (Becker *et al.*, 1988). This procedure was performed on 0.5cm depth intervals from cores with ^{210}Pb/^{137}Cs chronologies from 1800 onwards (STI$_{\text{core}}$, CT$_{\text{core}}$, EAS$_{\text{core}}$, LOU$_{\text{core}}$, EST$_{\text{core}}$, GRA$_{\text{core}}$, ELTIN$_{\text{core}}$, RYD$_{\text{core}}$, BLE$_{\text{core}}$, WNB$_{\text{core}}$ and WSB$_{\text{core}}$), whereas for those without chronologies, the full depth of the core was used (BT$_{\text{core}}$, LLT$_{\text{core}}$, ELTMID$_{\text{core}}$ and ELTOUT$_{\text{core}}$).

5.3 Ordination methods to determine algal community change over time

Ordination methods have been used and developed since the 1950s and have provided ecologists with the ability to investigate the species composition of ecological communities from single to numerous sampling sites, over an assortment of environmental gradients (Lepš and Šmilauer, 2003). If two species are plotted close to one another on a particular axis on an ordination plot, the distribution of these species is described as being similar (Lepš and Šmilauer, 2003).

PCA and other ordinations reduce multiple-dimensional datasets to two dimensions by rotating the data to explain the maximum variability in the first axis, followed by subsequent axes (Figure 5.1) (Palmer, 2014). PCA axis 1 scores can be used to describe species turnover or variation in a community dataset; in other words community change. This is done by reducing the square distance of each data point to the axis line from the centroid (often a vector of zeros when species have been centralised and standardised) (Palmer, 2014). Site scores for PCA axis 1 can therefore describe the species turnover or variation from the centroid at each data/sample interval. The more these scores deviate from the centroid, the more variation of the species at this interval is seen, independent of whether it is a negative or positive value.

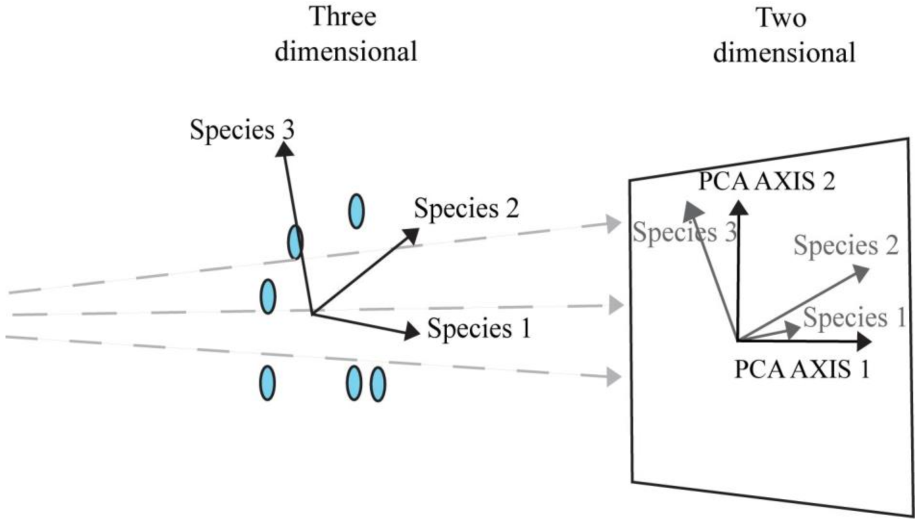


Figure 5.1 Schematic diagram of how a PCA transforms data from multiple response variables (e.g. species counts) onto a two-dimensional biplot. Modified from Palmer (2014).

Prior to PCA analysis, indirect gradient ordination or detrended correspondence analysis (DCA) was performed on the transformed seven stable sedimentary algal species concentrations to determine whether the distribution of the pigments was linear or unimodal. Generally if the length of axis 1 in the DCA is greater than 4.0 sd, there has been a complete turnover of the species (Lepš and Šmilauer, 2003). Thus, the data are too heterogeneous to undergo PCA. Each site’s DCA was performed using the decorana() function in the R package ‘vegan’, using log (x+1) transformed data which generated positive values as row sums of the community matrix must be greater than zero (a requirement of the package). All cores had gradient lengths of <2.0 for axis 1. Therefore, the data were analysed using the linear ordination method of PCA to obtain a single measure of algal community change, due to its homogenous, linear response (Hill and Gauch, 1980).

PCA axis 1 scores were used in this thesis to reduce the pigment assemblage data to a single summarising value that was interpreted as algal community change. This was performed on the pigment data described in section 5.2 at each 0.5 cm interval from 1800 onwards for cores with ^{210}Pb/^{137}Cs chronologies, and for the full depth for those without. This allowed piecewise regression, linear regression and regression tree (RT) analysis to be applied, which can only be used on a single response variable. PCA was achieved using the ()rda function in the ‘vegan’ package in R and the axis 1 scores extracted (Legendre and Legendre, 2012). The data inputted into the ()rda function was the centralised and standardised pigment data described in section 5.2**.**

5.4 Mann-Kendall tau rank correlation coefficient of stable pigments to determine trends in concentration

The Mann-Kendall trend test is a non-parametric statistical exploration of whether there is a monotonic upward or downward trend in a variable over time (Mann, 1945; Kendall, 1975; Gilbert, 1987). A Kendall tau rank correlation coefficient is the measure of association between random pair samples in the time series. It assigns the pairs a score: +1 if the sample is greater than the latter and -1 if it is lower (Gilbert, 1987). Thus, a Mann-Kendall coefficient with a negative value suggests a decreasing trend (coefficient between 0 and -1) whilst a positive value suggests an increasing trend (coefficient between 0 and +1) (Gilbert, 1987). The test assumes the variables are independent of one another. The null hypothesis, H_0, is that there is no trend in the time series, however a lack of adequate data can often lead to the null hypothesis being accepted (Gilbert, 1987). Mann-Kendall trend tests are a widely used method of exploring trends in datasets. They have been used to detect increasing cyanobacterial pigment trends across the northern hemisphere over the last ~200 years (Taranu *et al.*, 2015) and to compare trends in water chemistry such as TP with algal flora changes (Hobaek *et al.*, 2012).

The Mann-Kendall trend test was undertaken to investigate whether the concentration of each algal group present within the Windermere catchment increased, decreased or remained largely unchanged between 1800 and 2013.

The Mann-Kendall coefficient or tau was determined using the MannKendall() function in the R package ‘Kendall’ (McLeod, 2011). The transformed concentrations of the seven stable algal pigments described in 5.2 were inputted into the function, with the summary output providing the tau rank correlation coefficient and p-value.

5.5 Piecewise linear regression to address timing of major algal community change

A piecewise linear regression model is useful for determining a breakpoint or sharp change in the directionality of a dataset, by fitting two different linear regression models joined at a breakpoint (Toms and Lesperance, 2003). It can be used to identify shifts or critical thresholds in ecological communities which often occur when an ecosystem undergoes changes to environmental conditions and alternative stable states (Scheffer *et al.*, 2001). These thresholds and the timings at which they occur can be useful to managers in determining causal mechanisms (Scheffer *et al.*, 2001).

Piecewise linear regressions are widely used on both palaeolimnological and limnological datasets to investigate thresholds of change. They have been used to investigate correspondence of breakpoints between summer temperature and shifts in algal community structure i.e. from benthic to planktonic production and whole-lake primary production in arctic lakes (Rühland *et al.*, (2013). Elsewhere, they have been used to investigate other environmental change such as climate-mediated erosion events and diatom assemblage changes (Randsalu-Wendrup *et al.*, 2012). Thus, they are a well-established tool to determine shifts in past ecological change.

Several types of piecewise linear regression models exist. The continuous model (Figure 5.2a) constrains the distance between the two segments to be continuous, rather than the discontinuous model where the end and beginning of each segment may have a different y coordinate but the same x coordinate (Figure 5.2b) (Muggeo, 2003). The discontinuous model requires an iterative search to determine the best fit linear models (Lemoine, 2012). The continuous model is useful because the change in many response variables such as species turnover does not always exhibit a discrete jump or disjointed step change (Ewers and Didham, 2006).

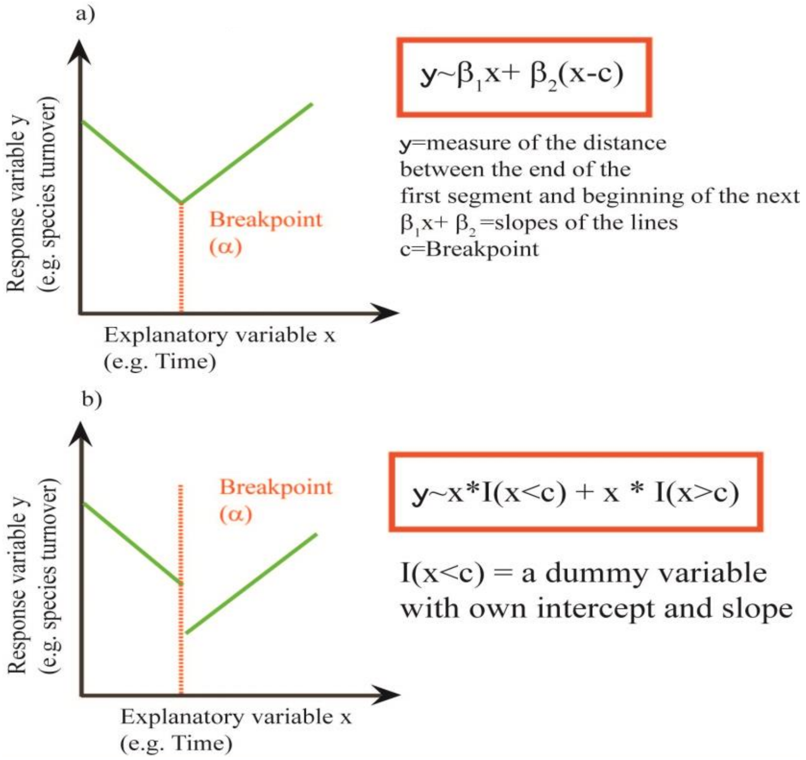


Figure 5.2 Conceptual examples and formula for a) continuous piecewise linear regression and b) discontinuous piecewise linear regression. Modified from Lemoine (2012).

A continuous piecewise linear regression was applied to the PCA axis 1 scores at 0.5cm depth intervals from each site with $^{210}Pb/^{137}Cs$ chronologies within the Windermere catchment to assess when and if a major shift in algal community change had occurred after 1800. A 95% confidence interval (95% CI) consisting of years before and after the breakpoint was additionally calculated in order to assess the usefulness of the piecewise model. The further these years were from the breakpoint the less confidence there is in there being a major/sharp change in the algal communities at that point. However, even in the absence of a sharp breakpoint this analysis can be useful in identifying broader periods of ecological change often witnessed in lakes experiencing additive nutrient sources and climate variation over time (Scheffer *et al.*, 2001).

Piecewise linear regression was performed using the R package ‘segmented’ using the segmented() function (Muggeo, 2008). This was chosen due to its ability to segment continuous explanatory variables such as time (Muggeo, 2008). The segmented() function requires an estimated breakpoint using the formula psi=x, where x= estimated year. The estimated breakpoint was determined by visual inspection of the plotted PCA axis 1 scores. The segmented() function first fits a linear model using the formula lm(y~x) with Y being the PCA axis 1 scores and X=year. Then the seg.Z=~x function segments the explanatory variable X. Subsequently the formula confint() was applied to the piecewise linear regression to determine the 95% CI in the breakpoint.

5.6 Synchrony analysis to address local vs catchment-wide centennial and decadal trends in stable pigments

Inter-lake synchrony (S) is defined as the extent to which limnological variables change in a similar manner over a designated time-scale between a series of lakes (Kratz *et al.*, 1998). It is measured by calculating the arithmetic mean of Pearson’s correlation coefficients (r) for a given variable across a time series for every lake pair and for multiple lake pairs to calculate regional S (Magnuson *et al.*, 1990). When a limnological variable behaves synchronously (S>0.5) over a large geographic region it suggests that regional or wider-scale factors such as climate or catchment-wide land use practices are controlling the observed modification (George *et al.*, 2000; Patoine and Leavitt, 2006). Biological variables often behave less synchronously than their physical or chemical counterparts due to site-specific trophic interactions and because seasonal cycles of community change tend to override regional forcings (Kratz *et al.*, 1998; Baines *et al.*, 2000; Patoine and Leavitt, 2006). However, looking at the S of both taxonomic specific and algal production as a whole is useful in identifying which algal groups are more resilient or susceptible to wider environmental processes and at what times (Patoine and Leavitt, 2006).

Spatial S analysis (or temporal coherence) is often performed on lake districts, catchments or chains of lakes to understand the temporal patterns of behaviour exhibited by limnological variables at regional to local scales (Liebhold *et al*., 2004). For instance, variations in climate (specifically NAO) led to synchronous changes in physical components such as surface temperature in five lakes of the English Lake District over 40 years, but longer-term, decadal S in chemical variables, such as nitrate-nitrogen, correlated with regional patterns of fertiliser application (George *et al*., 2000). Taxon-specific algal S has been shown to vary among algal groups with spring-blooming taxa such as cryptophytes (alloxanthin) and diatoms (diatoxanthin) being more synchronous than summer-blooming cyanobacteria (canthaxanthin, echinenone) and total algae (Pheophytin *a*, β-carotene) (Figure 5.3) (Patoine and Leavitt, 2006). In conclusion, S analysis provides the opportunity to understand taxon-specific algal responses to both regional and lake-specific forcings over centennial time scales, especially where the chemical stability of the pigments are the same.

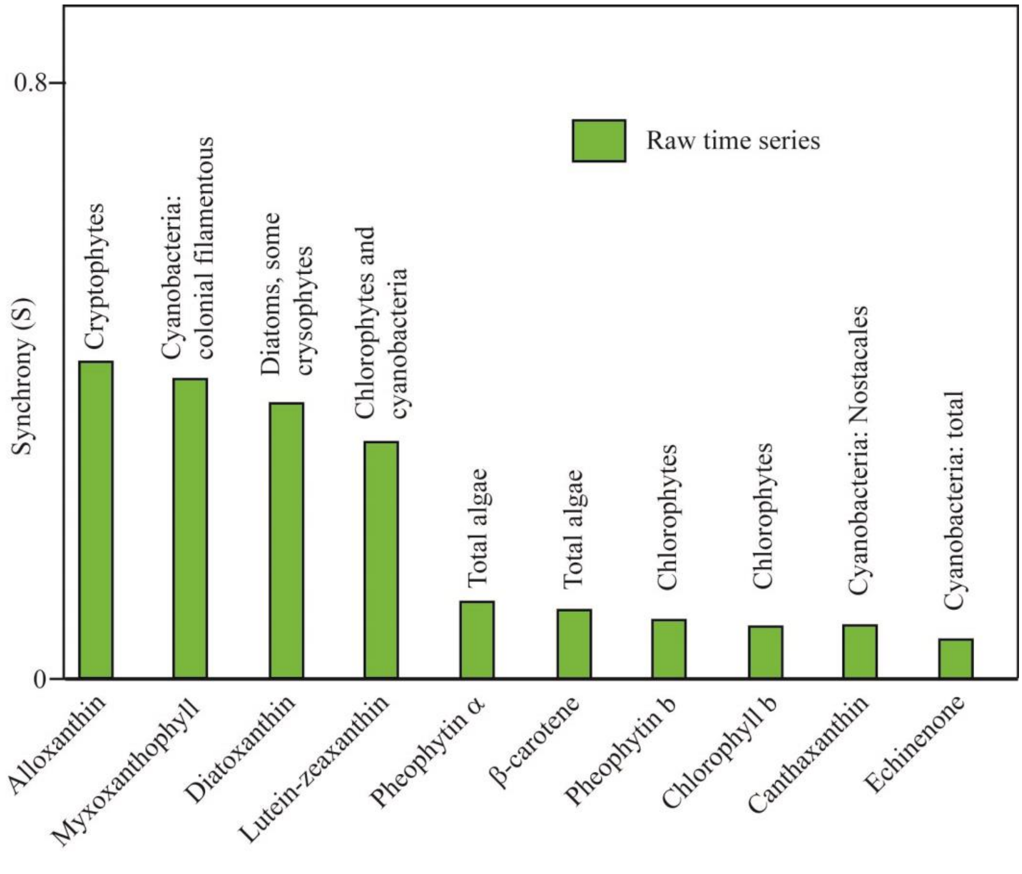


Figure 5.3 Synchrony of fossilised algal pigments from 1860-1994 in seven Qu'Appelle Valley lakes. Modified from Patoine and Leavitt (2006).

Inter-lake S of sedimentary algal pigments was calculated across the Windermere catchment to understand whether regional drivers of change or lake-specific drivers were more important in determining algal community change from 1800 onwards. This was performed on transformed concentrations of seven stable pigments from cores with ^{210}Pb/^{137}Cs chronologies at 5-year intervals for the following time series: 1800-2005; 1800-1905; 1900-2005; and 1950-2005. The year 2005 was chosen as the latest date to avoid post-depositional increases in sediments that can occur in the top few cms and which result in S increases (Patoine and Leavitt, 2006). In addition, WNB$_{core}$ and WSB$_{core}$ were collected in the decade prior to the others, so 2005 was deemed a useful end point (McGowan *et al*., 2012). The time periods were selected to address the following hypotheses:

a) All algal species and primary production (as determined by β-carotene) would increase and therefore behave synchronously from 1800 onwards due to increased catchment-wide nutrient input and a warming climate.
b) Post-war changes to sewage and agriculture in the catchment would lead to reduced synchronicity of the algal community due to differences in both the timing of these events and the ability of each individual lake's physical and chemical characteristics to filter or attenuate them.

The sites were then split into lowland sites (BLE$_{core}$, ELTIN$_{core}$, EST$_{core}$, GRA$_{core}$, LOU$_{core}$, RYD$_{core}$, WNB$_{core}$, WSB$_{core}$) and upland sites (CT$_{core}$, EAS$_{core}$, STI$_{core}$) to see if the lakes in these groups behaved more synchronously to one another than when pooled together across the aforementioned time-series.

S analysis was performed in the R package 'synchrony' using the meancorr() function on Z-transformed pigments to obtain the synchrony (S) value which is the mean Pearson's correlation coefficient (r) for all lake pairs among time series (Gouhier and Guichard, 2014). This results in the same S values as the computation of the intra-class correlation coefficient employed by Rusak *et al*., (1999). To obtain 5-yearly intervals for each Z-transformed pigment the mean was used where more than one value per five-year interval was found, and where missing values arose, they were estimated by the linear interpolation of adjacent samples (Patoine and Leavitt, 2006). Values of S=1 are perfectly synchronous whereas those where S=0 are asynchronous and values that are negative can arise when parameters are inversely correlated (Vogt *et al.*, 2011). An analysis of statistical significance was performed using monte-carlo permutations using the nrand= function in the R package ‘synchrony’. Whereby the observed mean S was compared with a distribution of r values derived from 999 randomizations of the original time series in order to obtain a p-value (Rusak *et al.*, 1999; Gouhier and Guichard, 2014).

5.7 Regression trees (RTs) to determine environmental explanatory variables of algal community change

RTs use binary recursive partitioning to explore complex, nonlinear, high-order species-environment relationships (De'ath and Fabricius, 2000). The method separates groups of species using partition criteria imposed by the environmental explanatory variables to minimise the dissimilarity between species groups (using the sum of squared Euclidean distances; SSD) (De'ath and Fabricius, 2000). The explanatory variable that leads to the lowest SSD is selected (Davidson *et al.*, 2010). The final groups of species are termed ‘leaves’ and the nodes are the splits or threshold changes in the explanatory variables, with the tree formed from both (Figure 5.4). The variance not explained by the tree is defined by the relative error (RE), where the R^2 for the tree is then calculated using 1- RE (De'ath, 2002). RTs are useful when investigating complex ecological relationships which often have nonlinear responses of species or environmental variables (Ouellette *et al.*, 2012). They detect abrupt changes in community composition as abrupt changes in the environmental variables are used to demarcate the leaves (Ouellette *et al.*, 2012).

RTs have been used by authors to investigate species-environment relationships in palaeolimnology. For example, Multivariate RTs have been used to identify 6 distinct cladoceran communities (leaves) in 39 shallow lakes in the UK and Denmark, according to splits in the two predictor variables zooplanktivorous fish (ZF) abundance and August Macrophyte Percentage Volume Infested (PVI), both of which were controlled by nutrient enrichment (Davidson *et al*., 2010). In another study, Multivariate RTs identified three distinct groups of lakes and sub-fossil cladoceran communities according to their latitudinal gradient: northern, southern and mid-European (Bjerring *et al*., 2009). These studies show that predictor variables are often both directly and indirectly responsible for changes in the community response, but represent the ability of the RT to handle high-order interactions (De'ath, 2002).

In addition, RTs can successfully pinpoint thresholds in the predictor variables. For instance, thresholds of electrical conductivity and magnesium/calcium ratios on the formation of endogenic minerals on lacustrine sediments from the Tibetan Plateau were obtained using Multivariate RTs (Wang *et al*., 2012). These results were then applied to the Late Glacial and Holocene sediment records from a single lake to infer past temperature and subsequent changes in salinity (Wang *et al*., 2012). This study and the aforementioned highlight the ability of RTs to determine thresholds of environmental change on historic species-response proxies, to aid understanding of complex species-environment relationships.

RTs were undertaken on each core with ^{210}Pb/^{137}Cs chronologies in order to explore hierarchal thresholds of past environmental drivers of algal community changes from 1800. PCA axis 1 scores were used as the response variable to represent algal community change. RTs were chosen for three main reasons:

a) They are able to generate hierarchal splits of environmental interactions.
b) They handle missing values, numeric and categorical explanatory variables.
c) They are easy to interpret (De'ath, 2002). Lake managers are often financially and time constrained and so information on what has caused the greatest ecological change and where is paramount so that this information can be relayed to a variety of stakeholders.

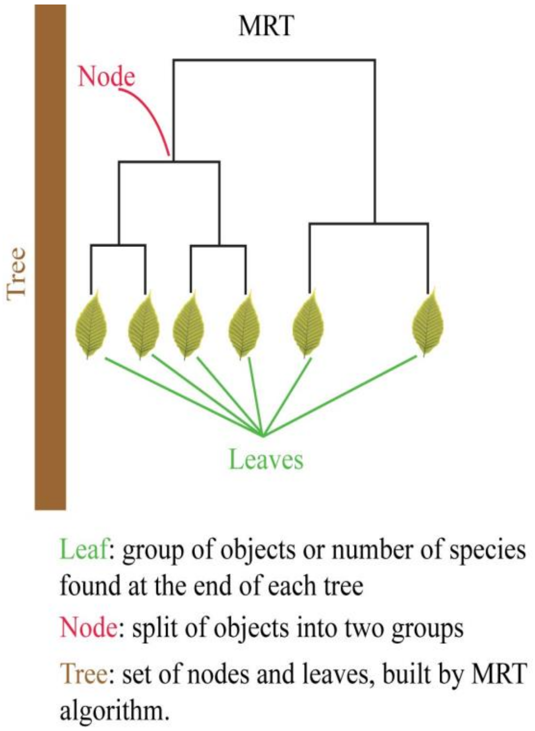


Figure 5.4 Example of RT. Nodes are formed by change in environmental variable. Modified from Ouelette *et al*., (2012).

RTs were performed using the statistical R library ‘mvpart’ using the mvpart() function used to create Multivariate RTs (De'ath, 2002). Prior to applying the function the explanatory environmental variables described in Table 5.2 for each site were matched to the chronologies of the corresponding sediment cores. Chiefly for the upland tarns ($\mathrm{CT}_{\mathrm{site}}$, $\mathrm{EAS}_{\mathrm{site}}$, $\mathrm{STI}_{\mathrm{site}}$) which have no or minimal human activity in their catchment, catchment human population and agricultural livestock and land use data were not selected for the analysis. In the lowlands, NOx and SO_2 emissions data were not included as the RT kept choosing these values over other local, longer time-scale datasets, notably WwTWs and livestock, and better model fit was found when NOx and SO_2 were removed. This is not uncommon in complex models, where certain indirect measurements can mask the importance of other more direct explanatory variables, and once removed can increase the variance explained or fit of the model (adjusted R^2/R^2) (e.g. Hill and Hamer, 1998). It has been found that different methods of selecting explanatory variables whether statistical or the iterative selection of explanatory variables enabled by RTs, often result in applicable models but are not always useful if the ecological processes involved are not considered (Murtaugh, 2009). Thus, if NOx and SO_2 were important drivers of ecological change in lowland lakes it would be expected that concomitant broad-scale changes in chemical and biological variables would have previously have been identified in the lowland lakes due to the diffuse nature of these pollutants. However previous studies in the Lake District found changes in algal community composition in nutrient-enriched lowland lakes but no changes in oligotrophic lowland lakes, suggesting atmospheric deposition is not a major driver of change in these systems (Bennion *et al*., 2000). Further, it is likely that NOx is an indirect measure of agricultural intensification or livestock density because of artificial N fertiliser use, thus, both livestock numbers and N fertiliser trends was used as a direct driver of change (Davidson, 2009). However, the upland lakes have been identified as sensitive to the effects of acidifying pollutants such as NOx and SO_2 due to being poor in dissolved ions but no evidence for acidification had been found for the lowland lakes and changes in diatom flora associated with reduction of sulphur deposition at STI_{site}, CT_{site} and EAS_{site} warrant the inclusion of NOx and SO_2 in the upland lakes RTs (Sutcliffe, 1983; Tipping *et al*., 2002). Individual livestock variables (sheep/cattle/pigs/poultry/horses numbers per hectare) were grouped together to improve model fit. Categorical variables, specifically presence or absence of site-specific hydromorphological alterations, WwTW installations and adaptations were applied to the individual site in question. PCA axis 1 scores were applied to the function as the response Y variable.

The mvpart() function was tricked into performing a Multivariate RT using a single response variable by the addition of a dummy variable. This was in order to produce the cross-validation model which is not achieved using the univariate RT approach (*pers comm*. Z. Taranu, 2015). RTs provide an over-fitted model where tree sizes are overestimated which thus requires simplification (De'ath and Fabricius, 2000; Crawley, 2002). This was performed using the mvpart() function by plotting the cross-validation results and pruning the tree according to the one standard error (1-SE) rule. This is where the tree chosen is the smallest tree whose estimated error rate is within 1-SE of the minimum error (Breiman *et al*., 1984). The 1-SE rule often prunes the trees to much smaller sizes but has the lowest associated error (De'ath and Fabricius, 2000). Tree sizes often vary with repeated cross-validations, so several cross-validations were run to ensure the 1-SE selected tree remained typical (De'ath and Fabricius, 2000). The output of the mvpart() function was the plotted RTs for each site showing thresholds of change in the environmental drivers which also define the percentage variation explained (PVE) in the sedimentary algal species turnover. This was calculated by 1- RE (relative error), and was performed for each single node, all nodes of each RT (described as R^2), and the sum of all nodes across the catchment to determine the PVE by each category of explanatory variables (see Figure 8.3 for list of categories).

Table 5.2 Environmental variables applied to each lake's RT.

Site **Environmental variable**	**BLE**	**CT**	**EAS**	**ELTIN**	**EST**	**GRA**	**LOU**	**RYD**	**STI**	**WNB**	**WSB**
Catchment livestock (numbers/ha), **1866-1988**	🟦			🟩	🟦	🟩	⬛	🟪		🟨	⬛
Catchment land cover (% Arable/Temp. grass/Perm. Grass/Rough grazing/Wood), **1866-1988**	🟦			🟩	🟦	🟩	⬛	🟪		🟨	⬛
UK P & N fertiliser use (kg/ha), **1974-2010**	🟦			🟩	🟦	🟩	⬛	🟪		🟨	⬛
Catchment population (numbers/ha), **1801-2001**	🟦			🟩	🟦	🟩	⬛	🟪		🟨	⬛
Annual rainfall Central Lake District (mm), **1842-2000**	🟦	🟧	🟥	🟩	🟦	🟩	⬛	🟪	🟥	🟨	⬛
Central England Temperature (°C), **1800-2011**	🟦	🟧	🟥	🟩	🟦	🟩	⬛	🟪	🟥	🟨	⬛
Annual NAO Index, **1865-2011**	🟦	🟧	🟥	🟩	🟦	🟩	⬛	🟪	🟥	🟨	⬛
NO_x emissions (thousand tonnes), **1970-2010**		🟧	🟥						🟥		
SO_2 emissions (thousand tonnes), **1970-2010**		🟧	🟥						🟥		
Presence/Absence. Outflow channel straightened, lowering lake level, **1830**	🟦										
Presence/Absence. Re-alignment of Inflow Fishpond beck, **1888**	🟦										
Presence/Absence. Housing & septic tank development at Outgate, **1900-1950**	🟦										
Presence/Absence. Piped water installed at Outgate, **1951**	🟦										
Presence/Absence. WwTw installed at Outgate, **1962**	🟦										
Presence/Absence. Great Langdale WwTw installed, discharge pipe at inner basin, **1973-74**				🟩							

Table 5.2 Continued

Site **Environmental variable**	**BLE**	**CT**	**EAS**	**ELTIN**	**EST**	**GRA**	**LOU**	**RYD**	**STI**	**WNB**	**WSB**
Presence/Absence. Diversion of WwTw discharge pipe to point downstream, **1999**				🟩							
Presence/Absence. WwTw installed at Hawkshead, **1973**					🟦						
Presence/Absence. Tertiary treatment installed at Hawkshead WwTw, **1986**					🟦						
Presence/Absence. Fish cages introduced in lake, **1981**					🟦						
Presence/Absence. Fish cages removed from lake, **2009**					🟦						
Presence/Absence. WwTw installed at River Rothay, **1971**						🟩		🟪			
Presence/Absence. Discharge pipe installed to hypolimnion of Grasmere from Rothay WwTw, **1982**						🟩		🟪			
Presence/Absence. Dam built at outflow, **1838**									🟥		
Presence/Absence. Dam re-built, **1959**									🟥		
Presence/Absence. Railway built to Windermere, **1847**										🟨	⬛
Presence/Absence. Piped water installed at settlements around Windermere, **1970**										🟨	⬛
Presence/Absence. WwTw installed at Ambleside, **1886**										🟨	
Presence/Absence. WwTw installed at Bowness, **1895**										🟨	
Presence/Absence. Upgrading of Ambleside WwTw, **1914**										🟨	
Presence/Absence. Tertiary treatment installed at Ambleside WwTw, **1991**										🟨	

Table 5.2 Continued

Site **Environmental variable**	**BLE**	**CT**	**EAS**	**ELTIN**	**EST**	**GRA**	**LOU**	**RYD**	**STI**	**WNB**	**WSB**
Presence/Absence. WwTw installed at TowerWood, **1886**											■
Presence/Absence. Upgrading of TowerWood WwTw, **1914**											
Presence/Absence. Tertiary treatment installed at TowerWood WwTw, **1991**											

5.8 Investigation into the relationship between physical site characteristics and Mann-Kendall trend coefficients of algal community change since the 19th century

Lakes within a lake district can exhibit very different biological, chemical and physical properties due to differences in morphometry, position in the landscape and the strength of interaction between the lakes and their catchments (Kratz *et al*., 1997). Therefore, understanding how these physical factors have influenced the magnitude of ecological community response to past environmental drivers of change helps to understand lake ecosystem dynamics and prevents a "one-size-fits-all" management approach (Kratz *et al*., 1997).

Several authors have investigated how lakes within a district respond to external pressures such as climate or land use depending on the lake's position in its landscape and its physical properties using different statistical approaches. For example, S analysis was used to show lake districts which had more heterogeneity in hydrological connectivity and topography were asynchronous in response to regional external pressures (Webster *et al*., 2000). Alternatively in lakes within the western boreal forest of Canada, investigations using simple and partial correlation and forward stepwise multiple regression analyses tested the strength in the relationship between the area of wetland and groundwater recharge on changes in the TP concentration (Devito *et al*., 2000). Thus, such statistical investigations can take many forms but are ultimately based on testing the strength of the relationship between the explanatory variables (physical lake and landscape) and response variables (change in lake-specific biological, chemical or physical).

Several steps were required to investigate the relationship between the landscape position and physical characteristics of the lakes and tarns in the Windermere catchment to algal community change using linear regression and t-tests. First, Mann-Kendall trend coefficients were used to summarise the algal community change as determined by the PCA axis 1 scores into a single value for every site. Mann-Kendall trend tests have been used by other authors on ordination scores such as PCA axis 1 scores of chironomid assemblages to determine the significance of trends (Frossard *et al*., 2013). The usefulness of the Mann-Kendall trend coefficient is that not only does it determine the significance of the trend but the magnitude of the temporal changes in community composition data. This then permitted the use of linear regression models to investigate gradients of algal community change across continuous physical site variables and the use of t-tests to investigate the relationship between two types of a physical variable.

The Mann-Kendall coefficients for algal community change were undertaken by importing the PCA axis 1 scores (from 1800 onwards for those cores $^{210}Pb/^{137}Cs$ chronologies and the full depth of core for those without) as described in section 5.4 into the function MannKendall() in the R package 'Kendall' (McLeod, 2011). Because the objective of the Mann-Kendall coefficient in this instance was to give a value for the extent or magnitude of algal community change and not to identify whether it showed an increasing or decreasing trend, absolute (non-negative) coefficient values were used. This enabled regression and t-test outputs to be simplified and more interpretable. Only sites with significant ($p<0.05$) Mann-Kendall coefficients were used in the analysis (CT_{core} and $ELTMID_{core}$ were excluded as $p>0.05$). This meant the analysis was restricted to significant and clearer community response trends, reducing ambiguous regression output.

5.8.1 Linear regression between physical site characteristics and algal community change

Simple linear regression models describe the relationship between a response Y variable to a single explanatory X variable using a straight line. This was performed using Equation 6 below :

$$Y=a+\beta_1X_1+\varepsilon \qquad \text{Equation 6}$$

Where: a is the intercept on the Y axis; β_1 is the slope which denotes the change in Y per unit change in the independent X1 variable; ε is the error term (McDonald, 2014).

Simple linear regression models use the ordinary least squares method which minimises the sum of squared residuals on a given plot to produce a line of best fit (Legendre and Legendre, 2012). It can be used to test the strength of association between the response and explanatory variables in question using the adjusted R^2 value (Legendre and Legendre, 2012). It ranges from 0 to 1, with 1 meaning that the Y variable can be predicted from the X variable without error. The adjusted R^2 measures how close the data are to the fitted regression line while taking into account the number of predictors or explanatory variables (Legendre and Legendre, 2012). The significance of the relationship between the two variables is given by the p-value (McDonald, 2014). This is a useful tool to explain ecological relationships but assumes the relationships are linear (Legendre and Legendre, 2012).

Linear regressions are a popular choice with ecologists when looking to explain the strength of a relationship between two variables. For instance, linear regressions were used to explore the relationship between climate variability and several different sediment proxies in seven remote European lakes (Battarbee *et al*., 2002b). The study found that coarse-scale climate trends were strongly associated with changes in OM, %C, %N and diatom assemblages in lacustrine sediment. Issues with temporal autocorrelation mean p-values must be interpreted with caution and often the R^2 is used to interpret regression models (Battarbee *et al*., 2002b). Although lake ecological communities are subject to many confounding factors and complex interactions, simple linear regressions are a useful step towards teasing out environment-community relationships.

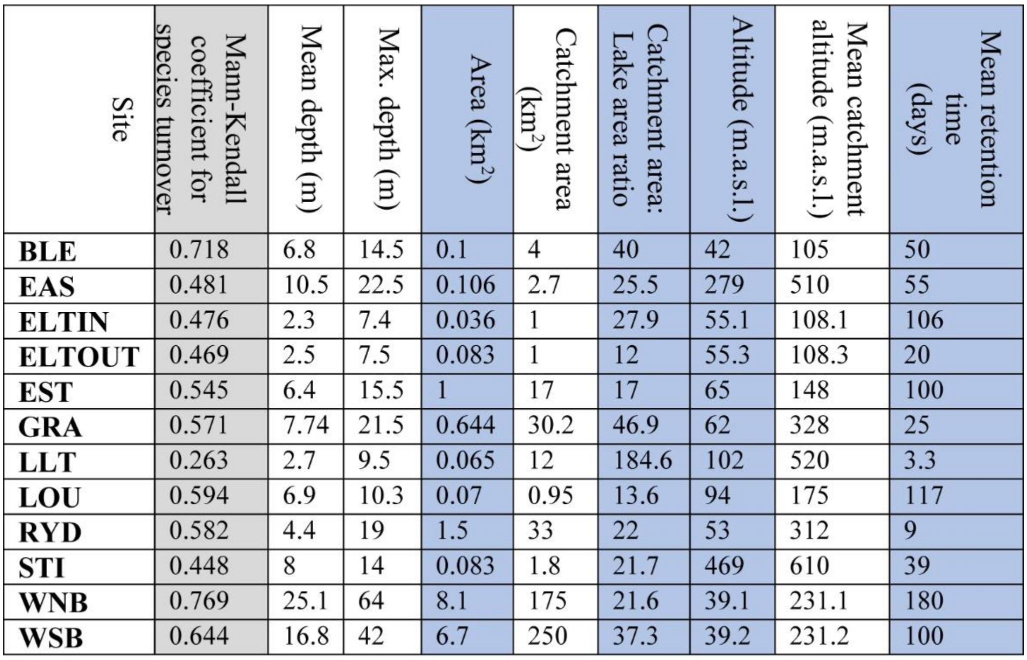
Linear regressions were used to understand which continuous physical site characteristics (Table 5.3) as the explanatory variables were important in determining algal community change (measured as Mann-Kendall coefficients of PCA axis 1 scores from 1800 in dated sediment cores and full core lengths for those not dated) as the response variables in the Windermere catchment. For example, was algal community change in deep lakes greater than those in shallow?, or greater in high altitude lakes than lowland lakes?, with the linear regression used to detect correlation between change in algal pigments over time (summarised by the Mann-Kendall trend coefficient) of each site against the corresponding measurement of the physical site characteristic in question at each site (McDonald, 2014). The output of such models is useful for future predictions of how algal communities may respond to other environmental drivers of change given a site's physical character. A linear regression model was used because pigment assemblage change over time was linear (section 5.3). The strength of relationship was determined by the adjusted R^2 and significance by the p-value. BT_{site} was omitted from this analysis due to the inability to source physical proxy data for this site.

Eight physical site and catchment characteristics were inputted into the cor() function in the R package 'vegan' to remove any highly correlated variables (Pearson's correlation coefficient $r>0.6$). This reduced the noise and improved the efficiency of the regression models which can be weakened by using highly correlated variables (Becker *et al.*, 1988). The variables that were not highly correlated ($r<0.6$) are shaded in dark blue in Table 5.3 and were used for linear regression. The linear regressions for each of the four site characteristics was performed using the lm() function in the R package 'vegan' (Becker *et al.*, 1988). The Mann-Kendall coefficients of the PCA axis 1 scores were the Y response variable and the physical proxy data the X independent variables to determine if there was a correlation (McDonald, 2014).

5.8.2 T-test to determine relationship between two categories of physical characteristics

T-tests are a useful statistical technique to determine if two datasets are statistically different from one another. Paired t-tests are useful if looking at the difference in datasets with similar units or the same response variable, with the test removing that variation that cannot be accounted for by the difference between the two plots (Hauer and Lamberti, 2011). In other words, it removes or reduces the influence of confounding factors on the response variables.

Table 5.3 Mann-Kendall coefficients for algal community change and the eight physical site characteristics for each site. Those characteristics not highly correlated and used for linear regression are shaded in dark blue. Data obtained from Table 2.1.



Site	Mann-Kendall coefficient for species turnover	Mean depth (m)	Max. depth (m)	Area (km^2)	Catchment area (km^2)	Catchment area: Lake area ratio	Altitude (m.a.s.l.)	Mean catchment altitude (m.a.s.l.)	Mean retention time (days)
BLE	0.718	6.8	14.5	0.1	4	40	42	105	50
EAS	0.481	10.5	22.5	0.106	2.7	25.5	279	510	55
ELTIN	0.476	2.3	7.4	0.036	1	27.9	55.1	108.1	106
ELTOUT	0.469	2.5	7.5	0.083	1	12	55.3	108.3	20
EST	0.545	6.4	15.5	1	17	17	65	148	100
GRA	0.571	7.74	21.5	0.644	30.2	46.9	62	328	25
LLT	0.263	2.7	9.5	0.065	12	184.6	102	520	3.3
LOU	0.594	6.9	10.3	0.07	0.95	13.6	94	175	117
RYD	0.582	4.4	19	1.5	33	22	53	312	9
STI	0.448	8	14	0.083	1.8	21.7	469	610	39
WNB	0.769	25.1	64	8.1	175	21.6	39.1	231.1	180
WSB	0.644	16.8	42	6.7	250	37.3	39.2	231.2	100

Paired t-tests were used to compare sedimentary proxies of two distinct lake characteristics in the Windermere catchment. They were performed to look for difference in values of C/N ratios, $\delta^{13}C_{org}$, $\delta^{15}N_{org}$, β-carotene concentrations, Mann-Kendall coefficients of PCA axis 1 scores between lowland and upland lakes. As well as $\delta^{15}N_{org}$ and Mann-Kendall coefficients of PCA axis 1 scores between lakes of high WRT (≥100 days) and low WRT (<100 days), Mann-Kendall coefficients of PCA axis 1 scores between lakes of BVG and SIL geology and Mann-Kendall coefficients of PCA axis 1 scores between upland low WRT (<100 days) lakes and lowland low WRT (<100 days) lakes. This was undertaken to see if the sedimentary proxies could be summarised categorically or more specifically if two distinct lake and catchment physical characteristics were different from one another.

Paired t-tests were performed using the t.test(y1,y2,paired='TRUE') formula in the R package 'vegan'. The p-value was used to determine the significant difference between the two site characteristics.

5.9 Summary

The statistical approaches used in this thesis have been chosen to address the three main aims described in section 1.6 using the sedimentary algal pigment and historical records collected as described in chapter 4. Methodological issues addressed by these numerical techniques include differences in core chronologies, algal preservation and historical records. Analyses were specifically chosen to overcome differential sediment chronologies. The DCA, PCA and Mann-Kendall trend tests were undertaken on all sediment cores as these are analyses that explore the trends in pigment concentrations from the bottom of the core to the top. The assumption for cores without ^{210}Pb chronologies (BT_{core}, LLT_{core}, $\text{ELTMID}_{\text{core}}$, $\text{ELTOUT}_{\text{core}}$) is that the bottom layers of the core are older than those of the top. Therefore these analyses still provide information on changing trends in sedimentary algal pigments and community change over time. The RT and S analyses are constrained by time so were only performed on the 11 cores with ^{210}Pb/^{137}Cs chronologies from 1800 onwards. This sample size (11 out of 15) was considered to be sufficient for investigating the timing of major changes in the Windermere catchment's algal communities. Finally, linear regressions and t-tests of algal community change over time/depth at each site (determined by the Mann-Kendall coefficient of PCA axis 1 scores since 1800 for ^{210}Pb/^{137}CS dated cores or full core length for those without) against the corresponding physical site characteristic measurements of each site was undertaken. All cores were used in these two analyses because they focussed predominantly on what may have caused differential algal community changes within the Windermere catchment, rather than when this change occurred. This chapter outlines the statistical methods used to synthesise the raw sediment and historical records presented in the following chapter. It was felt important to show the raw data to help interpret the results and utility of the statistical analyses.

CHAPTER 6. RESULTS AND INTERPRETATION OF INDIVIDUAL LAKE SEDIMENT RECORDS

This chapter gives a brief description and interpretation of the sedimentary proxies for each individual lake basin prior to the regional syntheses in chapters 7 and 8.

6.1 Regional climate trends (~1850 onwards)

Lake District annual rainfall was lower between 1960 and 1980, while mean decadal summer and autumn precipitation data (not shown) increased 37% and 16% between the 1990s and the 2000s respectively (Figure 6.1 (1)). The NAO index was in its positive phase from 1900-1957 and 1982–2004, which has been associated with warmer, wetter winters as determined by other authors (Figure 6.1 (1)) (see George *et al.*, 2007). These results indicate the discrepancy between annual precipitation and seasonal precipitation values, which may be important when considering climatic drivers of algal seasonal succession. There was an increased occurrence of extreme mean annual temperatures (>9°C) after 1950 and particularly from the late 1980s onwards when values increased to >9.5-10°C (Figure 6.1 (2)).

6.2 UK Nutrient trends (1975-2010)

Maximum fertiliser P and N application was between 1980 and 1990, peaking at 42 and 147 kg per ha in 1984 respectively, and afterward declined (Figure 6.1 (2)).

6.3 UK atmospheric emissions (1970-2010)

SO_2 emissions fell continuously from 6.42 million tonnes in 1970 to 0.406 by 2010 (Figure 6.1 (3)). NOx emissions fluctuated ~2600 thousand tonnes from 1970, but increased in the late 1980s, peaking at 2889 in 1989, after which they fell to their lowest values reaching 1105 in 2010 (Figure 6.1 (3)).

Results for $\mathrm{WNB_{core}}$ and $\mathrm{WSB_{core}}$ are described in McGowan *et al.*, (2012) and are shown in Figure 6.2 and Figure 6.3. Other results are presented in order of descending site altitude.

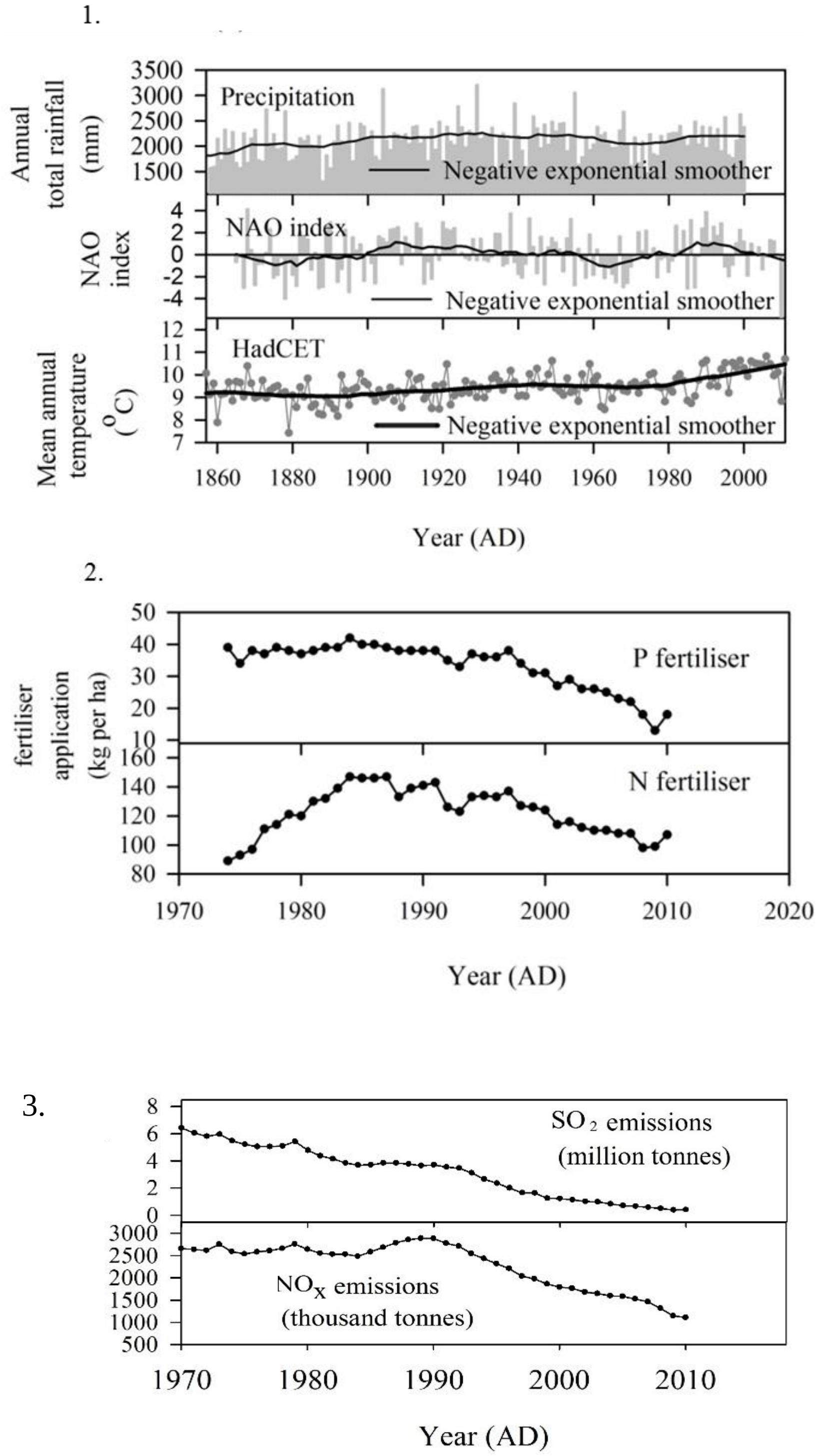


Figure 6.1 Changes in regional climate (1) and nutrient trends (2) in the U.K. (1) Central Lake District precipitation data supplied by Barker *et al*., (2004) with negative exponential smoother (black line); NAO index; CET data sourced from Crown copyright data supplied by the Met Office (Parker *et al.*, 1992) with negative exponential smoother (black line). (2) N and P fertiliser application are Crown copyright data supplied by DEFRA. (3) SO_2 and NO_x emissions (thousand tonnes) are Crown copyright data National Atmospheric Emissions Inventory supplied by DEFRA.

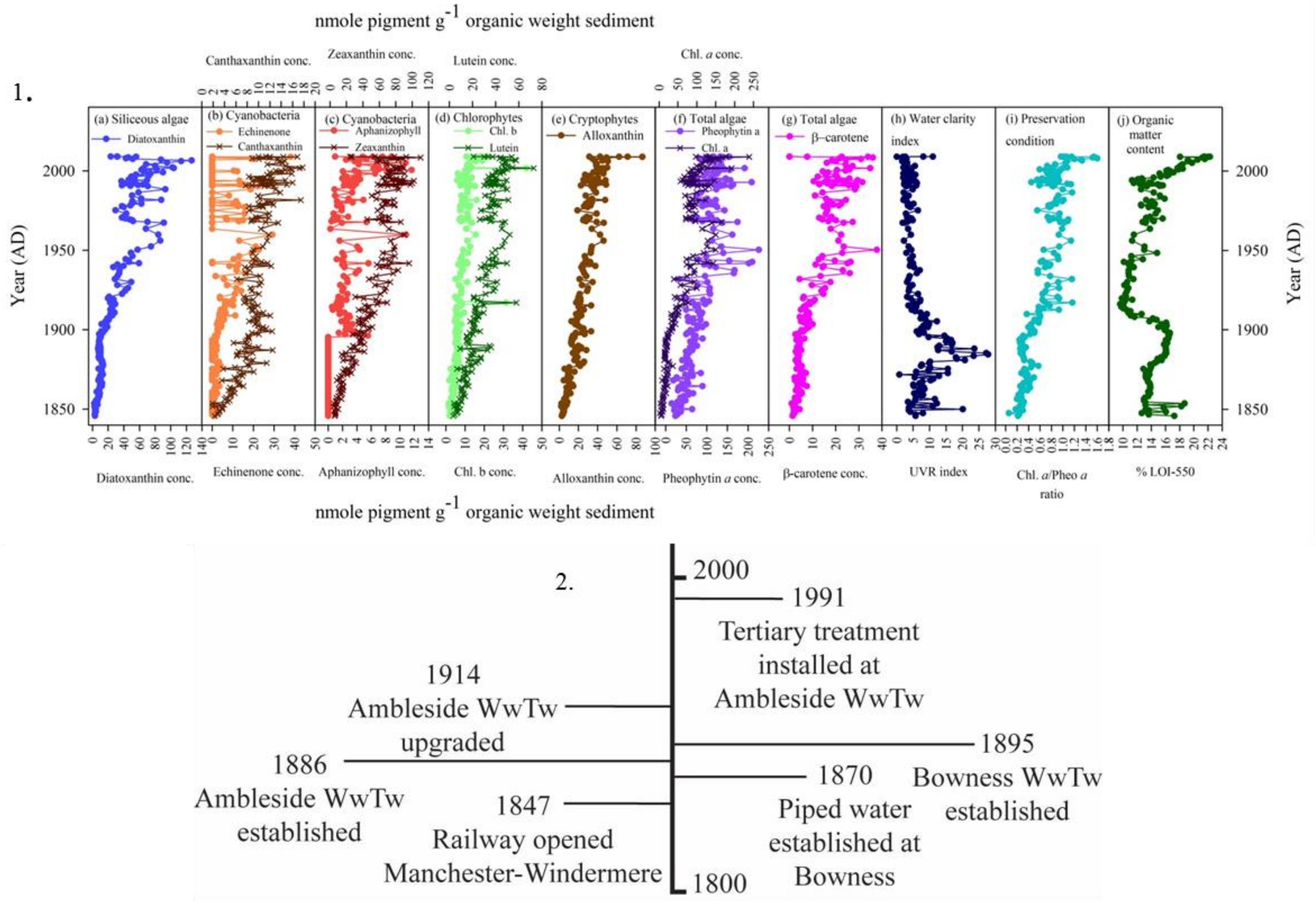


Figure 6.2 Changes in sedimentary chlorophylls and carotenoids from WNB$_{site}$ (1a-g), water clarity (1h), pigment preservation condition (1i) organic matter content (1j) from 1845 onwards (oldest date of core). Timeline of potential anthropogenic drivers of lake ecosystem in the WNB$_{site}$ catchment from 1845 onwards (2), after McGowan *et al*., (2012).

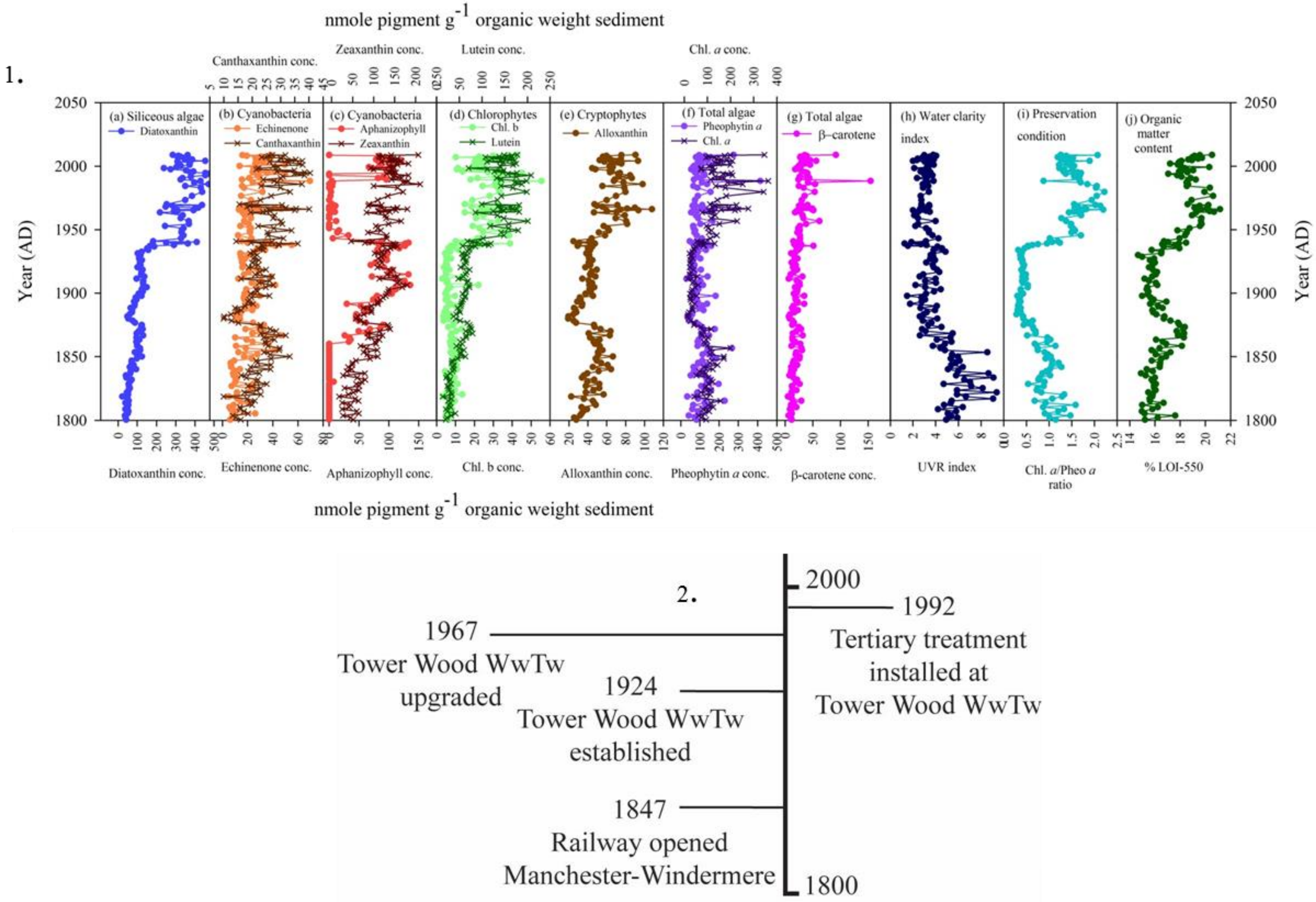


Figure 6.3 Changes in sedimentary chlorophylls and carotenoids from WSB_{site} (1a-g), water clarity (1h), pigment preservation condition (1i) organic matter content (1j) from 1800 onwards. Timeline of potential anthropogenic drivers of lake ecosystem in the WSB_{site} catchment from 1800 onwards (2), after McGowan *et al*., (2012).

6.4 Stickle Tarn (STI$_{site}$). Upland (469 m.a.s.l.)

Figure 6.4 Stickle Tarn, July 2013 (Photo: author) and location in Windermere catchment (red circle).

6.4.1 Field core description (STI$_{core}$)

From the bottom of the 17cm Glew core until 14.5cm, the sediment was light brown and clay-rich. The rest of the core consisted of a homogenous, dark brown, macrofossil rich sediment.

6.4.2 Sediment chronology

Total and supported ^{210}Pb reached equilibrium at 12.5cm (Figure 6.5 (1)). The deviation from an exponential decline in ^{210}Pb activity from 4.5cm to 6cm permitted the use of the CRS model to develop the core chronology. ^{137}Cs activity was greatest at 2.25cm, whereas ^{241}Am was detected from 2.25cm to 5.25cm (Figure 6.5 (2)). This indicated the 1986 ^{137}Cs fallout from Chernobyl blended with the 1963 record. The CRS age-depth model placed 1986 at 2.5cm and 1963 at 5cm, which was in agreement with the artificial radionuclide activities (Figure 6.5 (2-3)). Prior to the 1950s, dry bulk sediment accumulation rates (SARs) were stable at 0.014 g cm^{-2} yr^{-1}. By 1971 they had increased to a maximum of 0.0313 g cm^{-2} yr^{-1}, and fluctuated thereafter around ~0.02 g cm^{-2} yr^{-1} (Figure 6.5 (3)).

6.4.3 Sediment lithology

STI_{core} had the lowest mean OM content of all the upland lakes and second lowest mean carbonate content in the Windermere catchment reflecting the oligotrophic nature and volcanic rocky catchment of STI_{site} (Table 6.1). Water content (78-82%) and sediment density (0.17 to 0.25 g cm^{-3}) were quite stable between 1800 and 2011 (Figure 6.6 (1a/e)). OM declined from 33% in 1800 to 22% in 1970 when it then increased to 27% by 2011 (Figure 6.6 (1b)). Carbonate content was negligible throughout the core (Figure 6.6 (1c)). Minerogenic content increased most from 1910 and values stabilised ~76% from the 1950s to 1990s (Figure 6.6 (1d)).

6.4.4 Sediment C and N mass and stable isotopes

C and N relative mass and stable isotope values were relatively low in comparison to other sites in the Windermere catchment, with the second lowest mean $\delta^{15}N_{org}$ values after EAS_{core} (Table 6.1). %N increased from the 1870s to 1920 when it reached 0.79%, before declining until 1950, after which values increased (Figure 6.6 (2a)). %C also decreased from 1800 to ~1870, and increased to 15.6% in 1920 after which values stabilised ~10-11% from 1950 onwards (Figure 6.6 (2b)). C/N ratio values decreased from 23 in 1800 to 16 in 2006, suggesting increased autochthonous/algal matter in the sediments (Figure 6.6 (2c)). The $\delta^{15}N_{org}$ value decreased from 2.25‰ in 1970 to 0.8‰ by 1986 where values stabilised (Figure 6.6 (2d)). $\delta^{13}C_{org}$ values fluctuated between -27‰ and -28‰ (Figure 6.6 (2e)).

6.4.5 Sedimentary pigments

STI_{core} had low concentrations of all sedimentary pigments similar to other oligotrophic upland tarns in the catchment (Figure 6.6 (3)). Chl. *a* and its degradation product pheophytin *a* increased from 1800 onwards to a distinct maximum in the late 1970s (Figure 6.6 (3f)). Concentrations of β-carotene were low and undetectable in all but one sample, and so STI_{core} has the lowest mean total algal (β-carotene) concentration in the Windermere catchment (Figure 6.6 (3g); Table 6.1). Cyanobacteria (zeaxanthin), siliceous algae (diatoxanthin) and cryptophyte (alloxanthin) pigments and PCA axis 1 scores (37% variance explained) each increased from 1850 to the early 1900s after which they decreased (Figure 6.6 (3a/c/e)). Other pigments from cyanobacteria (echinenone, canthaxanthin, aphanizophyll) increased after 1900 (Figure 6.6 (3b/c)).

6.4.6 Historical records

The building of a dam at STI$_{site}$'s outflow in 1838, which increased the water level of the tarn, corresponded to a small peak in OM content of ~28 to 29%, but did not relate to any notable changes in the sedimentary pigments (Figure 6.6 (1-4)). Similarly, re-building the dam in 1959, which lowered the water level to its original state had little effect on the sedimentary record. Acidification documented in upland tarns elsewhere in the Lake District began during the Industrial Revolution (c.1850) and continued until the late 20th century, and there are increased concentrations of carotenoids within this period (Haworth *et al.*, 1987) (Figure 6.6 (3-4)). Human population and the area used for rough grazing increased in STI$_{site}$'s parish from 1900 onwards, although this would have been on the valley bottom so would not have impacted the tarn itself (Figure 6.7).

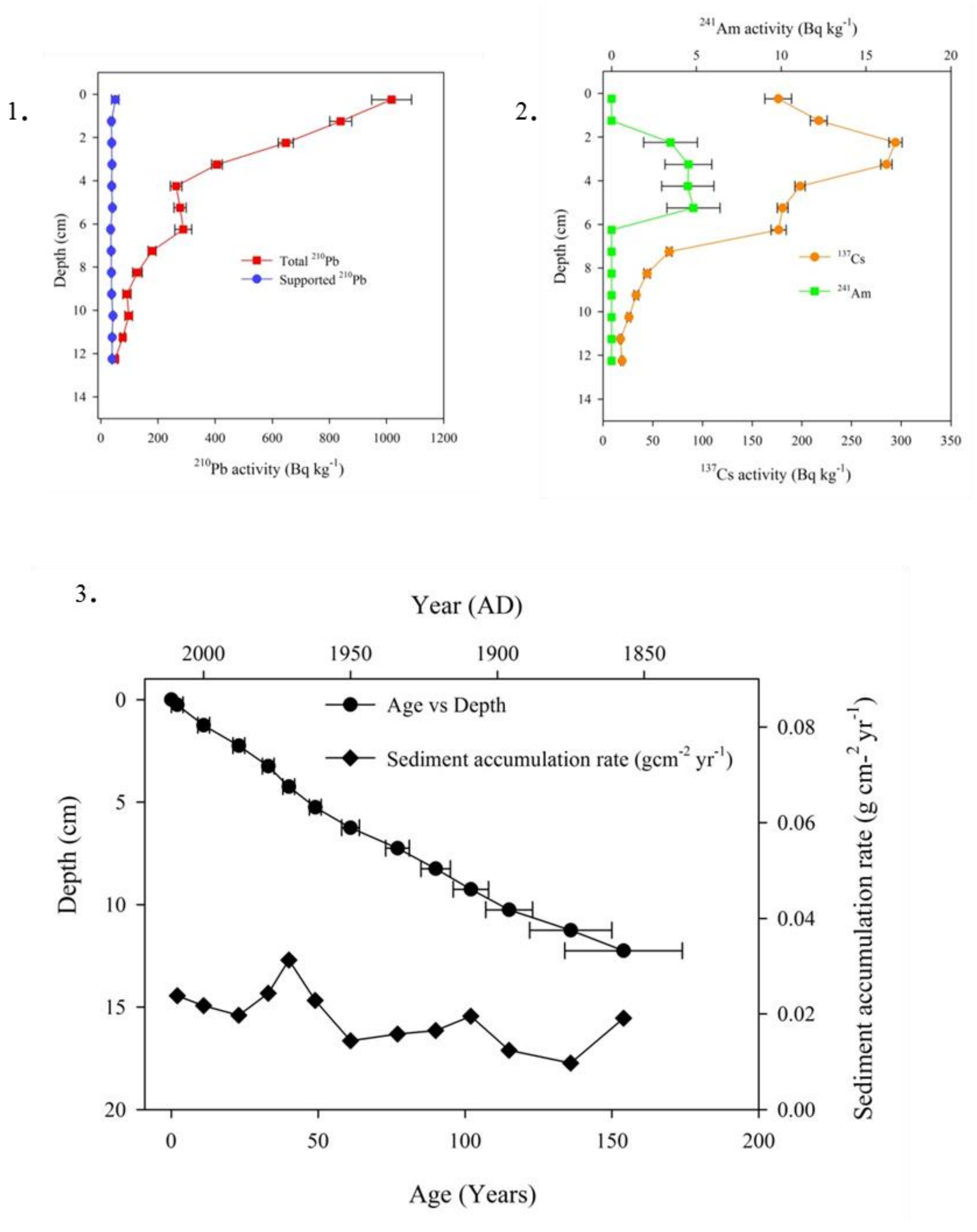


Figure 6.5 Changes in total and supported ^{210}Pb (1), ^{137}Cs and ^{241}Am activity (2), and CRS age-depth model and sediment accumulation rates for STI$_{core}$ (3).

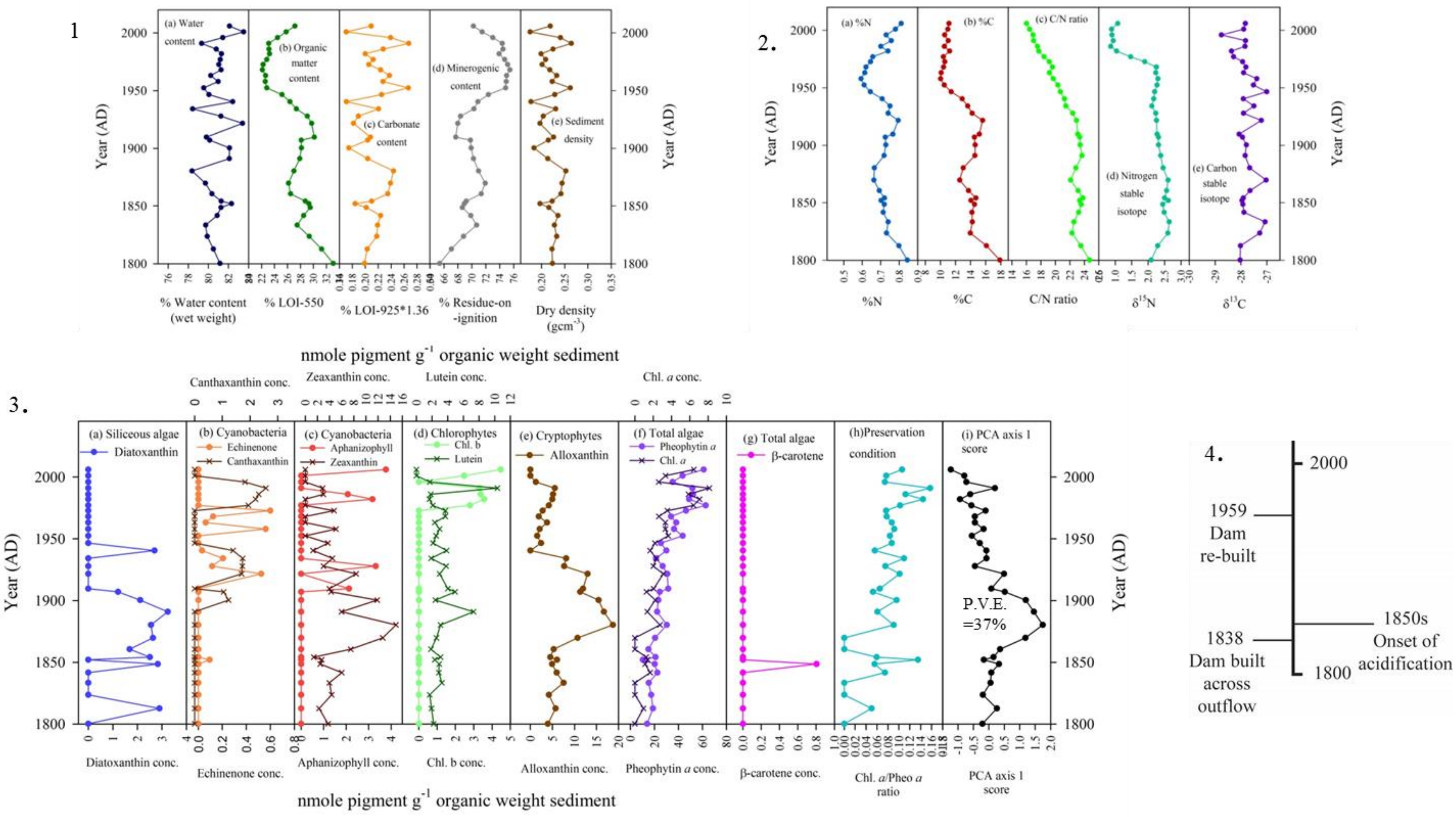


Figure 6.6 Changes in $\mathrm{STI}_{\mathrm{core}}$ sediment lithology (1a-e), bulk organic C and N and their isotopes (2a-e), sedimentary chlorophylls and carotenoids (3a-g), pigment preservation condition (3h) and the PCA axis 1 scores (3i) from 1800 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the $\mathrm{STI}_{\mathrm{site}}$ catchment from 1800 onwards (4).

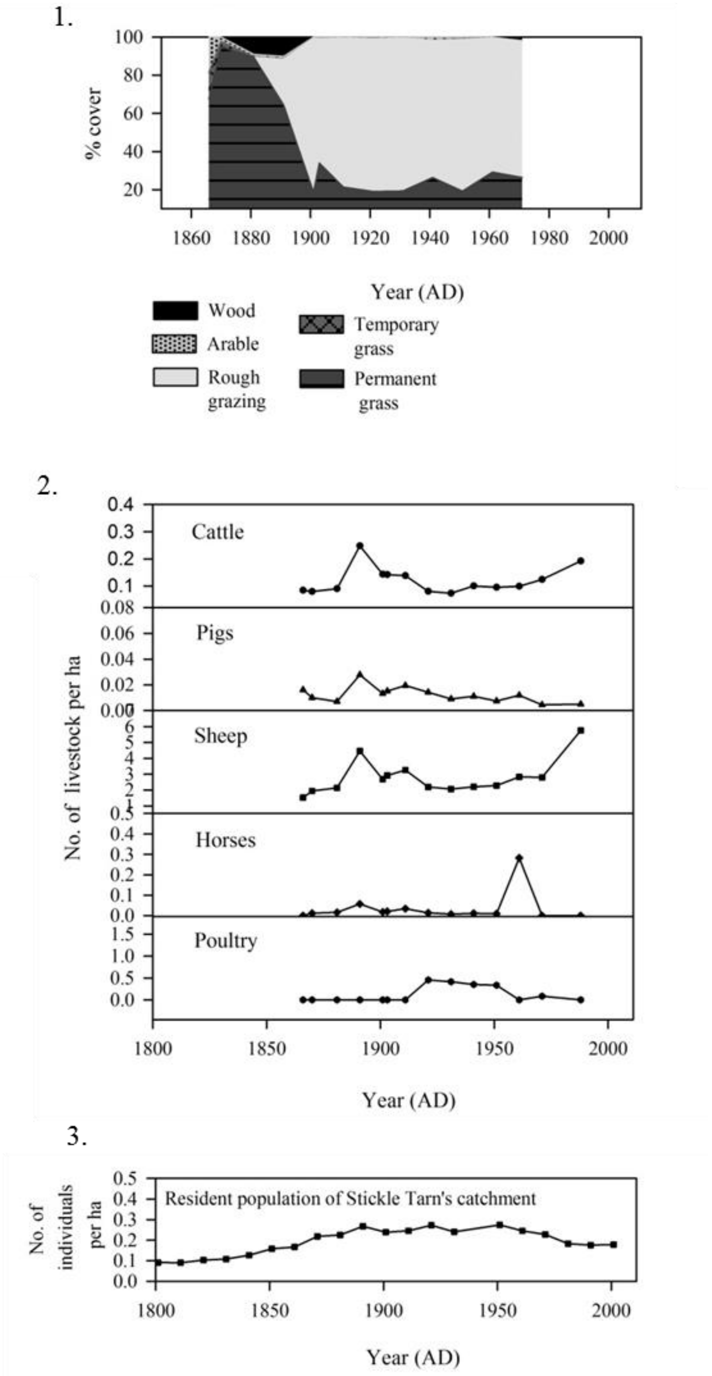


Figure 6.7 Changes in STI_{site} catchment land use (1), and livestock densities (2), both sourced from MAFF. Changes in the resident human population in the STI_{site} catchment (3) Crown copyright and reproduced with the permission of the Controller of HMSO and the Queen’s Printer for Scotland (Source: 1971 Census; Small Area Statistics). All data sources explained in Chapter 4.

6.5 Codale Tarn (CT_{site}). Upland (467 m.a.s.l.)

Figure 6.8 Codale Tarn, March 2013 (Photo: author), and location in Windermere catchment (red circle).

6.5.1 Field core description (CT_{core})

The 25.2cm Glew sediment core was sectioned at 0.6cm in the field due to a malfunction of the extruder (Figure 6.8). From the bottom of the core until 10cm depth the sediment was dark brown, with a fine grain size and consolidated organic-rich consistency, with higher water content and macrofossil-rich sediment in the uppermost 3cm.

6.5.2 Sediment chronology

Peak total ^{210}Pb activity peak occurred at 1.8cm depth and because there was a slight deviation from an exponential decline; the CRS age-depth model was used to develop the chronology (Figure 6.9 (1)). There were two peaks in ^{137}Cs activity at 1.5cm and 2.5cm corresponding to the two fallout episodes of 1986 and 1963 respectively (Figure 6.9 (2)). The CRS age-depth model was in good agreement with the ^{137}Cs activity although 1986 was at a slightly deeper depth in the CRS model (1.5-1.75cm) (Figure 6.9 (3)). CT_{core} had the lowest mean SAR of all the upland lakes in the Windermere catchment (Table 6.1). SARs ranged from 0.001-0.005 g cm^{-2} yr^{-1}, but increased from 1996 to 0.04 g cm^{-2} yr^{-1} by 2005 (Figure 6.9 (3)).

6.5.3 Sediment lithology

Mean OM values were the highest in the Windermere catchment, with values ~44% from 1845 onwards (Table 6.1, Figure 6.10 (1b)). Between the 1940s and 1970s, sediment water, OM and carbonate content decreased, and minerogenic and sediment density values increased (Figure 6.10 (1)). Conversely from the 1970s, sediment water, OM, and carbonate content values increased whereas minerogenic content and sediment density decreased.

6.5.4 Sedimentary pigments

Mean total algal (β-carotene) concentrations were the highest in CT_{core} compared to other oligotrophic upland lakes in the Windermere catchment (Table 6.1). Notable increases in carotenoid (diatoxanthin, canthaxanthin, zeaxanthin and alloxanthin) concentrations occurred ~1870 and ~1920 (Figure 6.10 (2a-c/e). However, most pigments increased mainly from 1970 onwards, and in particular from 1990 as summarised by the decline in PCA axis 1 scores (73% variance explained) (Figure 6.10 (2)). Preservation conditions began to increase after 1954 (Figure 6.9 (2h)).

6.5.5 Historical records

Like STI_{core} the increased carotenoids of CT_{core} correspond to timings of acidification throughout the Lake District from the late 19th and early 20th centuries (Haworth *et al.*, 1987) (Figure 6.10 (2-3)). The decrease in sediment water, OM and carbonate content and increase in minerogenic and sediment density values in the late 1960s, could suggest increased in-wash of catchment minerogenic matter which may relate to documented flooding in the Langdales at this time (Figure 6.10 (1)) (Watkins and Whyte, 2008). Increased rough grazing, livestock and residential populations occurred from 1870 onwards, although these changes would have occurred on the valley bottoms of CT_{site}'s catchment below the lake (Figure 6.11 (2-3)). Increased OM and sedimentary pigments from 1970 corresponded to increasing CET and precipitation values (Figure 6.10 (1-2); Figure 6.1 (1)).

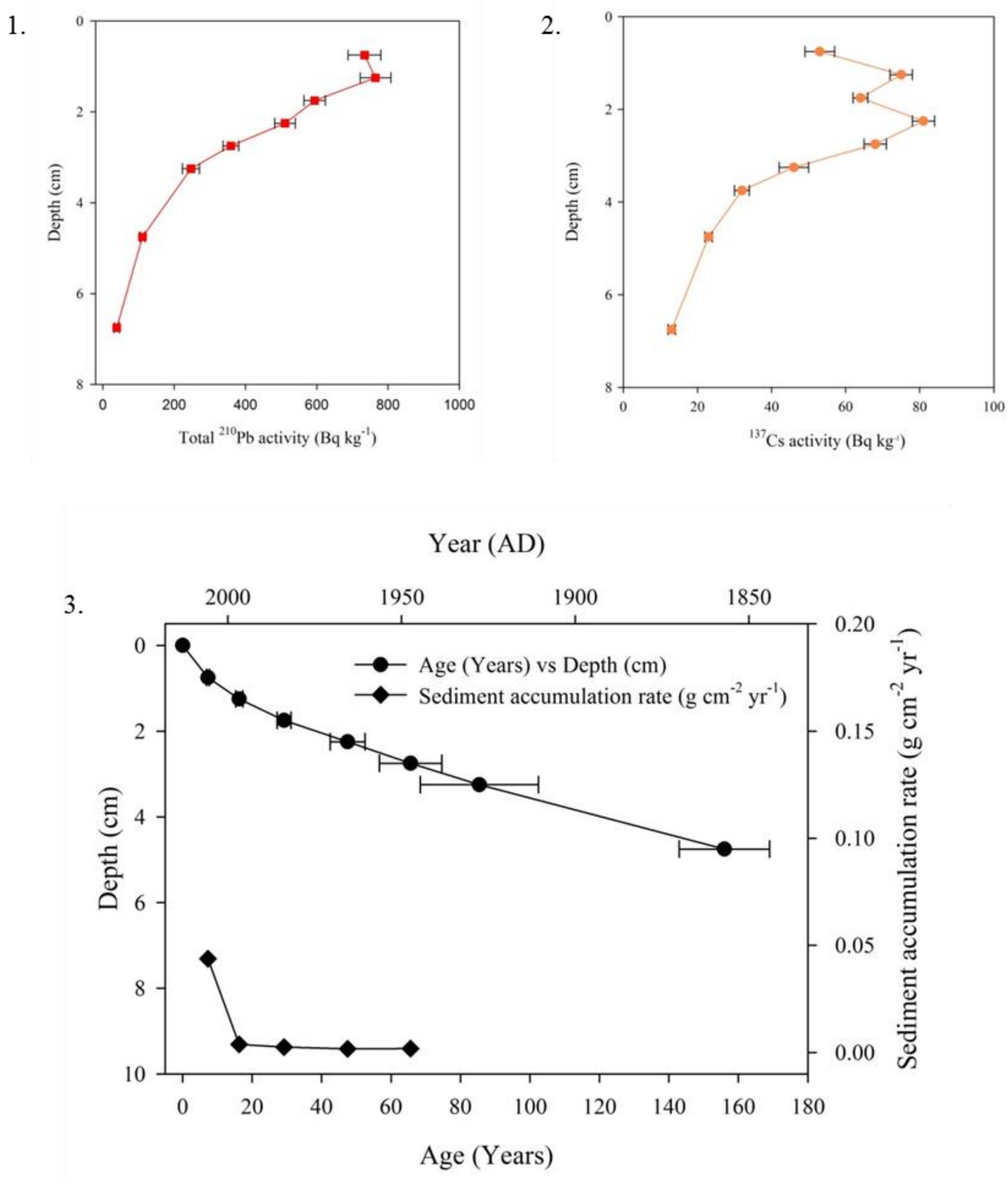


Figure 6.9 Changes in total ^{210}Pb (1), ^{137}Cs activity (2), and CRS age-depth model and sediment accumulation rates for CT$_{core}$ (3).

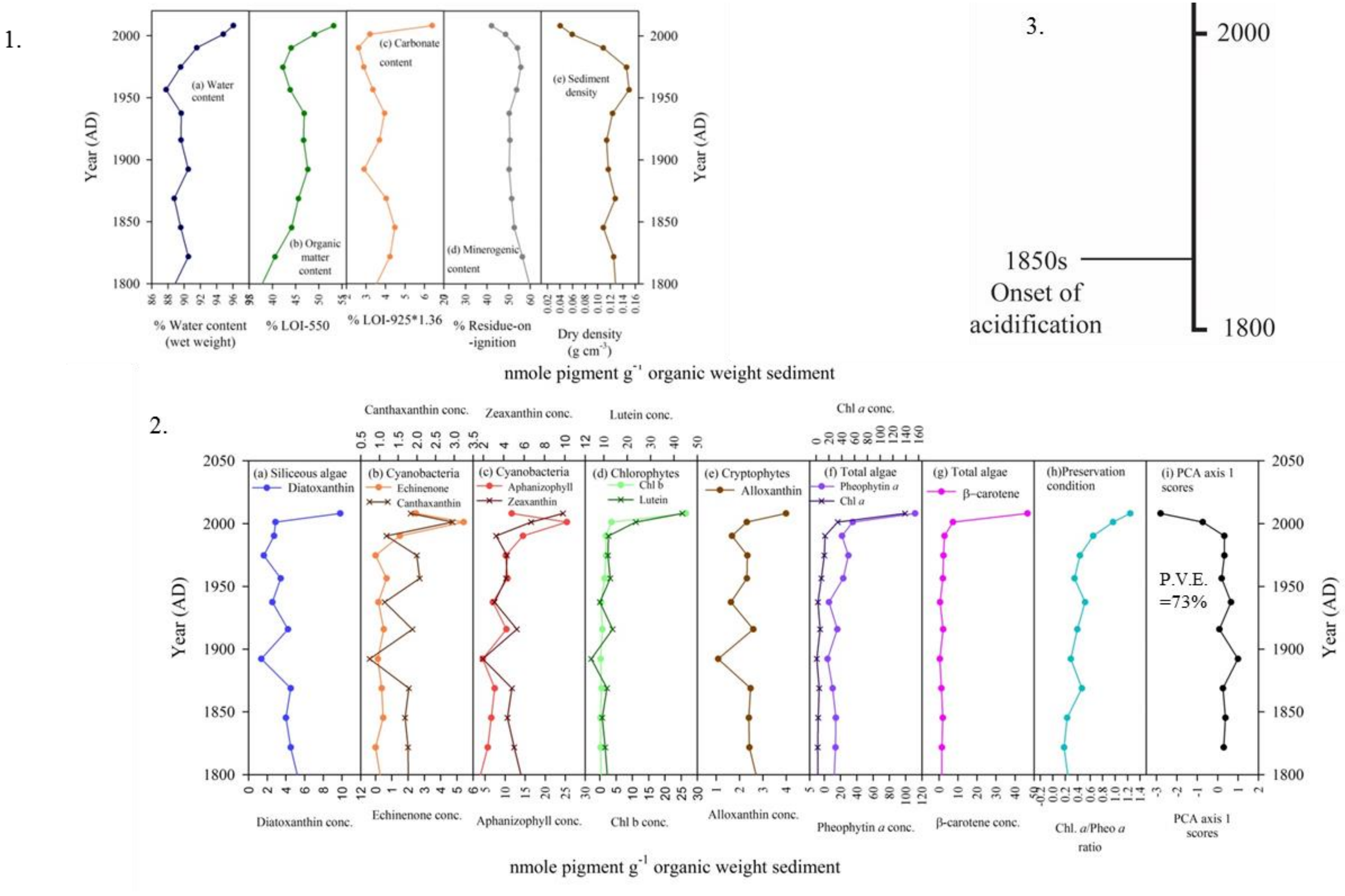


Figure 6.10 Changes in CT_{core} sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), pigment preservation condition (2h) and the PCA axis 1 scores (2i) from 1800 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the CT_{site} catchment from 1800 onwards (3).

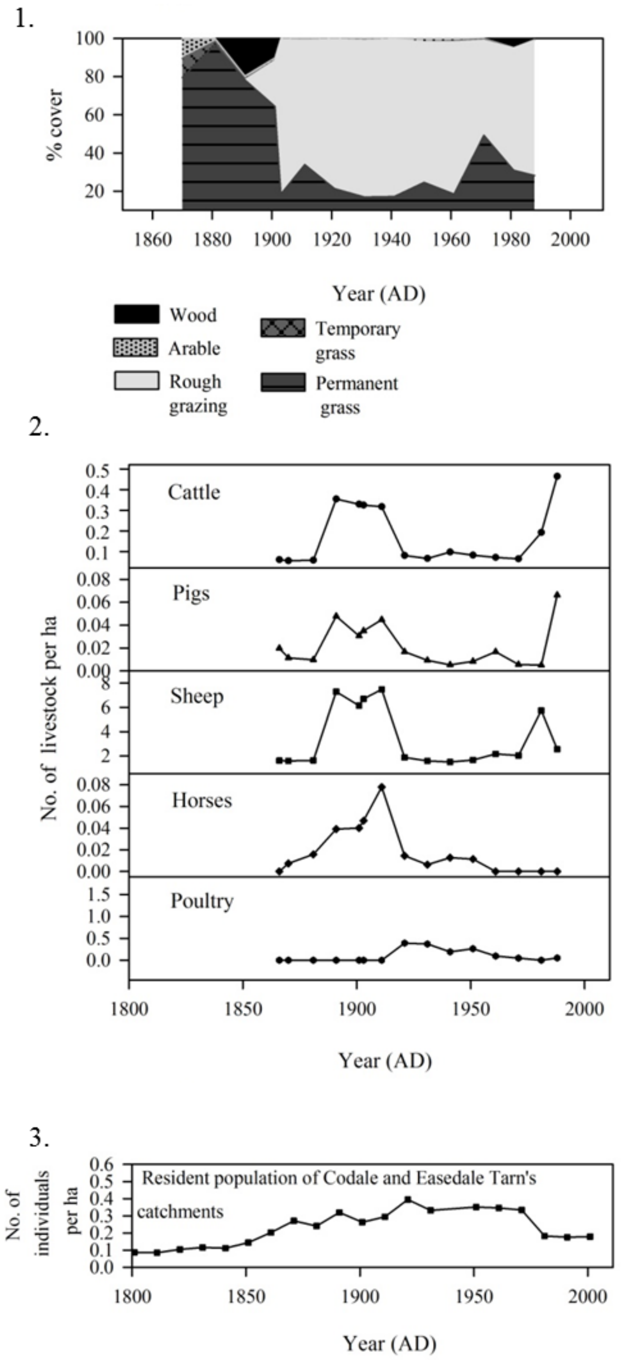


Figure 6.11 Changes in $\mathrm{CT_{site}}$ and $\mathrm{EAS_{site}}$ catchment land use (1) livestock densities (2) and resident human population (3).

6.6 Easedale Tarn (EAS_{site}). Upland (279 m.a.s.l.)

Figure 6.12 Easedale Tarn to the right, Codale Tarn to the left, July 2013 (Photo: author), and location in Windermere catchment (red circle).

6.6.1 Field core description

The 27.5cm Glew core de-watered itself prior to extrusion in the field, which could have been caused by a change in temperature, pressure or humidity on the structured water envelope of the sediment (Burst, 1976). From the bottom to 13cm the sediment was a reddish-brown gytjja[3]. Above 13cm there was dark brown, organic mud with abundant macrofossils, and the top 8cm consisted of light brown gyttja.

6.6.2 Sediment chronology

Total ^{210}Pb and supported ^{210}Pb reached equilibrium at 13cm depth (Figure 6.13 (1)). The total ^{210}Pb maximum at 2.5cm indicated increased sedimentation in recent years and there was a slight deviation from an exponential decline in lower core depths. Thus, the CRS model was chosen to develop the chronology. The ^{137}Cs peak at 3.25cm was assigned to the Chernobyl fallout in 1986, which may have masked the activity peak of 1963 (Figure 6.13 (2)). Peak ^{241}Am activity between 4.25cm and 5.25cm was attributed to the 1963 fallout (Figure 6.13 (2)). The CRS age-depth model places 1986 and 1963 between the depths 2.25-3.25cm and 4.25-5.25cm, which was in agreement

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[3] Gyttja in this thesis refers to organic-rich sediment with a mousse-like consistency.

with the ^{137}Cs and ^{241}Am activity (Figure 6.13 (3)). Mean SAR was lower than STI$_{core}$ but higher than CT$_{core}$ (Table 6.1). SARs increased steadily to 0.0203 g cm^{-2} yr^{-1} by 1964, before declining and increasing again post-1990 reaching 0.0376 g cm^{-2} yr^{-1} by 2009 (Figure 6.13 (3)).

6.6.3 Sediment lithology

EAS$_{core}$ had the lowest mean carbonate content in the Windermere catchment, and like the other upland lakes had a relatively high mean OM content compared to the lowlands (Table 6.1). Lithological proxies show reversal of their trends from 1920 onwards, whereby water and OM content decreased following a peak in values at 87% and 36% respectively (Figure 6.14 (1a-b)). The opposite occurred post-1920 in the carbonate, minerogenic and sediment density values which were lowest in 1920 (0.11%, 59% and 0.13 g cm^{-3} correspondingly) and increased after this date (Figure 6.14 (1c-d)).

6.6.4 Sediment C and N mass and stable isotopes

Mean $\delta^{15}N_{org}$ was the lowest in the catchment, whereas the mean C/N ratio was higher compared to the other upland STI$_{core}$ (Table 6.1). %N and %C values increased from 1800 to 1930 and decreased thereafter (Figure 6.14 (2a-b)). C/N ratios increased and peaked at values of 19 in the late 1890s after which they decreased to ~15 from 1980 onwards (Figure 6.14 (2c)). The $\delta^{15}N_{org}$ decreased after 1940 from values ~2‰ reaching 0.8‰ by 2006 (Figure 6.14 (2d)). The $\delta^{13}C_{org}$ also decreased from values -27.2‰ in ~1940 to -28.4‰ by 2006 (Figure 6.14 (2e)).

6.6.5 Sedimentary pigments

Mean total algal (β-carotene) concentrations were the second lowest in the Windermere catchment, with low concentrations of all sedimentary pigments throughout EAS$_{core}$ (Table 6.1). All algal groups and PCA axis 1 scores declined between 1800 to ~1880 and afterwards chlorophytes (Chl. b, lutein), diatoms (diatoxanthin), cyanobacteria (canthaxanthin, zeaxanthin) and total algae (Chl. *a*, pheophytin *a*) increased until ~1980, when they decreased again

(Figure 6.14 (3)). Elevated concentrations of filamentous cyanobacteria (aphanizophyll) were found from 1925 to 1960 (Figure 6.14 (3c)).

6.6.6 Historical records

Increased sedimentary carotenoids corresponded to acidification documented in other Lake District upland lakes from the mid-19th to late 20th century (Haworth *et al.*, 1987) (Figure 6.14 (3-4)). Increased rough grazing, livestock and residential populations occurred from 1870 onwards, although these changes would have occurred on the valley bottoms of EAS_{site}’s catchment (Figure 6.11). Increased minerogenic matter, SARs and decreased sedimentary pigments from ~1980 correspond to increasing CET and precipitation values, which could indicate climate-driven in wash of allocthonous minerogenic matter (Figure 6.13 (3); Figure 6.14 (1-2); Figure 6.1).

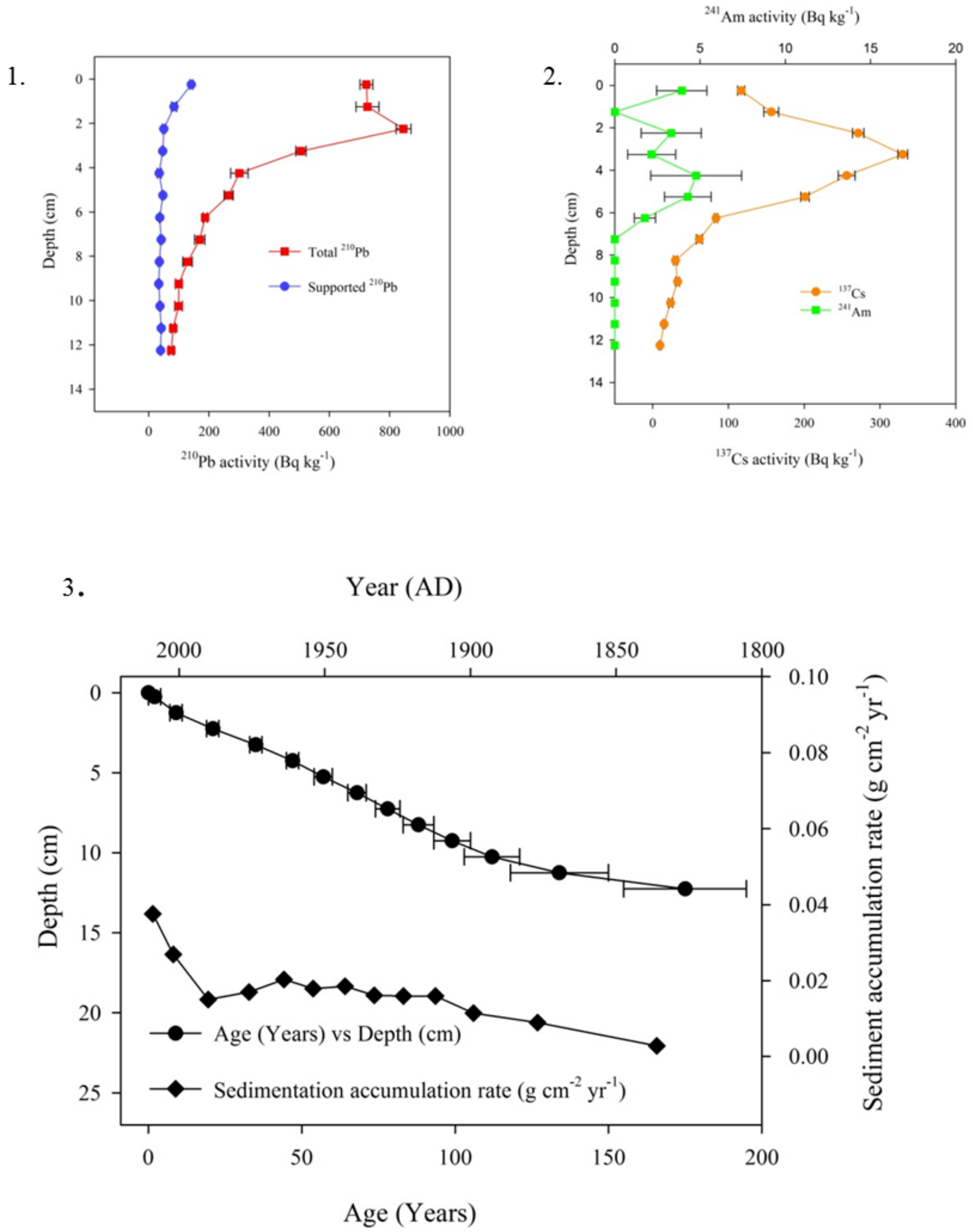


Figure 6.13 Changes in total and supported ^{210}Pb (1), ^{137}Cs and ^{241}Am activity (2), and CRS age-depth model and sediment accumulation rates for EAS$_{core}$ (3).

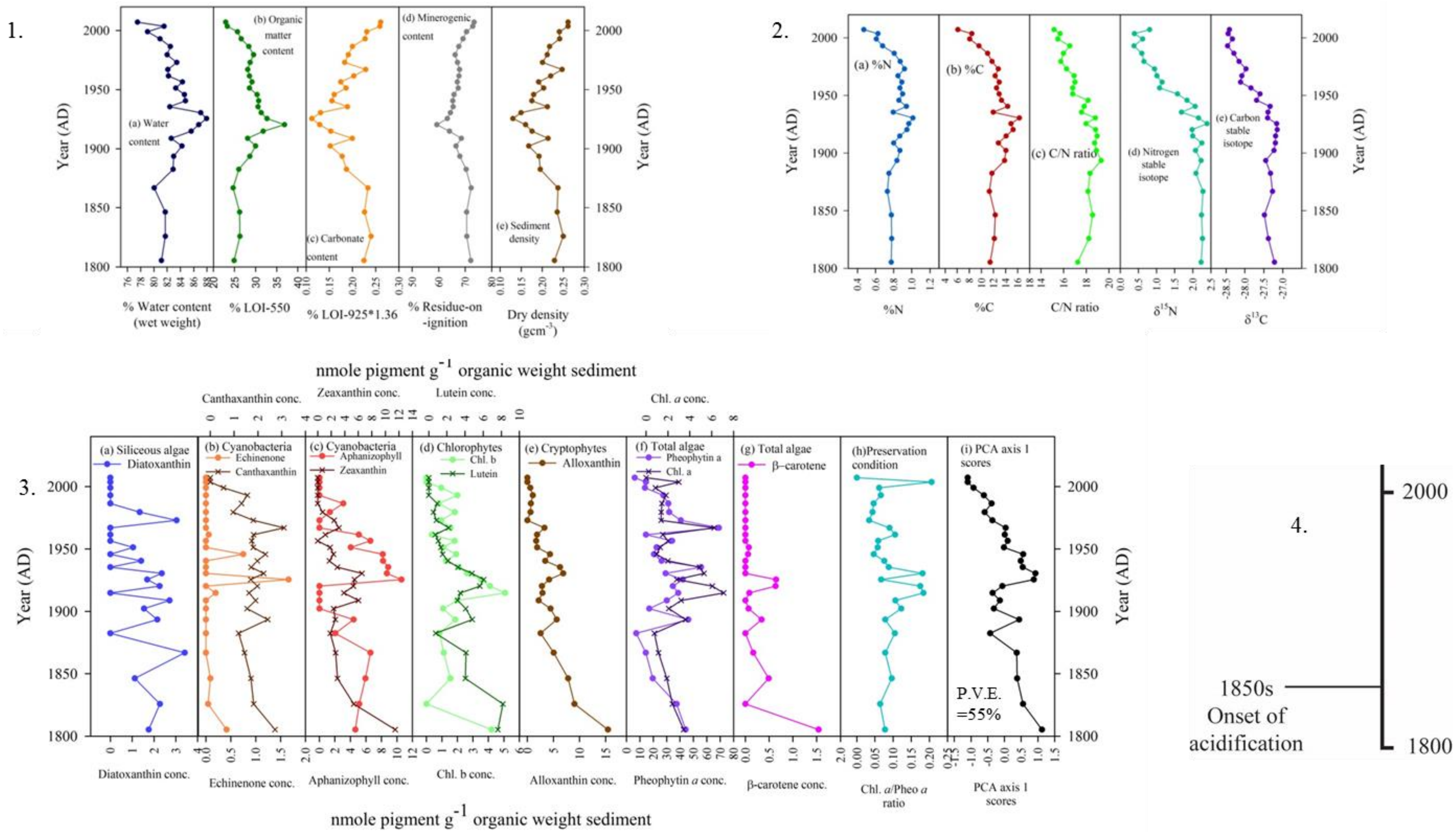


Figure 6.14 Changes in EAS$_{core}$ sediment lithology (1a-e), bulk organic C and N and their isotopes (2a-e), sedimentary chlorophylls and carotenoids (3a-g), pigment preservation condition (3h) and the PCA axis 1 scores (3i) from 1800 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the EAS$_{site}$ catchment from 1800 onwards (4).

6.7 Blea Tarn (BT$_{\text{site}}$). Upland (192 m.a.s.l.)

Figure 6.15 Blea Tarn, November 2012 (Photo: author), and location in Windermere catchment (red circle).

6.7.1 Field core description

The 43.5cm long HON-Kayak sediment core comprised organic and macrofossil-rich gyttja, which was dark brown and consolidated up to 20cm. The core was less consolidated from 20cm to 17cm and was very floccy with high water content above 17cm. This core was not dated.

6.7.2 Sediment lithology

Mean OM and carbonate content were the second highest in the Windermere catchment, although minerogenic material was predominant throughout BT$_{\text{core}}$ (Table 6.1; Figure 6.16). Water content fluctuated between 82-92% throughout but increased markedly in the uppermost 2cm (Figure 6.16 (1a)). OM increased from ~30% at the bottom of the core to ~40% at the top (Figure 6.16 (1b)). Sediment density ranged mostly between 0.10-0.20 g cm^{-3} throughout the core (Figure 6.16 (1e)).

6.7.3 Sedimentary pigments

Mean total algal (β-carotene) concentration was higher than STI$_{\text{core}}$, EAS$_{\text{core}}$ and CT$_{\text{core,}}$ but still relatively low considering the high OM content (Table 6.1). All sedimentary pigments were also relatively low throughout BT$_{\text{core}}$ that suggests the OM was mainly allocthonous in origin (Figure 6.16 (2)). The most notable change in BT_{core} was the early decrease in siliceous diatoxanthin at 35cm, followed by a later increase in other sedimentary pigments (Figure 6.16 (2)). The pigments from cyanobacterial (canthaxanthin, aphanizophyll, zeaxanthin), chlorophyte (Chl. *b*, lutein), cryptophyte (alloxanthin) taxa, and total algae (Chl. *a*, pheophytin *a*, β-carotene) and preservation condition increased mainly above 9.5cm to the top of the core, as reflected in the increasing PCA axis 1 scores (60% variance explained) (Figure 6.16 (2)). In contrast, the cyanobacterial pigment echinenone decreased ~4cm onwards (Figure 6.16 (2b)).

6.7.4 Historical records

Increased carotenoids from the bottom of the core to ~35cm could relate to acidification documented elsewhere in the Lake District beginning c.1850 (Figure 6.16 (2-3)) (Haworth *et al.*, 1987). Alternatively, the increased carotenoids could have been a result of deforestation in the catchment in 1940, which would have increased erosion, as suggested by the high % minerogenic content from the bottom of the core up to 35cm (ranging from 66-60%) (Figure 6.16 (1d/3)) (Hürrig, 1999). The deforestation could have led to increased nutrient delivery from the catchment to the lake and stimulated algal production, causing the increase in OM from the bottom of the core up to 35cm (28-34%) (Figure 6.16 (1b/2)) (Leavitt and Carpenter, 1989). Rough grazing was the dominant land cover which reached a maximum of 80% in 1931 and then declined to ~60% onwards, as permanent grass increased (Figure 6.17 (1)). Sheep stocking density grew steadily from the late 19th century onwards although this would have been from the two farms found lower down the catchment closer to LLT_{site} (Figure 6.17 (2)) (Haworth, 1969).

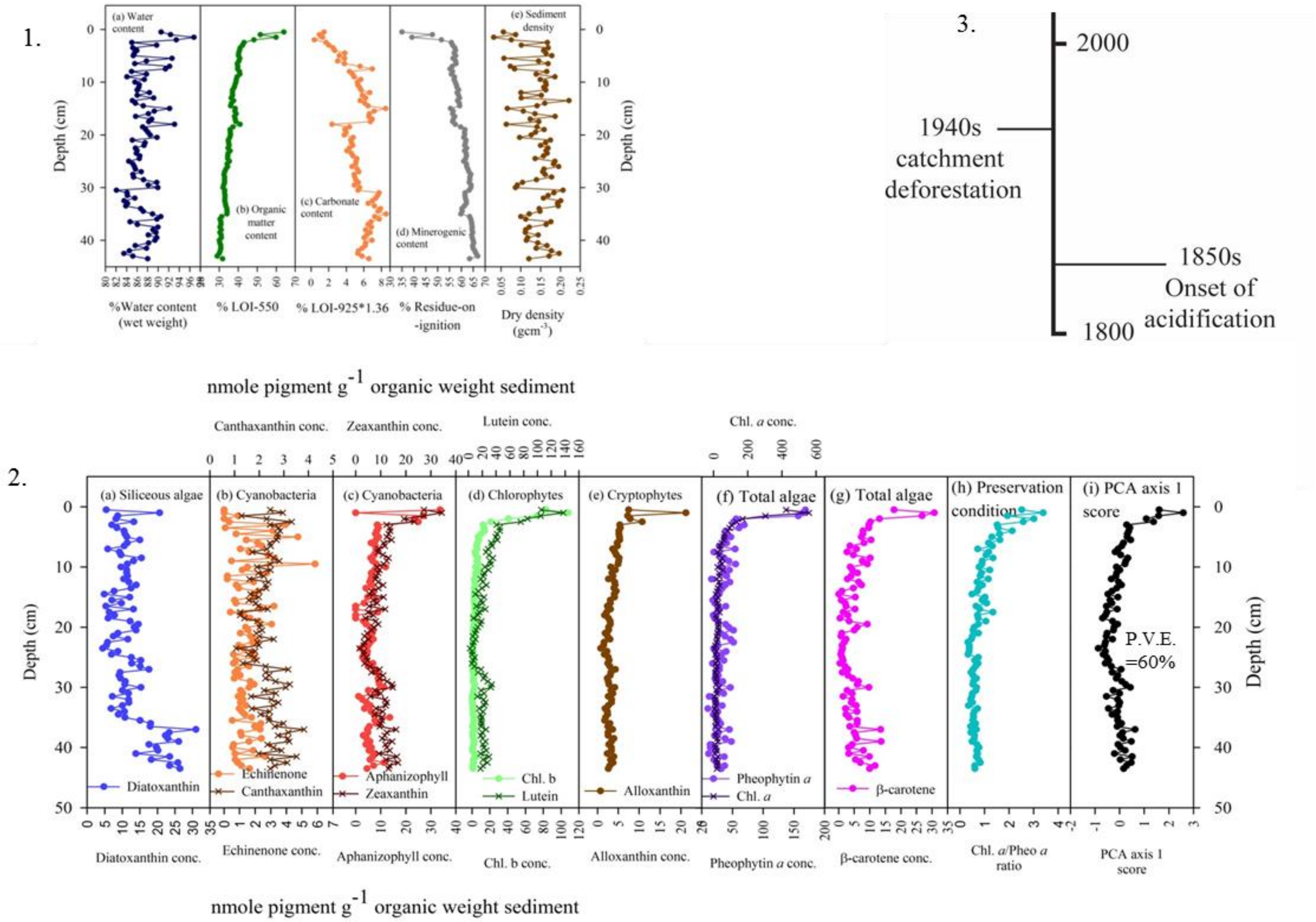


Figure 6.16 Changes in BT_{core} sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), pigment preservation condition (2h) and the PCA axis 1 scores (2i) for full core length (cm). Timeline of potential anthropogenic drivers of lake ecosystem change in the BT_{site} catchment from 1800 onwards (3).

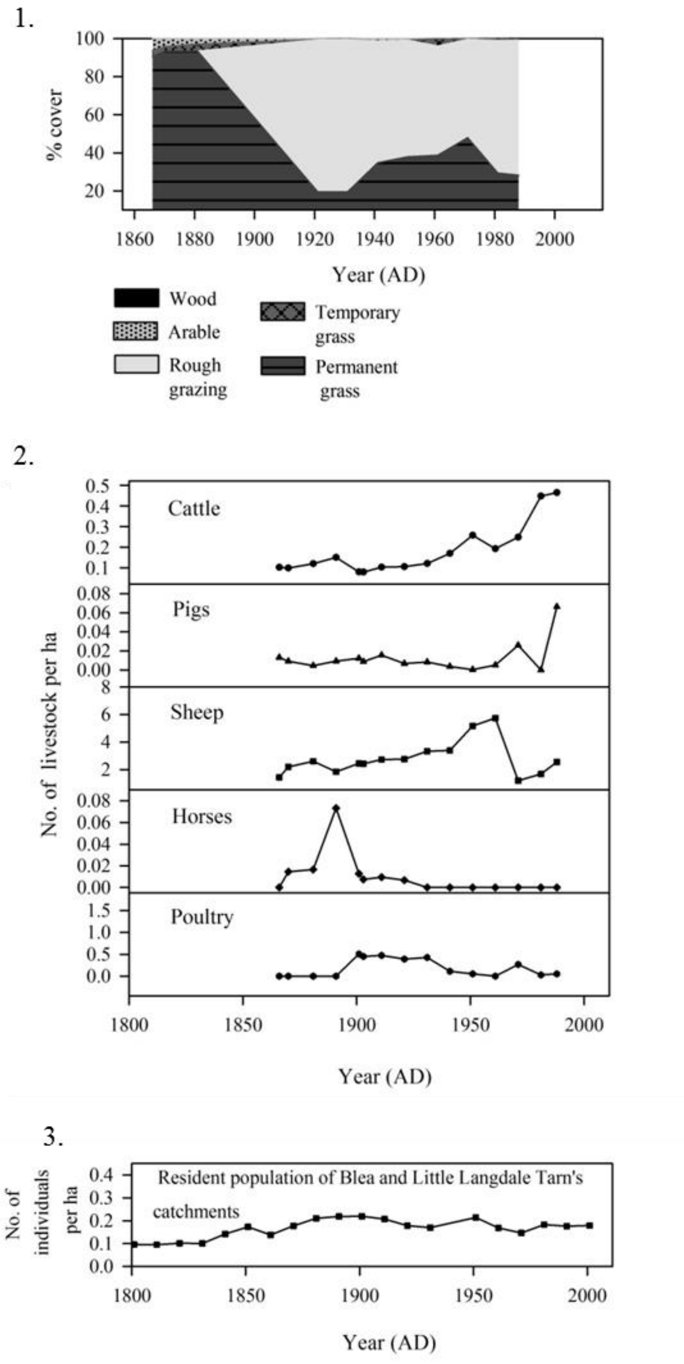


Figure 6.17 Changes in BT_{site} and LLT_{site} catchment land use (1), livestock densities (2) and resident human population (3).

6.8 Little Langdale Tarn (LLT$_{site}$). Upland (102 m.a.s.l.)

Figure 6.18 Little Langdale Tarn, July 2013 (Photo: author), and location in Windermere catchment (red circle).

6.8.1 Field core description

The 27.5cm long HON-Kajak core was composed of grey clay and organic-rich sediment below 25cm. Above 20cm the sediment was rich in macrofossils and was a fine, dark brown, organic-rich material. This core was not dated so no chronology exists for the sequence.

6.8.2 Sediment lithology

Mean OM content and mean carbonate content were both higher than STI$_{core}$ and EAS$_{core}$ but not as high as the other upland lakes in the Windermere catchment (Table 6.1; Figure 6.19 (1d)). Water content increased up the core from ~81 to 88%, whereas sediment density decreased from ~0.2 to 0.1 g cm^{-3} (Figure 6.19 (1a/e)). OM content increased from the bottom to 14.5cm, and then it decreased before increasing to values ~35% to the top of the core (Figure 6.19 (1b)). Carbonate content values peaked at 4.7% at 14.5cm and stabilised ~3% to the top of the core (Figure 6.19 (1c)).

6.8.3 Sedimentary pigments

Mean total algal (β-carotene) concentration was the highest of all the upland lakes, but still lower than the productive lowlands in the Windermere catchment (Table 6.1). Elevated concentrations of diatoxanthin (diatom) and canthaxanthin (cyanobacteria) occurred at 21cm, and decreased from ~5cm and these patterns were particularly pronounced for diatoxanthin (Figure 6.19 (2a-b)). Alloxanthin (cryptophytes) increased from 10cm onwards, whereas zeaxanthin (cyanobacteria) increased slightly until 5cm before decreasing (Figure 6.19 (2c/e)). Peaks in lutein (chlorophytes), zeaxanthin (cyanobacteria), Chl. *a* and β-carotene (total algae) in the top 1cm corresponded to improvements in the preservation condition (Figure 6.19 (2c-d/f-h)). Zeaxanthin (cyanobacteria), lutein (chlorophytes) and β-carotene (total algae) maxima occurred at 14.5cm as reflected in the PCA axis 1 scores (48% variance explained) (Figure 6.19 (2c-d/g/i)).

6.8.4 Historical records

The straightening of the tarn's inflow and outflow in 1840 may correspond to the increased % minerogenic content from the bottom of the core up to 20cm (73-60%) (Figure 6.19 (1d/3)) (Oswald *et al.*, 2001). However, it may also relate to the later increased minerogenic input to the sediments of $\mathrm{LLT_{site}}$ recorded from c.1889-1907 associated with the Greenburn copper mine (active from ~1840 although potentially in operation from the 17th century) (Hürrig, 1999). Evidence from past palaeolimnological studies suggested atmospheric pollution led to a pH decline at $\mathrm{LLT_{site}}$ from 1900 onwards and increased the number of benthic diatoms (Hürrig, 1999). This could correspond to the increased carotenoid concentrations from 24 to 17cm, which would support the previous hypothesis that mining activity in the late 18th and early 20th centuries upstream of $\mathrm{LLT_{site}}$ enhanced erosion into the tarn (Figure 6.19 (2)). SARs in $\mathrm{LLT_{site}}$ have been documented as increasing since the mid-1900s and have been attributed to multiple sources including ploughing in the catchment up to the 1950s, the bursting of the Greenburn reservoir in 1979, dredging of the tarns inflow in 1983, and evidence of erosion from sheep stocking in the 1990s (Figure 6.19 (3)) (Hürrig, 1999; Oswald *et al.*, 2001). However, in the mid-1970s sheep numbers were reduced by more than half in one farm in the catchment (Figure 6.17 (2)) (Oswald *et al.*, 2001).

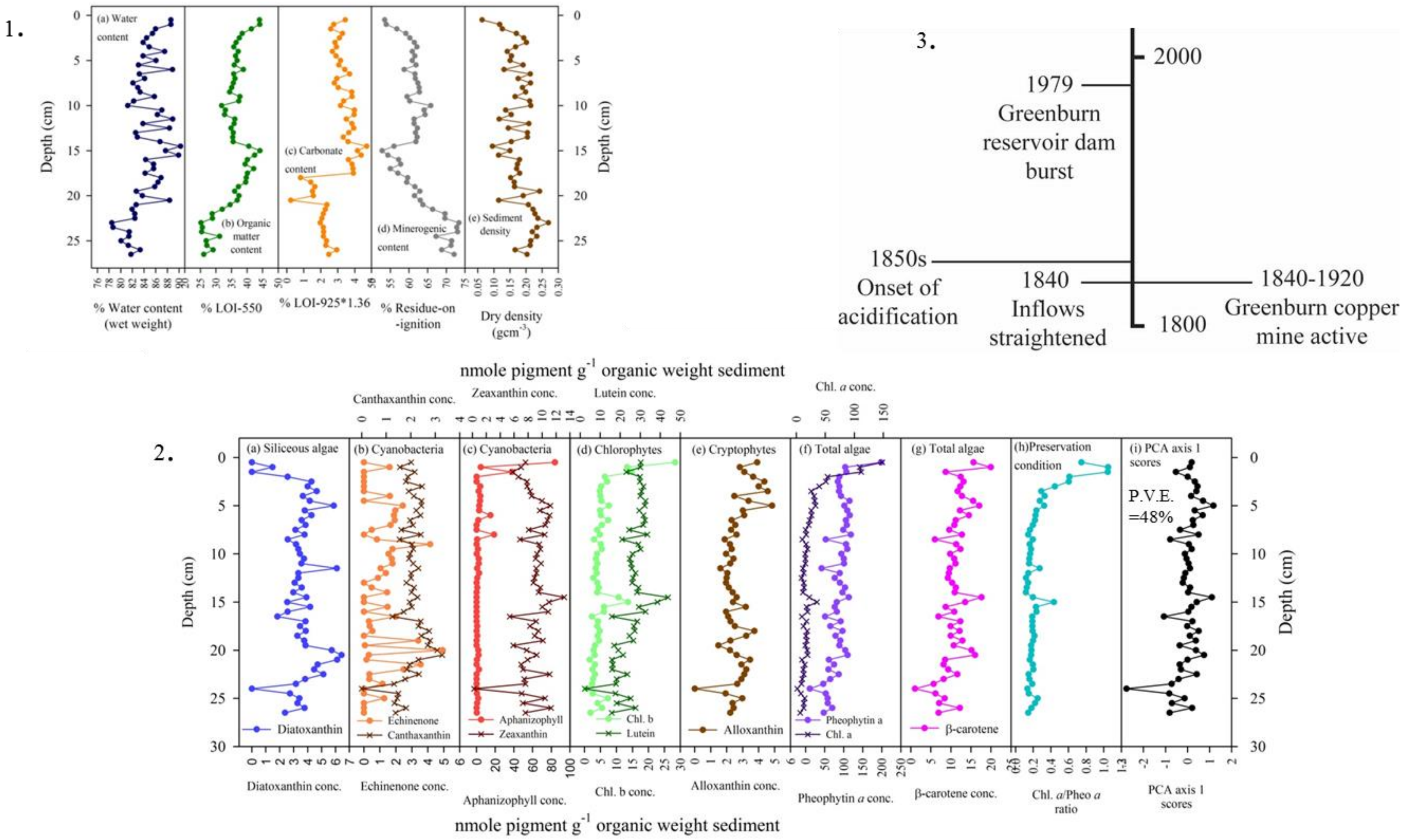


Figure 6.19 Changes in LLT$_{core}$ sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), pigment preservation condition (2h) and the PCA axis 1 scores (2i) for full core length (cm). Timeline of potential anthropogenic drivers of lake ecosystem change in the LLT$_{site}$ catchment from 1800 onwards (3).

6.9 Loughrigg Tarn (LOU$_{site}$). Lowland (94 m.a.s.l.)

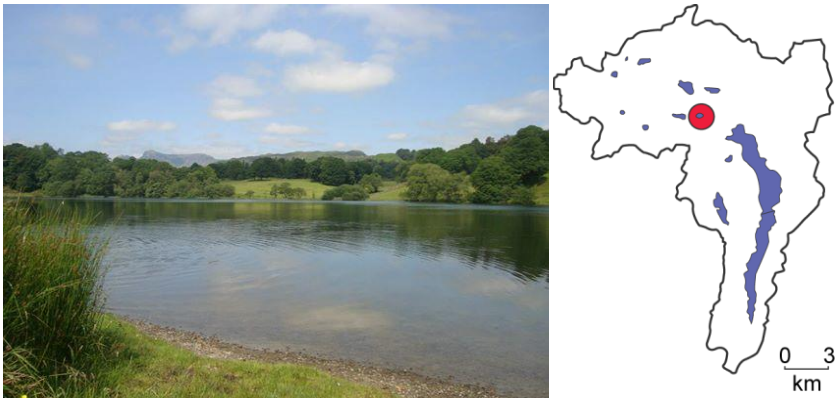


Figure 6.20 Loughrigg Tarn, July 2013 (Photo: author), and location in Windermere catchment (red circle).

6.9.1 Field core description

Throughout the 41.5cm HON-Kajak core, the sediment was dark brown and organic-rich. Above 6.5cm the water content increased and the upper 3cm of the core was unconsolidated.

6.9.2 Sediment chronology

Total ^{210}Pb activity peaked at 3.5cm, with deeper samples deviating from an exponential decline, so the CRS model was used to develop the chronology (Figure 6.21 (1)). There was one ^{137}Cs activity maximum at 10.5cm, which indicated a mixing of the 1986 and 1963 fallout records (Figure 6.21 (2)). The CRS age-depth model established 1986 at 7cm and 1963 at 10.25cm and was in agreement with the elevated ^{137}Cs activity from 7-15cm (Figure 6.21 (2-3)). The mean SAR was average compared to other lowlands in the Windermere catchment (Table 6.1). SARs were at their highest from 1988 to 1998 (~0.1 g cm^{-2} yr^{-1}), after which they declined to 0.05 g cm^{-2} yr^{-1} by 2008 (Figure 6.21 (3)).

6.9.3 Sediment lithology

Mean carbonate content was the highest in the Windermere catchment, whereas mean OM content was the third highest of the lowlands (Table 6.1). Water and OM content increased from 1800 to 2012, with a marked increase between 1900-2012 when values increased from 89 to 99% and 33 to 43% respectively (Figure 6.22 (1a-b)). Carbonate content fluctuated ~4-5% from 1800 until the late 1990s when it increased to ~7% (Figure 6.22 (1c)). Minerogenic content increased from 1800, peaked at 72% in 1880 and decreased afterwards (Figure 6.22 (1d)). Sediment density decreased from 0.16 g cm^{-3} in 1800 to 0.05 g cm^{-3} by 2012 (Figure 6.22 (1e)).

6.9.4 Sedimentary pigments

Mean total algal (β-carotene) concentrations were the highest of all sites in the Windermere catchment, reflecting LOU$_{site}$'s eutrophic status (Table 6.1). Most sedimentary pigments increased from 1850 onwards. Siliceous (diatoxanthin), cyanobacterial (canthaxanthin, zeaxanthin), chlorophyte (lutein) and total algae (Chl. *a*, β-carotene) had elevated concentrations from ~1910 up to the late 1950s after which they decreased to concentrations higher than pre-1850 (Figure 6.22 (2a-d/f-g)). Cyanobacterial (canthaxanthin, aphanizophyll, and zeaxanthin), chlorophyte (lutein), cryptophyte (alloxanthin) and total algae (Chl. *a*, pheophytin *a*, β-carotene) had pronounced increases in concentrations within the late 1990s onwards before declining again in 2010 (Figure 6.22 (2b-g)). These trends are reflected in the increased preservation conditions and PCA axis 1 scores (75% variance explained) (Figure 6.22 (2h-i)).

6.9.5 Historical records

Dominant catchment land cover transitioned from arable in 1866 (36%) to permanent grass from 1870-1881 (93-98%), to rough grazing by 1921 (77%) that peaked at 79% in 1951 (Figure 6.23 (1)). Henceforth, rough grazing declined slightly and permanent grass cover increased to 28% by 1988 (Figure 6.23). Sheep and cattle densities increased most from 1971 to 1988, reaching 5.7 and 0.19 individuals per hectare respectively, similar to other lake catchments in the region (Figure 6.23 (2)). This increase in stocking corresponded to increased cyanobacterial pigment (zeaxanthin) concentrations from the 1980s up to the late 2000s (Figure 6.22 (2c)). The resident human population gradually increased from 1801 and reached 0.27 individuals per hectare by 1961 but then declined thereafter, with most algal pigments following the same trend (Figure 6.22 (2); Figure 6.23 (3)).

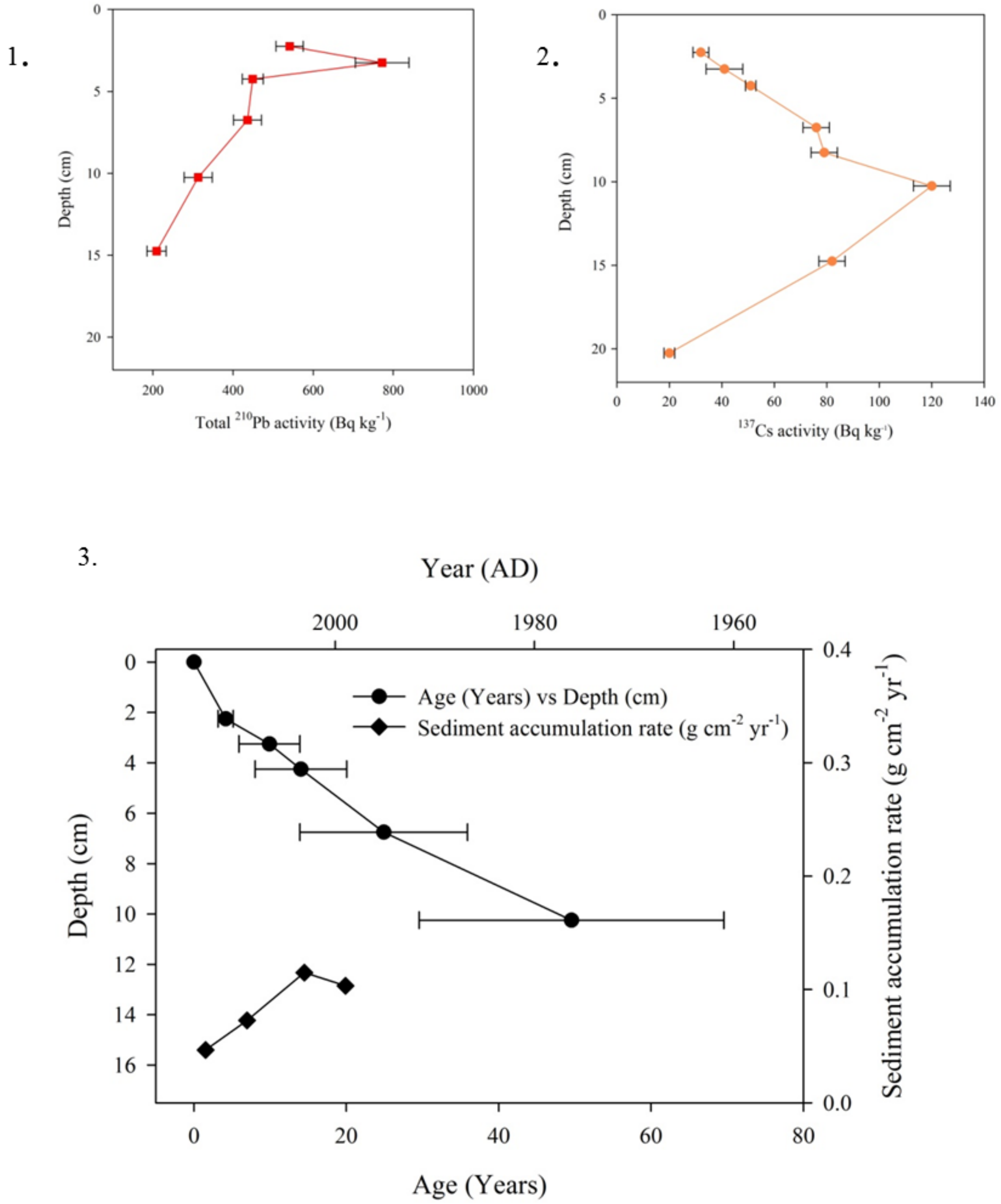


Figure 6.21 Changes in total ^{210}Pb (1), ^{137}Cs activity (2), and CRS age-depth model and sediment accumulation rate for LOU$_{core}$ (3).

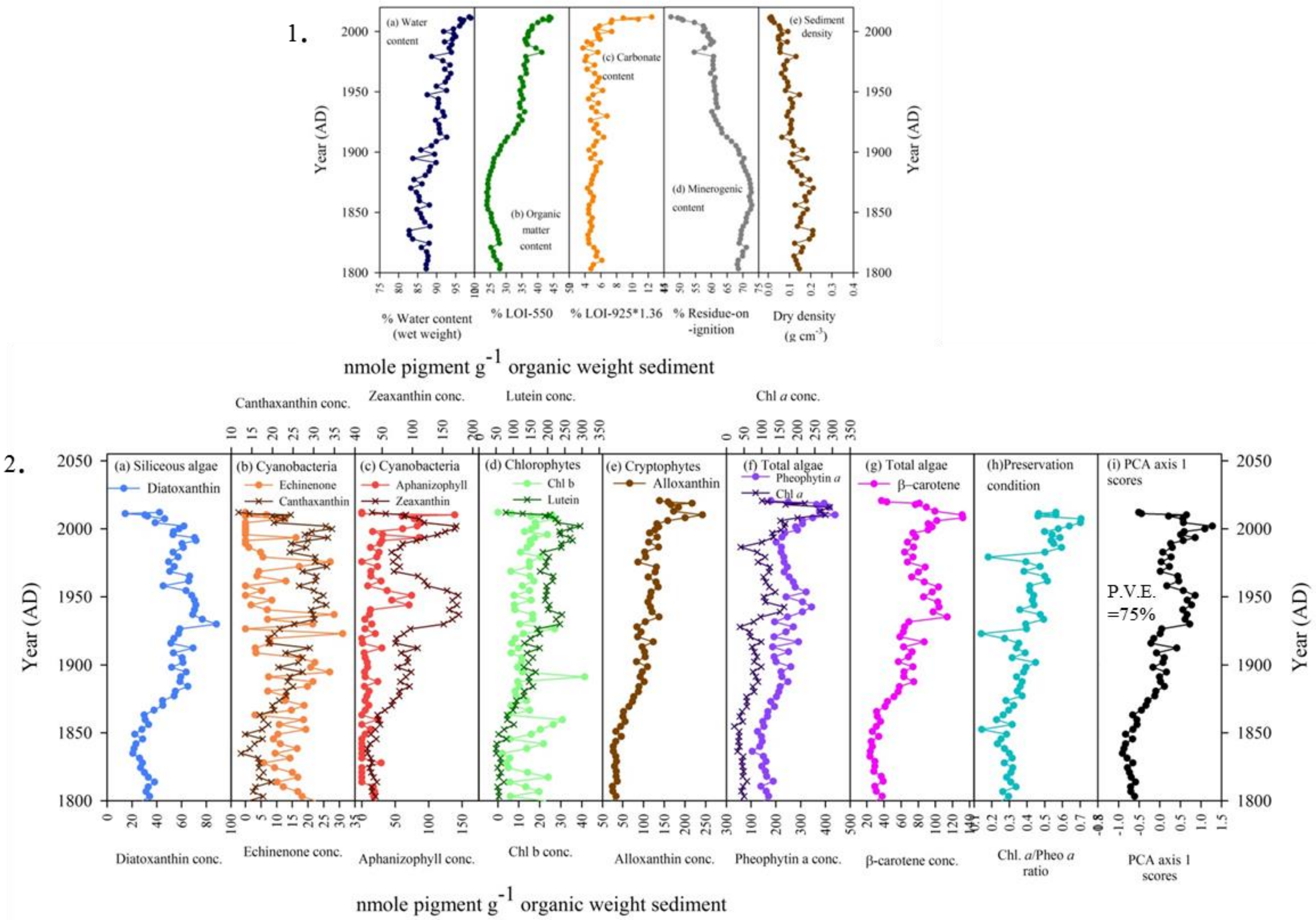


Figure 6.22 Changes in LOU_{core} sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), pigment preservation condition (2h) and the PCA axis 1 scores (2i) from 1800 onwards.

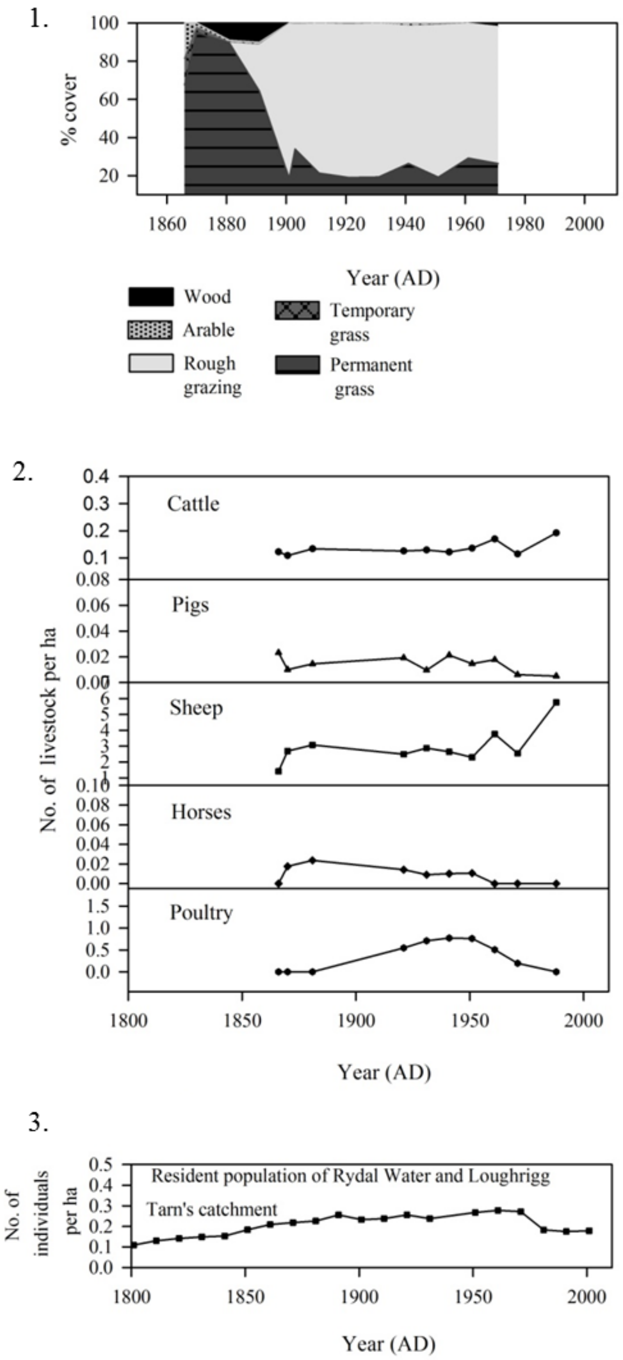


Figure 6.23 Changes in $\mathrm{LOU}_{\mathrm{site}}$ and $\mathrm{RYD}_{\mathrm{site}}$ catchment land use (1), livestock densities (2) and resident human population (3).

6.10 Esthwaite Water (EST$_{site}$). Lowland (65 m.a.s.l.)

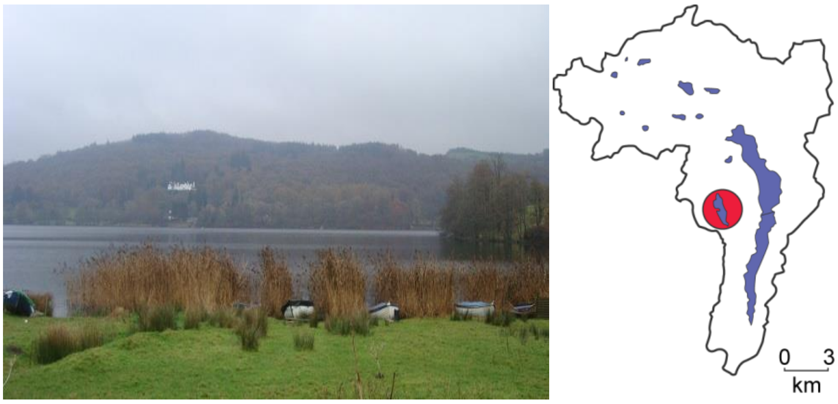


Figure 6.24 Esthwaite Water, November 2011 (Photo: author), and location in Windermere catchment (red circle).

6.10.1 Field core description

From the bottom of the 84.5cm Mackereth core up to 50-60cm the sediment consisted of clay-rich gyttja. Above this, the sediment was dark brown, fine and organic-rich.

6.10.2 Sediment chronology

Total supported ^{210}Pb reached equilibrium at 54cm (Figure 6.25 (1)). The non-monotonic trends in the ^{210}Pb activities determined that the CRS model be used to develop the chronology. There were two well-resolved ^{137}Cs peaks at 20.25cm and 35.25cm, designated as 1986 and 1963 respectively, with the peak in ^{241}Am activity at 35.25cm supporting this assumption (Figure 6.25 (2)). The CRS age-depth model placed 1986 at 21cm and 1963 at 38cm which was deeper than the ^{137}Cs 1986 and 1963 activity peaks (Figure 6.25 (2-3)). The CRS model was still considered to be in good agreement with the artificial radionuclide records. Mean SAR although not the highest in the Windermere catchment, was higher than other productive lowlands such as those in LOU$_{core}$, BLE$_{core}$ and WSB$_{core}$ (Table 6.1). SARs increased steadily peaking at 0.2595 g cm^{-2} yr^{-1} in 1976 (Figure 6.25 (3)). SARs declined then increased again in 1987 to 0.2122 g cm^{-2} yr^{-1} when they declined but to rates greater than pre-1960.

6.10.3 Sediment lithology

Mean OM and carbonate content were relatively low compared to other lowlands in the Windermere catchment (Table 6.1). Marked shifts in lithology occurred from 1900 onwards, particularly post-1950 (Figure 6.26 (1)). Water and OM content increased from 1900 to 2011 (77 to 85% and 20 to 29% respectively) (Figure 6.26 (1a-b)). Whereas carbonate, minerogenic and sediment density values decreased during this period, although carbonate content was negligible (Figure 6.26 (1c-e)).

6.10.4 Sediment C and N mass and stable isotopes

The mean $\delta^{13}C_{org}$ value was the lowest of all the lowland sites in the Windermere catchment, whereas the mean $\delta^{15}N_{org}$ and C/N ratio was the median (Table 6.1). %N and %C distinctly increased from 1975-2011 (Figure 6.26 (2a-b)). C/N ratios increased from 13 in 1800 to 15 in 1950, after which they declined to ~12-13 in the last two decades (Figure 6.26 (2c)). The $\delta^{15}N_{org}$ values fluctuated between 4-5‰ from 1800 to 2011 (Figure 6.26 (2d)). The $\delta^{13}C_{org}$ values were relatively stable at -28 to -29‰ but in the late 1970s decreased to values -29 to -30‰ (Figure 6.26 (2e)).

6.10.5 Sedimentary pigments

Mean total algal (β-carotene) concentration was lower than the other eutrophic lowland sites (LOU_{core}, $ELTIN_{core}$ and WSB_{core}), but still high compared to the remaining sites in the Windermere catchment (Table 6.1). All pigments continually increased from ~1850 onwards. After 1960 the highest concentrations of cyanobacterial pigments and an increased occurrence of filamentous cyanobacterial pigment aphanizophyll, indicated increased cyanobacterial production (Figure 6.26 (3)). Diatom (diatoxanthin), cyanobacterial (echinenone, canthaxanthin, zeaxanthin), chlorophyte (Chl. b, lutein) and cryptophyte (alloxanthin) pigments declined temporarily in the late 1970s to 1991, corresponding to an increased water clarity index (Figure 6.26 (3a-e/h)). All pigments peaked markedly in 2002, which could be related to an algal bloom (Figure 6.26 (3)). PCA axis 1 scores summarised both this feature and the increasing pigment trend from 1850 (60% variance explained) (Figure 6.26 (3i)).

6.10.6 Historical records

Previous work at $\mathrm{EST_{site}}$ noted that prior to the 1970s eutrophic diatom taxa were not found (Dong *et al*., 2011). Multiple nutrient sources may have led to eutrophication at $\mathrm{EST_{site}}$ including the development of Hawkshead WwTW in 1973, which treated effluent from the villages of Hawkshead and Near Sawrey (Figure 6.26 (4)) (Dong *et al*., 2011). Tertiary treatment began in 1986 and prior to this fish culture cages where established in 1981 but were later removed in 2009 (Figure 6.26 (4)) (Dong *et al*., 2011). From 1881-1891 woodland cover was ~40% but decreased markedly following an increase in permanent grass cover by 1901 to 95% (Figure 6.27 (1)). From 1911 onwards rough grazing increased to ~40% but gradually decreased as permanent grass cover increased to 70% by 1971. The higher permanent grass cover indicates increased land use intensification as fertiliser application and drainage were used to maintain these pastures. The densities of livestock were relatively low compared to other lake catchments, but were at their highest in $\mathrm{EST_{site}}$'s catchment from the late 19th century and never reached these densities in the 20th century, though increases in sheep and cattle were seen in the latter half (Figure 6.27 (2)). Resident human population gradually increased from 1800 up to the 1970s to 0.3 individuals per hectare, after which it declined (Figure 6.27 (3)).

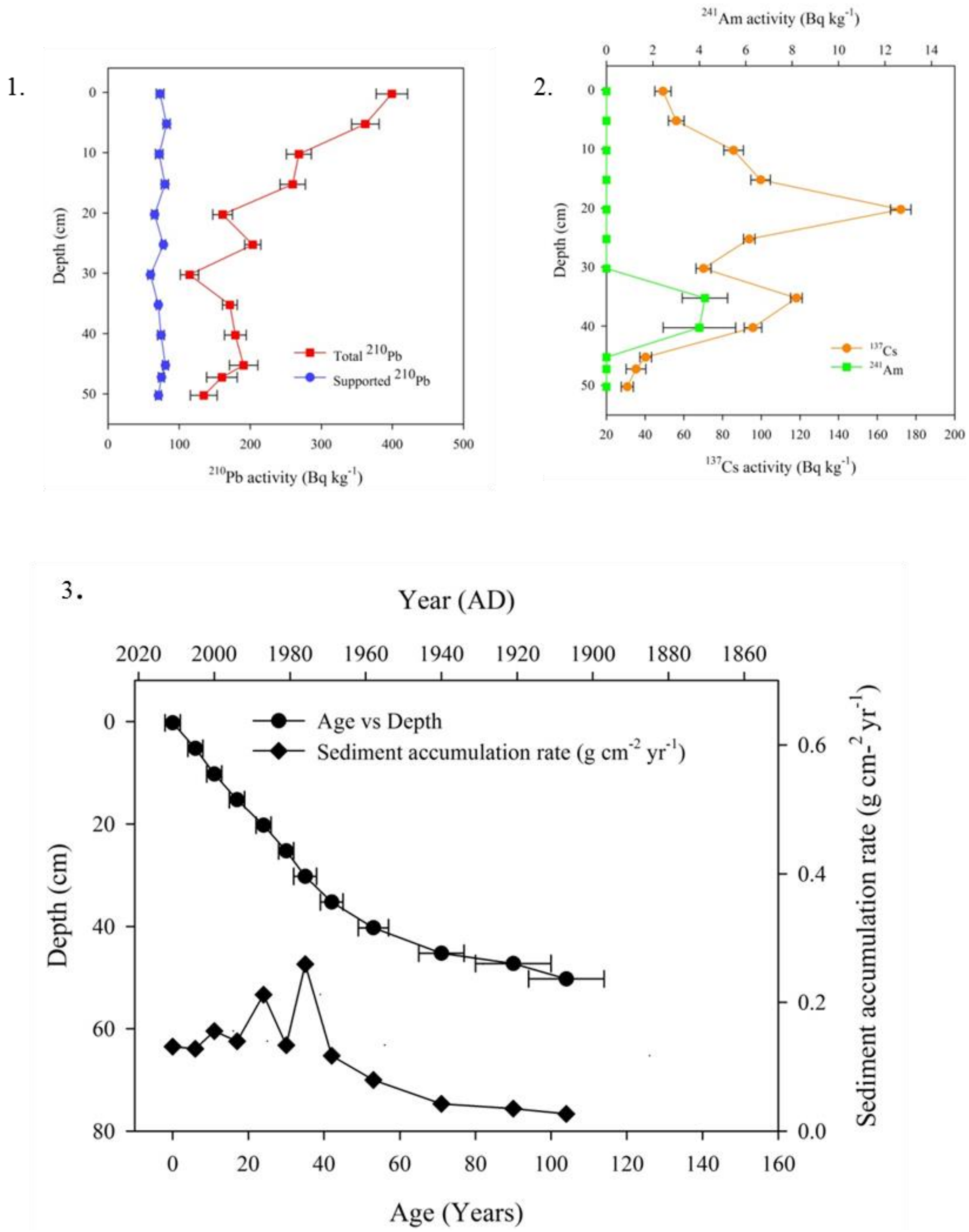


Figure 6.25 Changes in total and supported ^{210}Pb (1), ^{137}Cs and ^{241}Am activity (2), and CRS age-depth model and sediment accumulation rates for EST$_{core}$ (3).

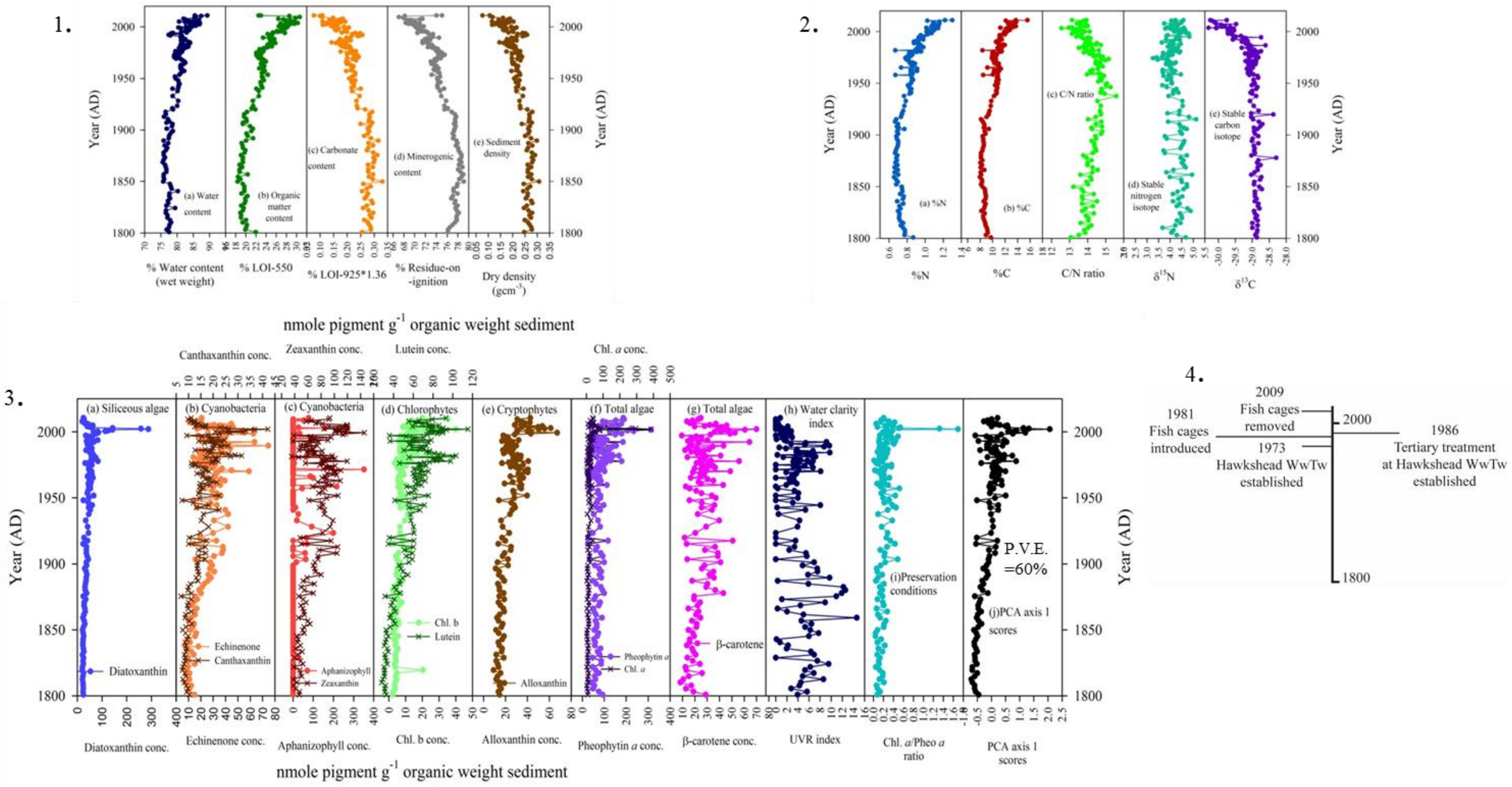


Figure 6.26 Changes in EST$_{core}$ sediment lithology (1a-e), bulk organic C and N and their isotopes (2a-e), sedimentary chlorophylls and carotenoids (3a-g), water clarity (3h), pigment preservation condition (3i) and the PCA axis 1 scores (3j) from 1800 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the EST$_{site}$ catchment from 1800 onwards (4).

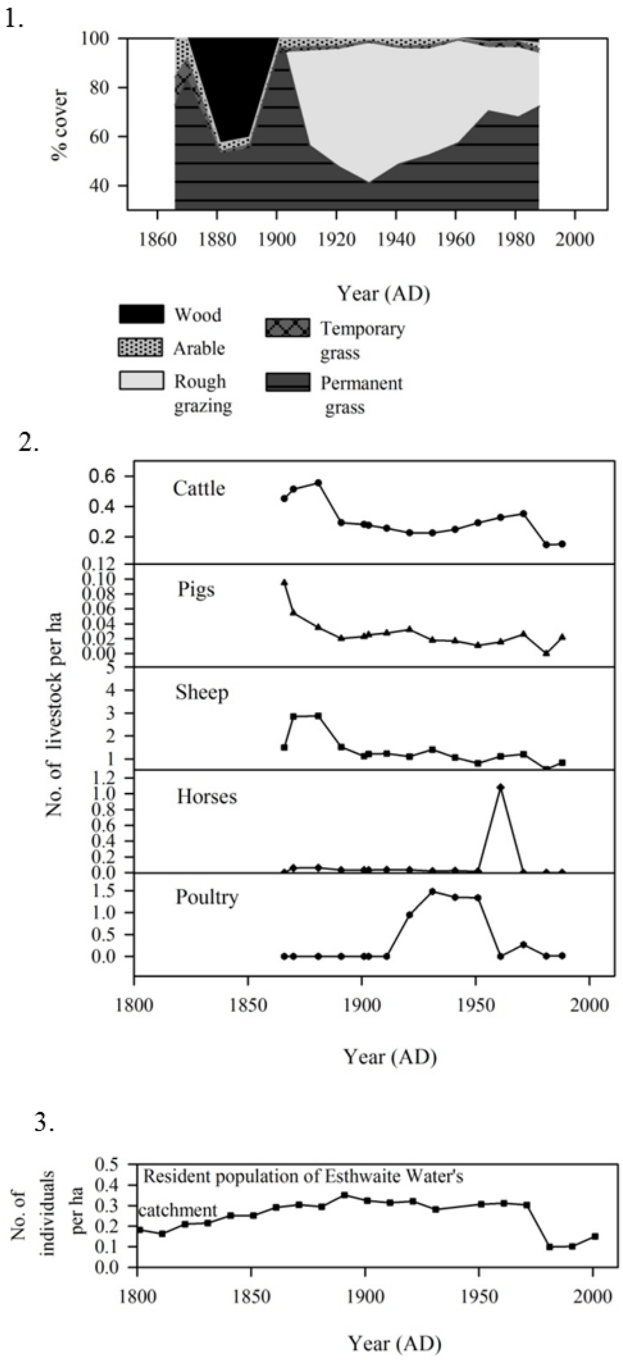


Figure 6.27 Changes in EST_{site} catchment land use (1), livestock densities (2) and resident human population (3).

6.11 Grasmere (GRA$_{site}$). Lowland (62 m.a.s.l.)

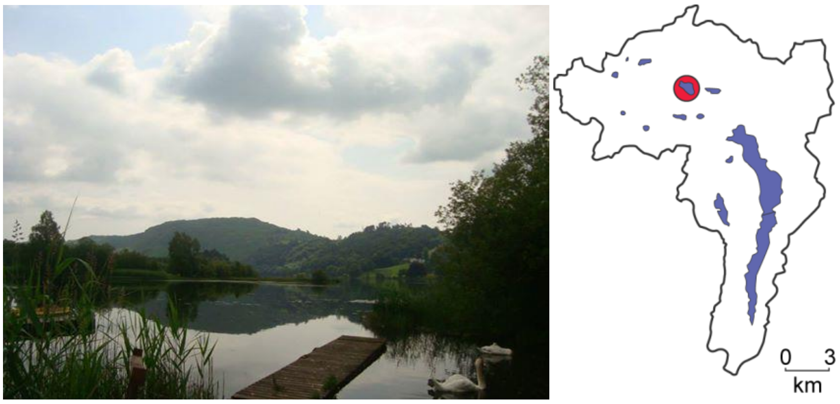


Figure 6.28 Grasmere, July 2013 (Photo: author), and location in Windermere catchment (red circle).

6.11.1 Field core description

From the bottom of the 50cm HON-Kayak core up to 40cm, the sediment was consolidated and red-brown in colour, possibly indicating oxidation. Above 40cm depth, the sediment became a fine, dark brown-black, organic-rich material with a green sheen.

6.11.2 Sediment chronology

As for ELTIN$_{core}$ (see 6.10.2), ^{210}Pb activity counts were very low and so, ^{137}Cs activity was used to determine the chronology. Two ^{137}Cs maxima at 7.5cm and 18cm were determined to be the 1986 and 1963 fallout peaks respectively (Figure 6.29 (1)). At 30cm ^{137}Cs activity was 0 and was designated as the year 1940, which again is a best estimate due to lack of clarity about the exact date when weapons testing began, although 1953 is often cited (Appleby, 2001). Thus, there was more error associated with dates interpolated between 1963 and 1940 (shaded in grey in Figure 6.29 (2)). Mean SAR was the second highest in the Windermere catchment, although like ELTIN$_{core}$ this was calculated differently to the other sites (Table 6.1). SARs steadily increased between 1847 and 1952 (0.29 g cm^{-3} yr^{-1}) and then declined to 0.04 g cm^{-3} yr^{-1} by 2002, which could have been caused by the high water content (80-90%) of the core after 1952 (Figure 6.29 (2); Figure 6.30 (1a)). To help validate the

^{137}Cs chronology, %LOI$_{550}$ and diatom (diatoxanthin) trends were compared with those found in core 6 by Barker *et al.*, (2005), which was retrieved from a similar location in GRA$_{site}$ (Figure 6.29 (3)). A comparable increase in %LOI$_{550}$ values occurred in core 6 (from 24-28%), and GRA$_{core}$ (from 20-24%) from 1945 to 1965 (Figure 6.29 (3a-b)). From the late 1960s onwards, total diatom flux and *A. formosa* flux increased at GRA$_{site}$ (Barker *et al.*, 2005). Concentrations of the diatom pigment diatoxanthin increased notably from 6.1 nmole pigment g^{-1} organic weight sediment before 1967 to 29.3 after 1967 (Figure 6.29 (3b)), suggesting that the ^{137}Cs chronology is robust.

6.11.3 Sediment lithology

Mean OM content was fairly low, whereas mean carbonate content was the second highest of the lowlands in the Windermere catchment (Table 6.1). There were marked shifts in lithological variables after 1915 (Figure 6.30 (1)). Water, OM and carbonate content increased from 77 to 98%, 17 to 31% and ~3 to 7% respectively from 1915 to 2011 (Figure 6.30 (1a-c)). Over the same period, minerogenic and sediment density values decreased from 80 to 63% and 0.3 to 0.01 g cm^{-3} correspondingly (Figure 6.30 (1d-e)).

6.11.4 Sedimentary pigments

Mean total algal (β-carotene) concentration was the fourth highest of the lowlands in the Windermere catchment (Table 6.1). All sedimentary pigments increased markedly after 1950, with the highest water clarity index in 1944 followed by lower values thereafter (Figure 6.30 (2)). Declines in diatom (diatoxanthin), cyanobacterial (echinenone, canthaxanthin, and zeaxanthin), chlorophyte (Chl. *b*, lutein) pigments and total production (β-carotene) occurred after 1982 (Figure 6.30 (2a-e/g)). Preservation conditions were greater in GRA$_{core}$ relative to the other sites in the Windermere catchment (Figure 6.30 (2i)), which could have been attributed to its strong stratification and hypolimnetic anoxia which would have reduced oxidative degradation (Jones *et al.*, 1980; Leavitt, 1993). PCA axis 1 scores decreased ~1960 matching the increased pigment concentrations (78% variance explained) (Figure 6.30 (2j)).

6.11.5 Historical records

From 1916 to 1927, complaints of foul-smelling drains and sewage matter flooding onto local land were recorded (Grasmere Urban District Council minutes, 1902-1927). This continued until 1971, as domestic sewage from houses and hotels in GRA_{site}'s catchment entered cess pools and septic tanks which were not adequately maintained and so, slowly seeped into the lake (Smyly, 1978). In 1971, a WwTW delivered treated effluent to GRA_{site}'s main inflow; the River Rothay, and corresponded to declines in hypolimnetic oxygen at GRA_{site} (Figure 6.30 (3)) (Hall *et al.*, 1978). Abundant surface runoff and septic tank reliance continued to deliver untreated waste to the River Rothay however, but in 1982 the WwTW was upgraded and the outfall pipe moved to GRA_{site}'s eastern basin's hypolimnion (Reynolds *et al.*, 2012). In 1996, the WwTW was upgraded again and included stripping of ammonium (NH_4) and phosphate (Reynolds *et al.*, 2012). GRA_{site}'s human population increased steadily from 1800 and in 1972 was recorded as 1500 persons, although tourism increased this number in the summer months substantially (Figure 6.31 (3)) (Reynolds *et al.*, 2012). Rough grazing was the dominant land cover from 1900 onwards (70-80%) (Figure 6.31 (1)). Sheep and cattle densities were relatively high between 1901-1911, after which they decreased but increased again to their highest values of 5.7 and 0.19 individuals per hectare respectively by 1988 (Figure 6.31 (2)).

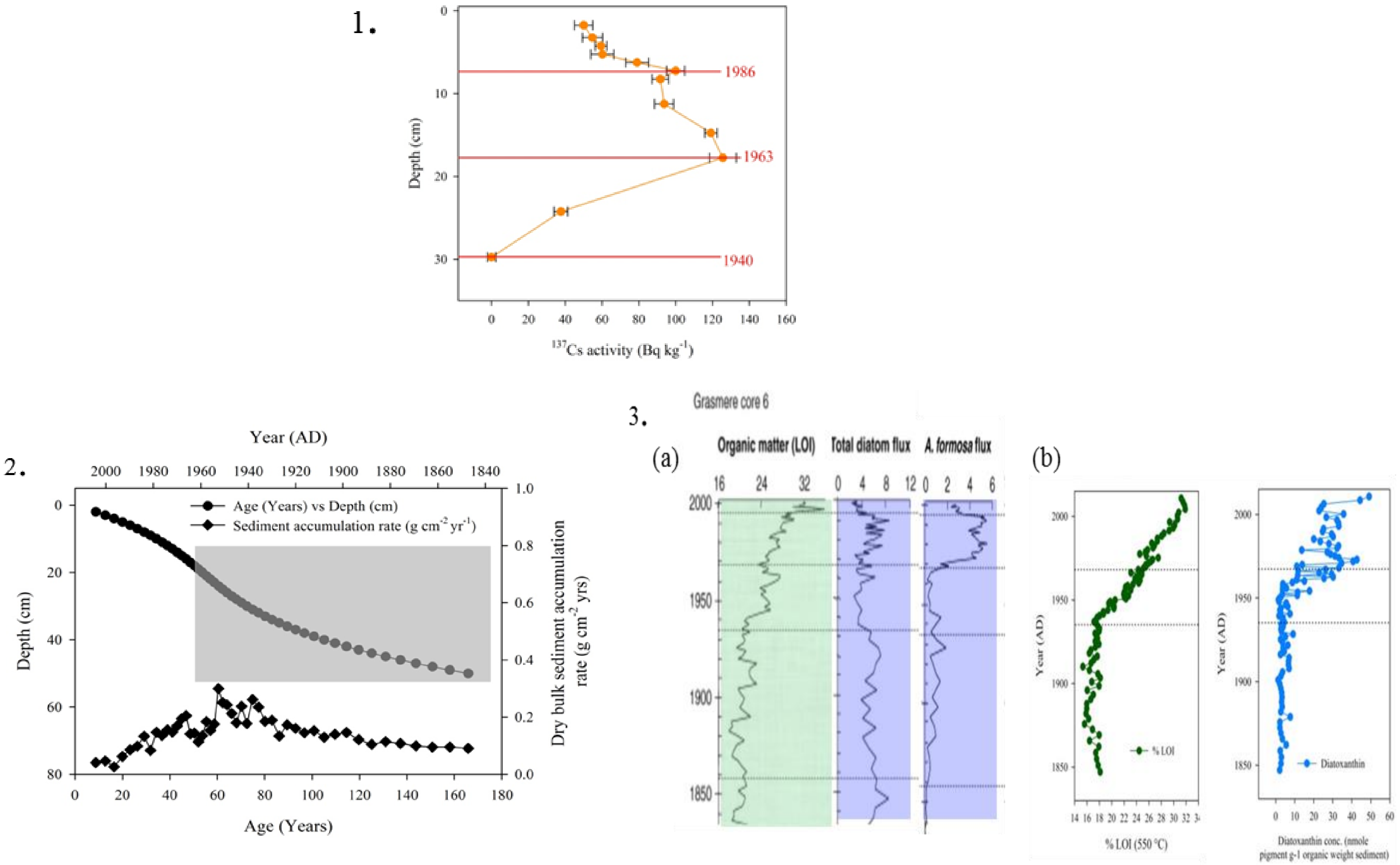


Figure 6.29 Changes in ^{137}Cs activity in GRA$_{core}$. Red lines locate peaks used to determine chronology (1). ^{137}Cs derived age-depth model and sediment accumulation rates for GRA$_{core}$. Grey shading depicts potential error (2). Changes in sedimentary organic matter and diatom influx from ~1835 onwards taken from Barker *et al*., (2005) (3a), juxtaposed against organic matter and the carotenoid diatoxanthin found in diatoms from GRA$_{core}$ from 1847 onwards (3b). Dashed lines depict 1945 and 1965 determined by Barker *et al.*, (2005) to have increased organic matter (3a-b).

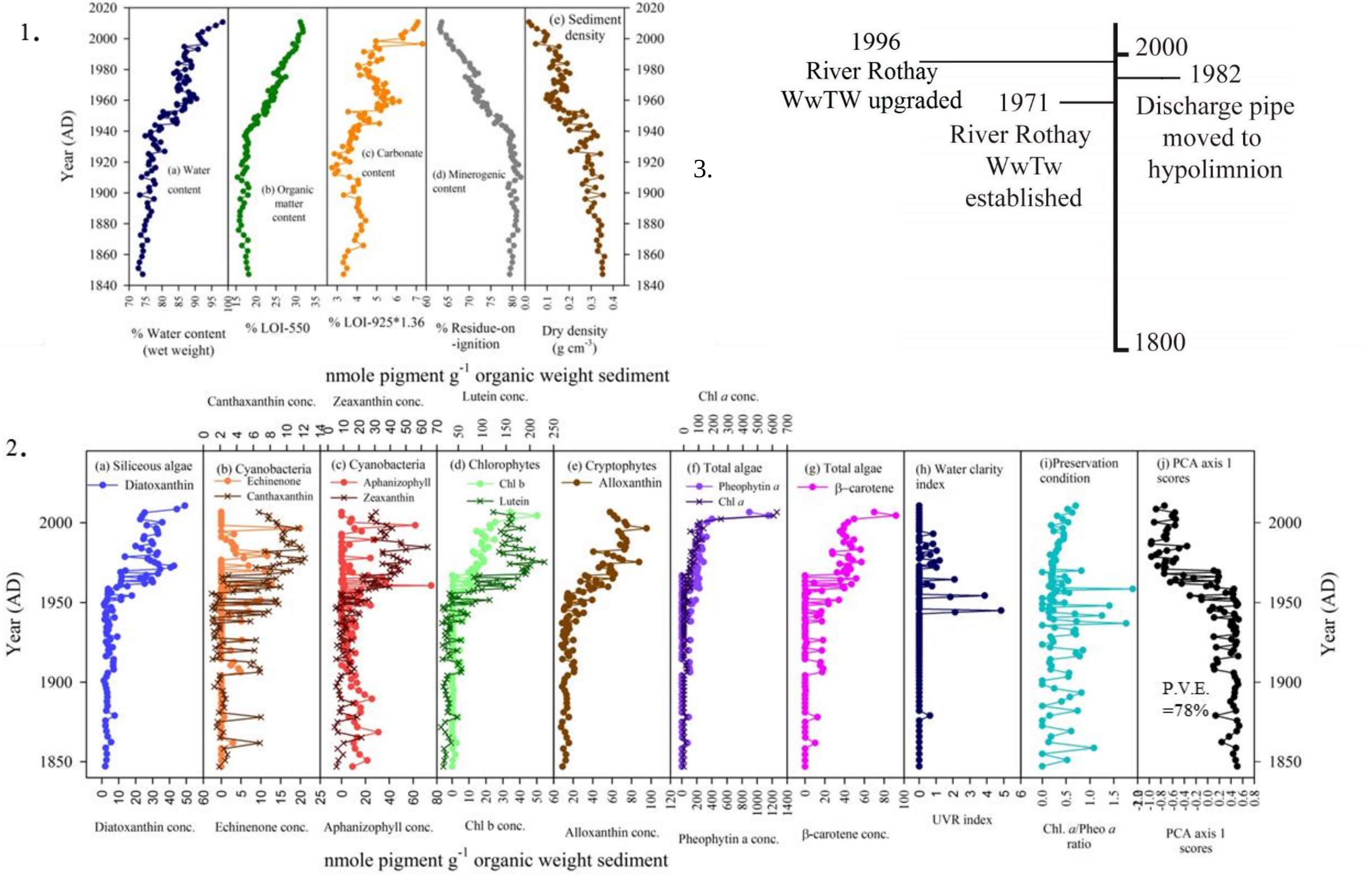


Figure 6.30 Changes in GRA$_{core}$ sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), water clarity (2h), pigment preservation condition (2i) and the PCA axis 1 scores (2j) from 1847 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the GRA$_{site}$ catchment from 1847 onwards (3).

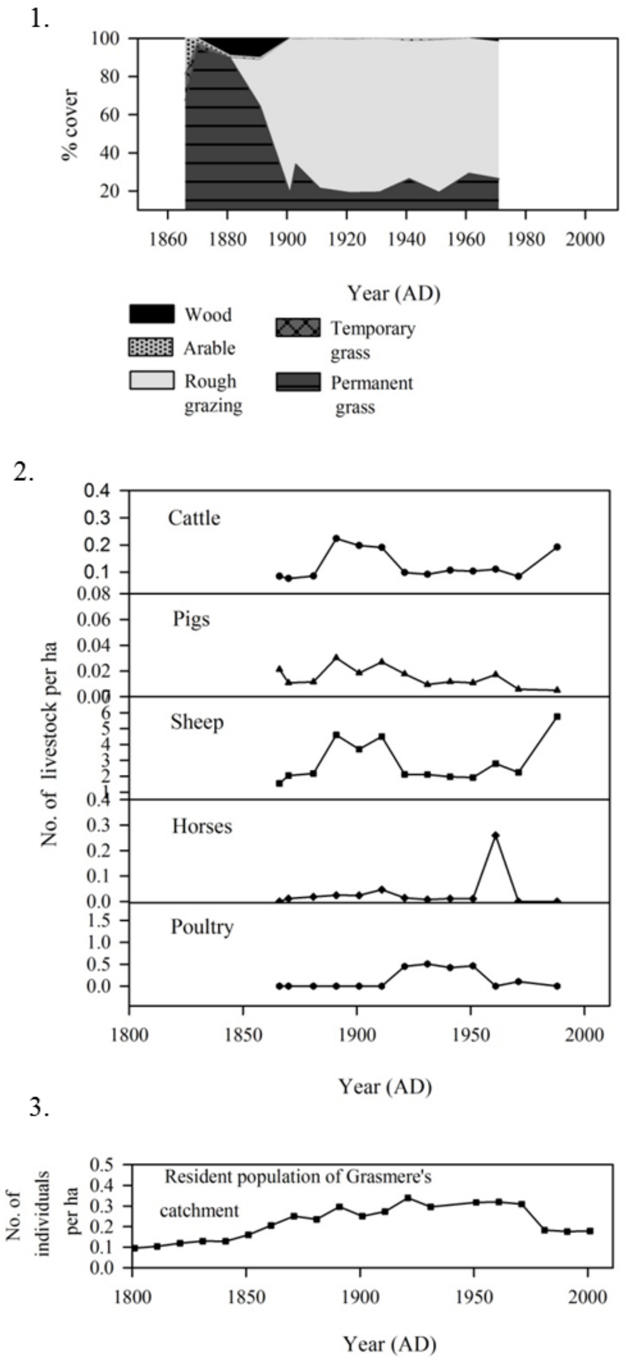


Figure 6.31 Changes in GRA_{site} catchment land use (1), livestock densities (2) and resident human population (3).

6.12 Elterwater Inner Basin (ELTIN$_{site}$). Lowland (55 m.a.s.l.)

6.12.1 Field core description

The 35cm HON-Kajak core consisted of consolidated light brown gytjja from the bottom up to 20cm, followed by dark brown-black organic-rich sediment. The upper 5 cm of sediment was floccy with higher water content.

6.12.2 Sediment chronology

^{210}Pb counts for ELTIN$_{core}$ were below detection limits even for extended count times, possibly due to the low density of dried sediment. Therefore, chronologies were based solely on the ^{137}Cs activity, which had a subsurface maximum at 15.5cm (Figure 6.32 (1)). This peak was assigned to the 1986 Chernobyl peak (as with EAS$_{core}$, LOU$_{core}$ and RYD$_{core}$ which also exhibited a single peak maxima), and was based on the assumption that sedimentation rates would be high at this eutrophic lake with a long WRT. The interpolated dates place 1963 at 23cm, which was only slightly deeper than the small peak in ^{137}Cs at 21.5cm attributed to 1963 weapons testing. However, additional ^{137}Cs sampling between 21.5cm and 31cm would be required to validate the peak in 1963 ^{137}Cs activity at 21.5cm. The year 1940 was estimated to be the lowest recorded activity point at 31cm prior to atmospheric weapons testing and the years extrapolated between 1986 and 1940 (shown in grey on the age-depth model) are a best estimate with the data available (Figure 6.32 (1-2)). Mean SAR was the highest within the Windermere catchment (although like GRA$_{core}$ was calculated differently), which may reflect the long WRT and hypereutrophic status of this basin (Table 6.1). SARs fluctuated between 0.2 to 0.1 g cm^{-3} yr^{-1} from 1931 to 2012 (Figure 6.32 (2)). Lack of published long-term monitoring and palaeolimnology from ELTIN$_{site}$ made it difficult to validate the chronology but documented blooms of the green alga *Volvox* and centric diatoms from water samples taken from 1974 to 1976 match the high concentrations of sedimentary chlorophyte (lutein) and diatom (diatoxanthin) pigments in these years as determined by the ^{137}Cs chronology (Lund, 1981) (Figure 6.32 (3)). Furthermore, Lund (1981) described the ELTIN$_{site}$ algal community as “similar to that common in sewage-oxidation ponds” pointing again and in line with the ^{137}Cs chronology, that the effluent entering the inner basin from the Great Langdale WwTW led to changes in the algal communities here (Figure 6.32 (3); Figure 6.33 (2)). An increase in preservation conditions in 1974 is also consistent with the hypothesis that stimulated algal development from WwTW effluent led to anoxia in the hypolimnion from degradation of OM which would have improved pigment preservation (Leavitt, 1993) (Figure 6.33 (2i)).

6.12.3 Sediment lithology

Mean OM and carbonate content were relatively high compared to all sites in the Windermere catchment (Table 6.1). From 1931 to 2012, water, OM and carbonate content continually increased (from 76 to 96%, 23 to 43% and 3 to 4% respectively) (Figure 6.33 (1a-c)). Minerogenic and sediment density values were relatively high at ~75% and ~0.3 g cm^{-3} respectively in the 1930s, after which they continually declined to values reaching 52% and 0.03g cm^{-3} respectively by 2012 (Figure 6.33 (1d-e)).

6.12.4 Sedimentary pigments

Mean total algal (β-carotene) concentrations were the second highest in the Windermere catchment (Table 6.1). All sedimentary pigments increased distinctly after 1973, with a temporary decline in the water clarity around this period (Figure 6.33 (2)). Cryptophytes (alloxanthin) and total algae (Chl. *a*, pheophytin *a*) continued to increase until 2013, whereas the other algal pigments and water clarity decreased after 1998 (Figure 6.33 (2)). These major trends were reflected by the increased PCA axis 1 scores in the 1970s and again in the late 1990s (79% variation explained) (Figure 6.33 (2j)).

6.12.5 Historical records

From the 1820s to 1830s several farms were bought, marshes drained and channels straightened in the Elterwater catchment to create extensive areas of meadowland from which land cover was dominated by permanent grass from

1866 to 1901 and ranged from 64-94% (Figure 6.34 (1)) (Cooper, 1966). However, this occurred prior to the oldest dates of the sediment record (1931) (Figure 6.34). After 1901, rough grazing became the dominant land cover, which peaked at 77% by 1931, but remained ~68-70% thereafter as % permanent grass increased (Figure 6.34 (1)). In the 1930s, the Elterwater gunpowder works on the River Brathay upstream of $\mathrm{ELTOUT}_{\mathrm{site}}$ was in full employment but closed in 1937 (Figure 6.33 (3)) (Cooper, 1966). Treated effluent from the Great Langdale WwTW was released into a tributary of $\mathrm{ELTIN}_{\mathrm{site}}$ from 1973 to 1999, after which it was diverted downstream of $\mathrm{ELTOUT}_{\mathrm{site}}$ into the River Brathay (Figure 6.33 (3)). From 1999 to 2011, sewage overflow continued to enter Great Langdale Beck; $\mathrm{ELTOUT}_{\mathrm{site}}$'s main inflow (APEM, 2012).

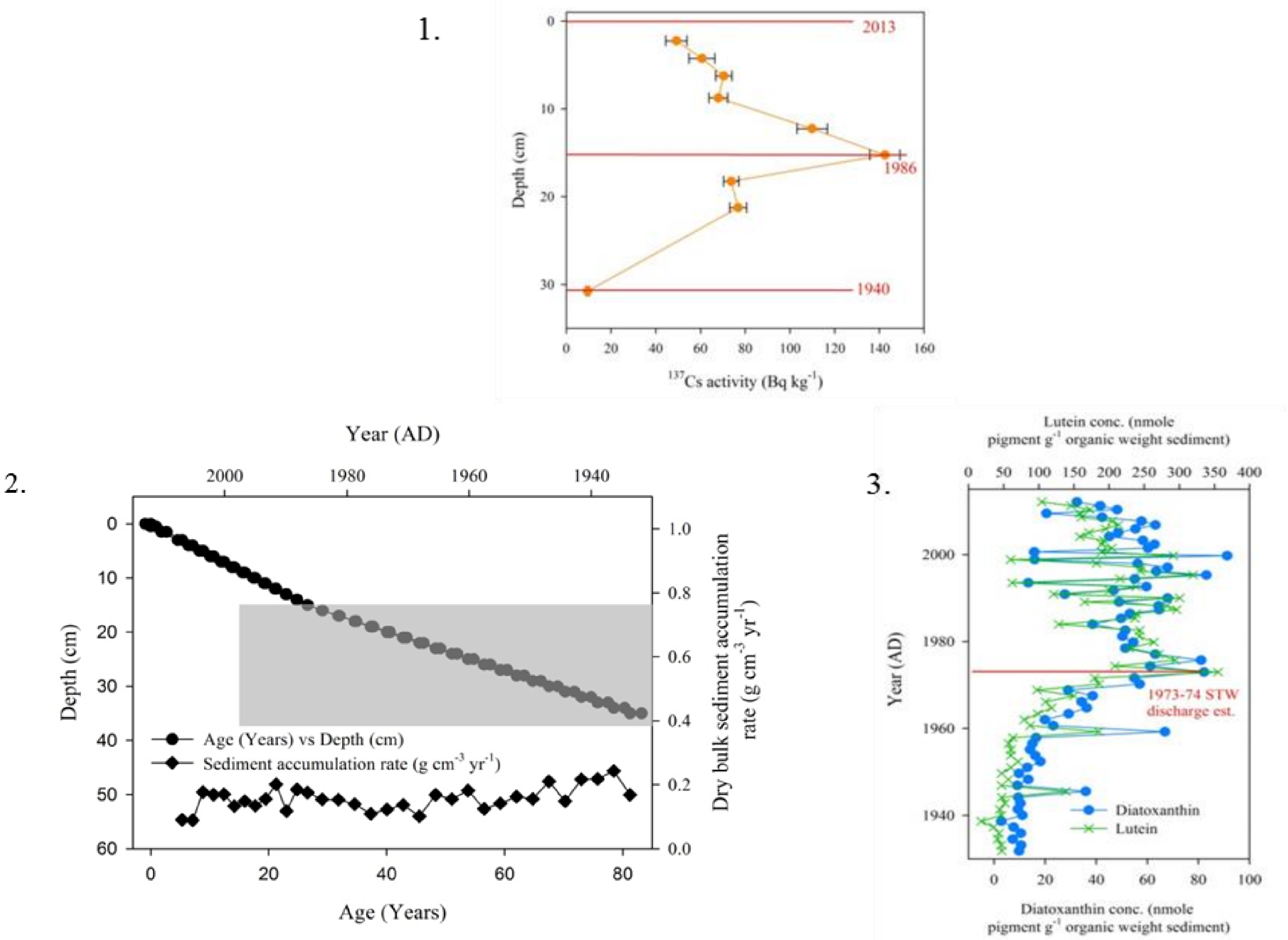


Figure 6.32 Changes in ^{137}Cs activity in ELTIN$_{core.}$ Red lines locate peaks used to determine chronology (1). ^{137}Cs derived age-depth model and sediment accumulation rates for ELTIN$_{core}$. Grey shading depicts potential error (2). Changes in the sedimentary carotenoids diatoxanthin and lutein using the ^{137}Cs derived chronology, with the red line depicting the River Rothay WwTW installation which corresponded to increased biomass of diatoms and green algae from 1974 to 1976 (Lund, 1981) (3).

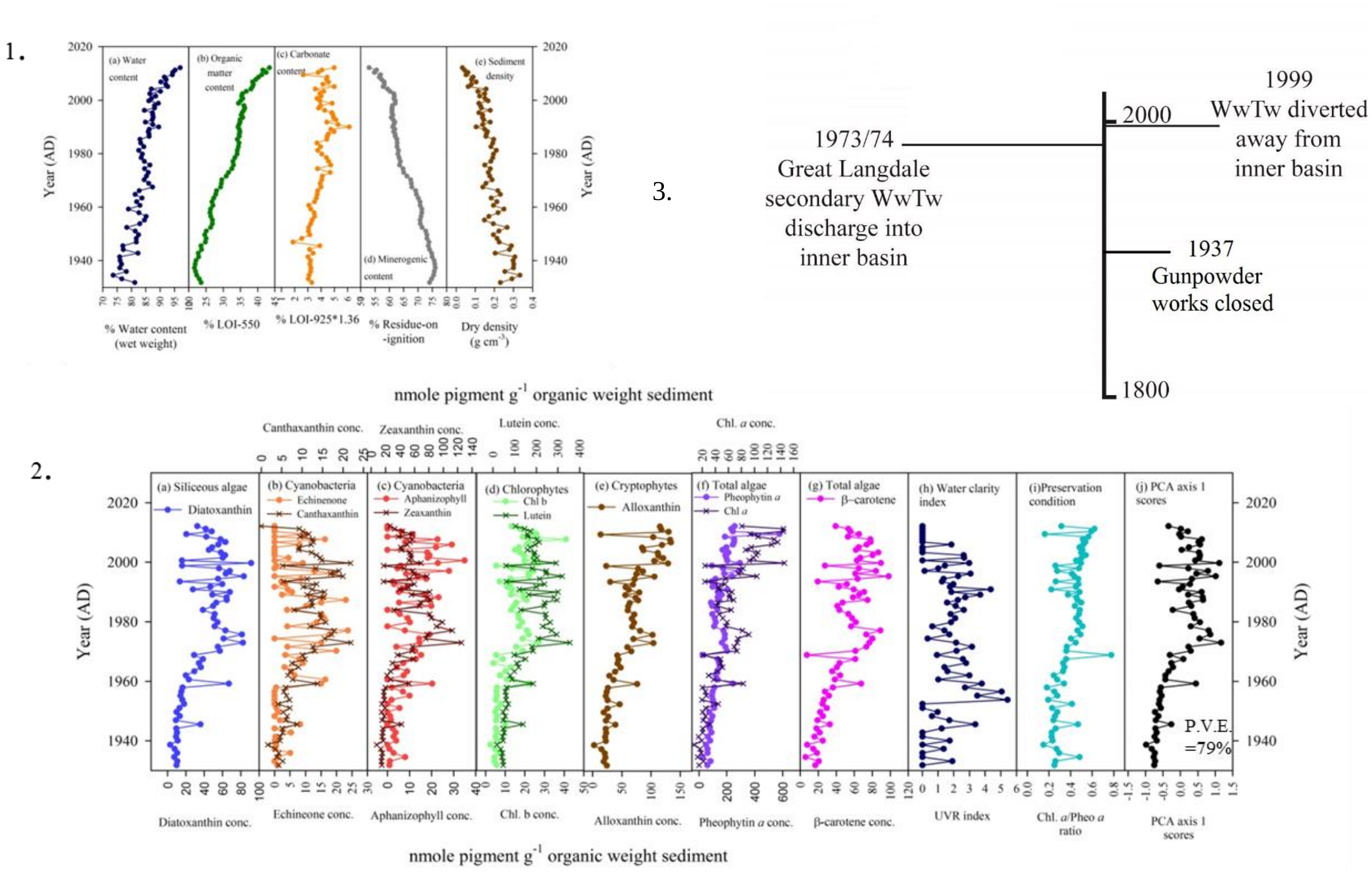


Figure 6.33 Changes in ELTIN$_{core}$ sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), water clarity (2h), pigment preservation condition (2i) and the PCA axis 1 scores (2j) from 1933 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the ELTIN$_{site}$ catchment from 1933 onwards (3).

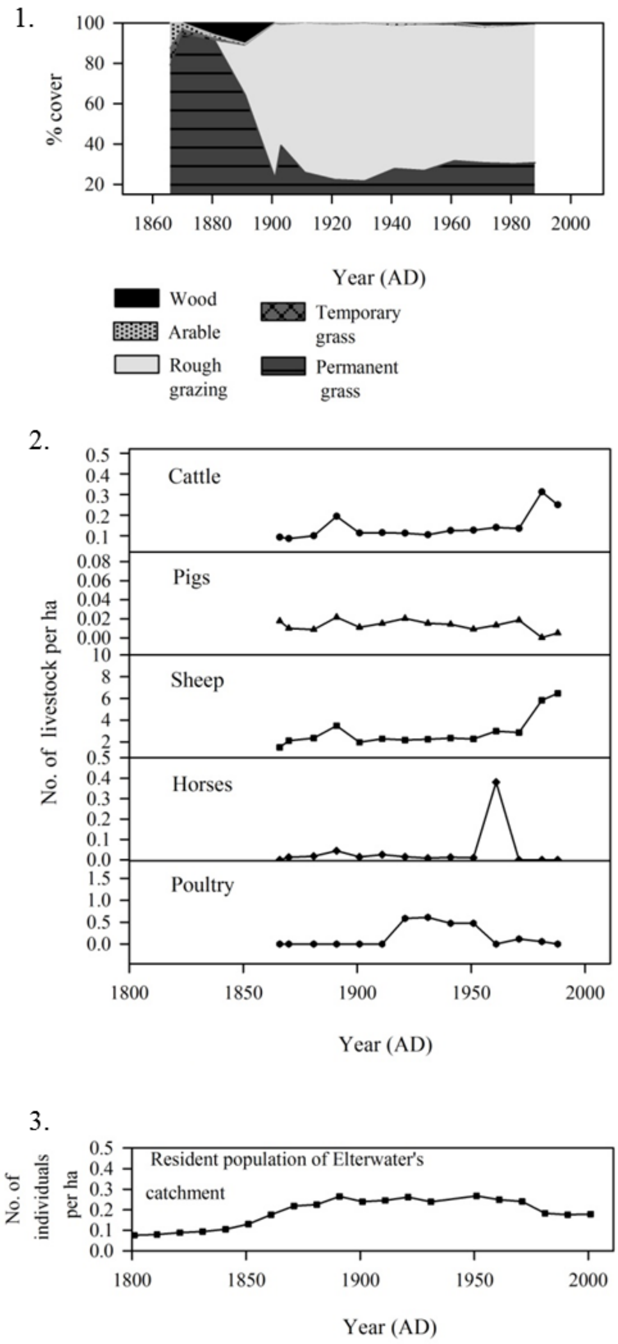


Figure 6.34 Changes in ELT_{site} catchment land use (1), livestock densities (2), and resident human population (3).

6.13 Elterwater Middle Basin (ELTMID$_{site}$). Lowland (55 m.a.s.l.)

6.13.1 Field core description

The 30cm long HON-Kajak core had abundant macrofossil material from the bottom up to 24.5cm. From 24.5cm to 16cm, the sediment was a light brown gytjja and above this depth became a darker brown, fine, organic-rich material. This core was not dated.

6.13.2 Sediment lithology

Both mean OM and carbonate content were relatively high compared to other lakes in the Windermere catchment (Table 6.1). Water and OM content gradually increased from 78 to 98% and 28 to 44% respectively, from the bottom to the top of the core (Figure 6.35 (1a-b)), whereas minerogenic content and sediment density steadily decreased (Figure 6.35 (1d-e)). Interestingly, carbonate content declined from 16.5 to 14.5cm to 2-1%, after which it increased to 3-4%, similar to values at the bottom of the core (Figure 6.35 (1c)).

6.13.3 Sedimentary pigments

Mean total algal (β-carotene) concentration was fairly low compared to other lowland sites in the Windermere catchment, especially the adjacent basin ELTIN$_{core}$ (Table 6.1). Diatom (diatoxanthin), cyanobacteria (zeaxanthin, canthaxanthin, and echinenone), chlorophyte (lutein) values and PCA axis 1 scores (64% variance explained) increased from the bottom of the core up to a maxiumum at 20cm from which they maintained relatively high concentrations until ~12cm after which they decreased (Figure 6.35 (2a-d/i)). Filamentous cyanobacteria (aphanizophyll) and total algal production (β-carotene) decreased above 6.5cm depth, whereas cryptophytes (alloxanthin) decreased in the top 4cms (Figure 6.35 (2c/e/g)). In the top 5cms, concentrations of Chls *a* and *b* (chlorophytes and total algae) peaked, which corresponded to increased preservation conditions (Figure 6.35 (2d/f/h)).

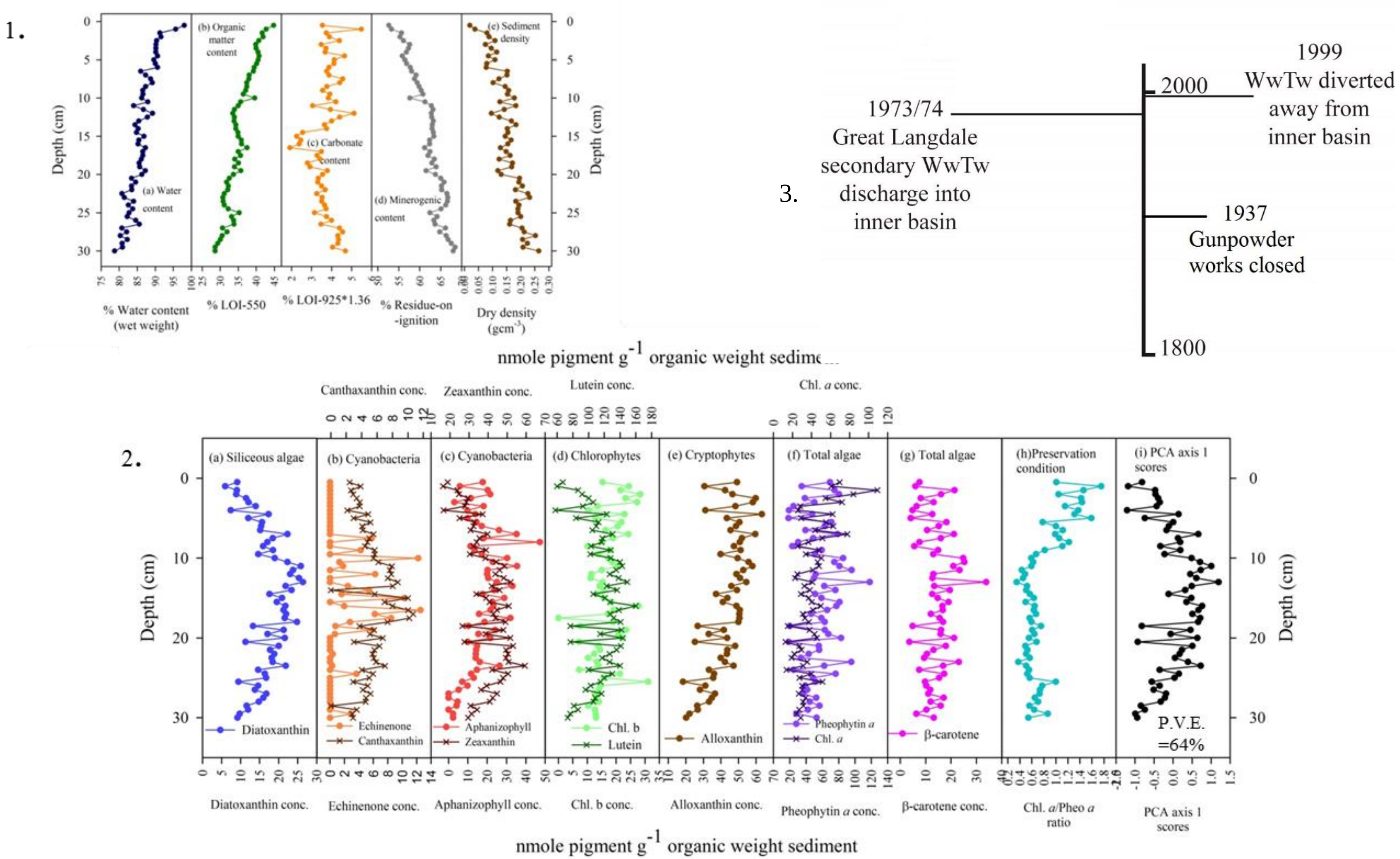


Figure 6.35 Changes in ELTMID$_{core}$ sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), pigment preservation condition (2h) and the PCA axis 1 scores (2i) for the full core length (cm). Timeline of potential anthropogenic drivers of lake ecosystem change in the ELTMID$_{site}$ catchment from 1930 onwards (3) (oldest calculated age of ELTIN$_{core}$ chronology).

6.14 Elterwater Outer Basin ($\text{ELTOUT}_{\text{site}}$). Lowland (55 m.a.s.l.)

Figure 6.36 Elterwater outer basin from middle basin, July 2013 (Photo: author), and location in Windermere catchment (red circle).

6.14.1 Field core description

From the bottom of the 40cm HON-Kajak core up to 30cm, the sediment was macrofossil rich. From 30cm to 10cm, it was a light brown gytjja. Above this, the sediment was dark brown, fine and organic-rich, with the top few centimetres being very floccy with clumps of filamentous algal material. This core was not dated.

6.14.2 Sediment lithology

$\text{ELTOUT}_{\text{core}}$ had the lowest mean OM and highest carbonate content compared to the other ELT_{core} basins (Table 6.1). Water and OM content steadily increased from the bottom to the top of the core (79 to 93% and 19 to 40% respectively) (Figure 6.37 (1a-b)), whereas minerogenic content and sediment density steadily declined (77 to 55% and 0.25 to 0.07 g cm^{-3} respectively) (Figure 6.37 (1d-e)). Carbonate content increased from the bottom to 28.5cm after which it dropped to 2-3% and then increased and maintained stable values of ~4% above 13.5cm (Figure 6.37 (1c)).

6.14.3 Sedimentary pigments

Mean total algal (β-carotene) concentration was the second lowest of all the lowlands in the Windermere catchment, reflecting the low WRT and mesotrophic status of ELTOUT$_{\text{site}}$ (Table 6.1). Changes in siliceous algal (diatoxanthin), cyanobacteria (zeaxanthin, echinenone), cryptophyte (alloxanthin) and total algal (β-carotene) pigments were similar to ELTMID$_{\text{core}}$, in which pigments increased to a maximum between 30cm to ~20cm (Figure 6.37 (2a-c/e/g)). From 9cm to the top of the core, total algae (Chl. *a*, pheophytin *a*, β-carotene), preservation conditions, cyanobacteria (echinenone, aphanizophyll), chlorophytes (Chl. b, lutein) and cryptophytes (alloxanthin) increased (Figure 6.37 (2b-h)). These two episodes are reflected in the higher PCA axis 1 scores (46% variance explained) at 20cm and after 10cm (Figure 6.37 (2i)).

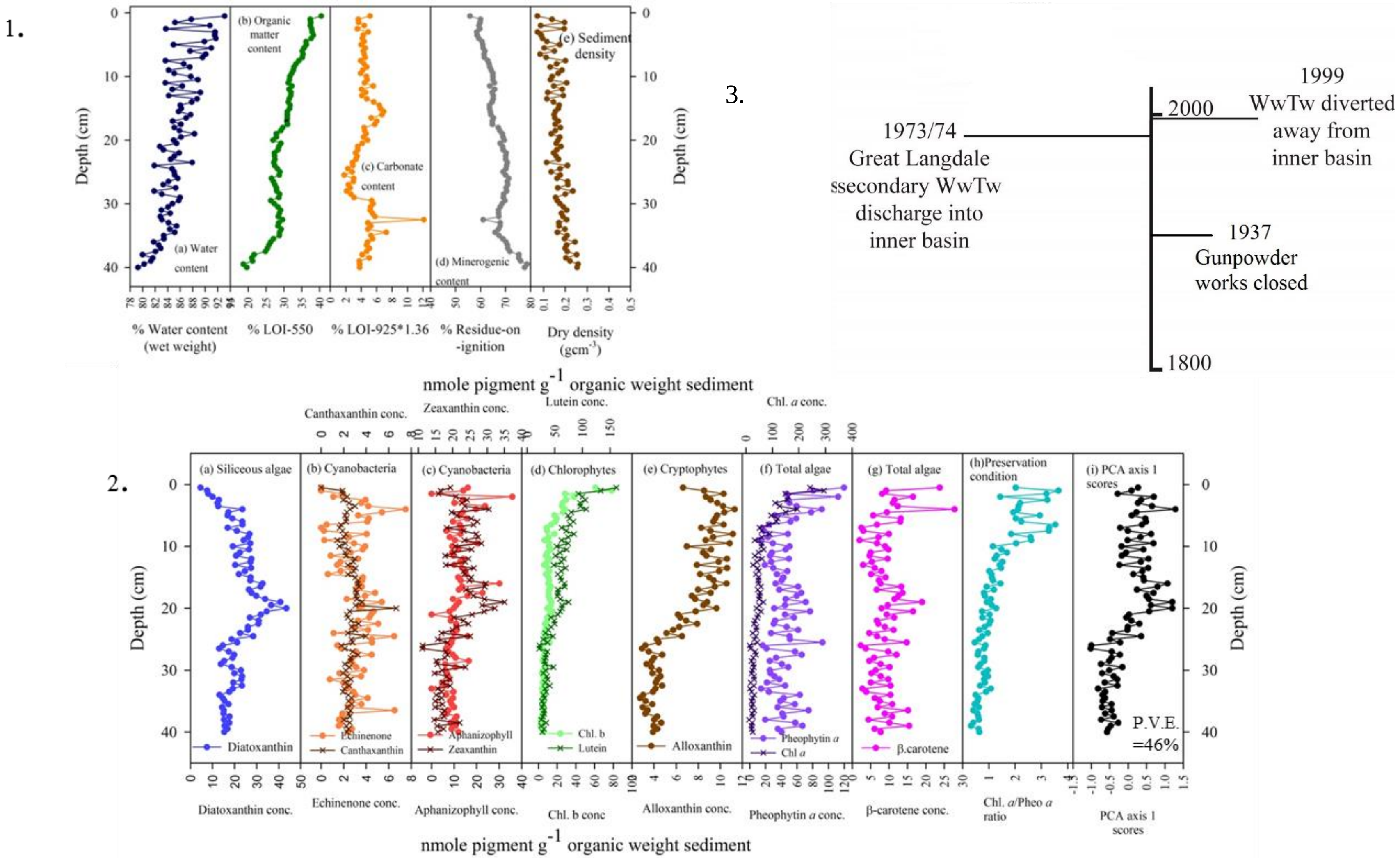


Figure 6.37 Changes in ELTOUT$_{core}$ sediment lithology (1a-e), sedimentary chlorophylls and carotenoids (2a-g), pigment preservation condition (2h) and the PCA axis 1 scores (2i) for the full core length (cm). Timeline of potential anthropogenic drivers of lake ecosystem change in the ELTOUT$_{site}$ catchment from 1930 onwards (3) (oldest calculated age of ELTIN$_{core}$ chronology).

6.15 Rydal Water (RYD$_{site}$). Lowland (53 m.a.s.l.)

Figure 6.38 Rydal Water, March 2012 (Photo: Brayshaw, S), and location in Windermere catchment (red circle).

6.15.1 Field core description

The bottom 10cm of the 85cm Mackereth core was clay-rich with abundant macrofossils. Up to 30cm the sediment was a light brown gyttja with abundant macrofossils. Above 30cm the sediment was darker brown-black and organic-rich. The upper 10cm consisted of dark black-green fine sediment, which smelled strongly of sulphur.

6.15.2 Sediment chronology

Total ^{210}Pb and supported ^{210}Pb activity reached equilibrium around 20.5cm depth (Figure 6.39 (1)). The CRS model was used to develop the chronology of the core because of the non-exponential decline in ^{210}Pb activity. ^{137}Cs activity was highest between 5.25cm and 11.75cm, which indicated a blend of the 1986 and 1963 fallout, and the peak in ^{241}Am activity at 11.75cm was assigned to the 1963 fallout maximum (Figure 6.37 (2)). The CRS age-depth model was in good agreement with the artificial radionuclides, with 1986 placed at 7.75cm and 1963 between 11.5 and 12cm in the CRS model (Figure 6.37 (2-3)). Mean SAR was the lowest of all the lowlands in the Windermere catchment, reflecting the very low WRT of RYD$_{site}$ (Table 6.1). SARs increased from 0.0113 g cm^{-2} yr^{-1} in 1892 to 0.02117 g cm^{-2} yr^{-1} by 1920, after which they remained stable until 1964 when they steadily increased until the late 1990s and increased markedly to reach 0.0452 g cm^{-2} yr^{-1} by 2012 (Figure 6.37 (3)).

6.15.3 Sediment lithology

RYD_{core} had the second lowest mean carbonate content in the Windermere catchment and fairly low OM content (Table 6.1). Water and OM content increased steadily between 1800 and 2011 (Figure 6.40 (1a-b)), except when OM values decreased to 20-21% from 1950 to 1980, after which they increased to ~25% (Figure 6.40 (1b)). Carbonate content increased slightly until ~1850 after which values steadily decreased, except ~ 1950 and ~ 1995 when values decreased more notably (Figure 6.40 (1c)). Whilst minerogenic content steadily decreased from 1800 until 1950 after which values increased to 76% by 1980, and then decreased thereafter (Figure 6.40 (1d)). Sediment density followed the same trend as carbonate content (Figure 6.40 (1e)).

6.15.4 Sediment C and N mass and stable isotopes

Mean $\delta^{13}C_{org}$ was the highest, mean C/N ratio was the second highest, and mean $\delta^{15}N_{org}$ was the lowest out of all the lowland sites in the Windermere catchment (Table 6.1). %N and %C increased from 1800 to 2011 (0.9 to 1.4% and 11.2 to 14.5% respectively), with a more marked increase from the late 1960s onwards (Figure 6.40 (2a-b)). C/N ratios were relatively stable at ~12 from 1800 to the 1960s, after which values decreased reaching 10.5 in 2011 (Figure 6.40 (2c)). The $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$ values decreased from 1900, and this decline was more pronounced after 1950 (Figure 6.40 (2d-e)).

6.15.5 Sedimentary pigments

Mean total algal (β-carotene) concentration was the lowest of all the lowland sites in the Windermere catchment (Table 6.1). Sedimentary pigment concentrations increased after 1940 but the most marked increase occurred after 1996 (Figure 6.40 (3)). The PCA axis 1 scores followed this trend in reverse (64% variance explained) (Figure 6.40 (3i)). There were sporadic peaks in colonial cyanobacteria (canthaxanthin), filamentous cyanobacteria (aphanizophyll) and all cyanobacteria (echinenone) throughout the 1800-2012 period (Figure 6.40 (3b-c)).

6.15.6 Historical records

The water quality and past environmental changes of RYD_{site} are closely connected to that of upstream GRA_{site}. A 30% increase in epilimnetic TP concentration was recorded at RYD_{site} in 1971 following the establishment of the River Rothay WwTW upstream at GRA_{site} (Figure 6.40 (4)) (Jones, 1972). RYD_{site} catchment data followed that of LOU_{site} (Figure 6.23). The notable increases in pigments from 1940 onwards, corresponded to an increase in rough grazing from 70-79% from 1941 to 1951, although this declined to 71% as permanent grass increased to 28% by 1988 (Figure 6.40 (3); Figure 6.23 (1)).

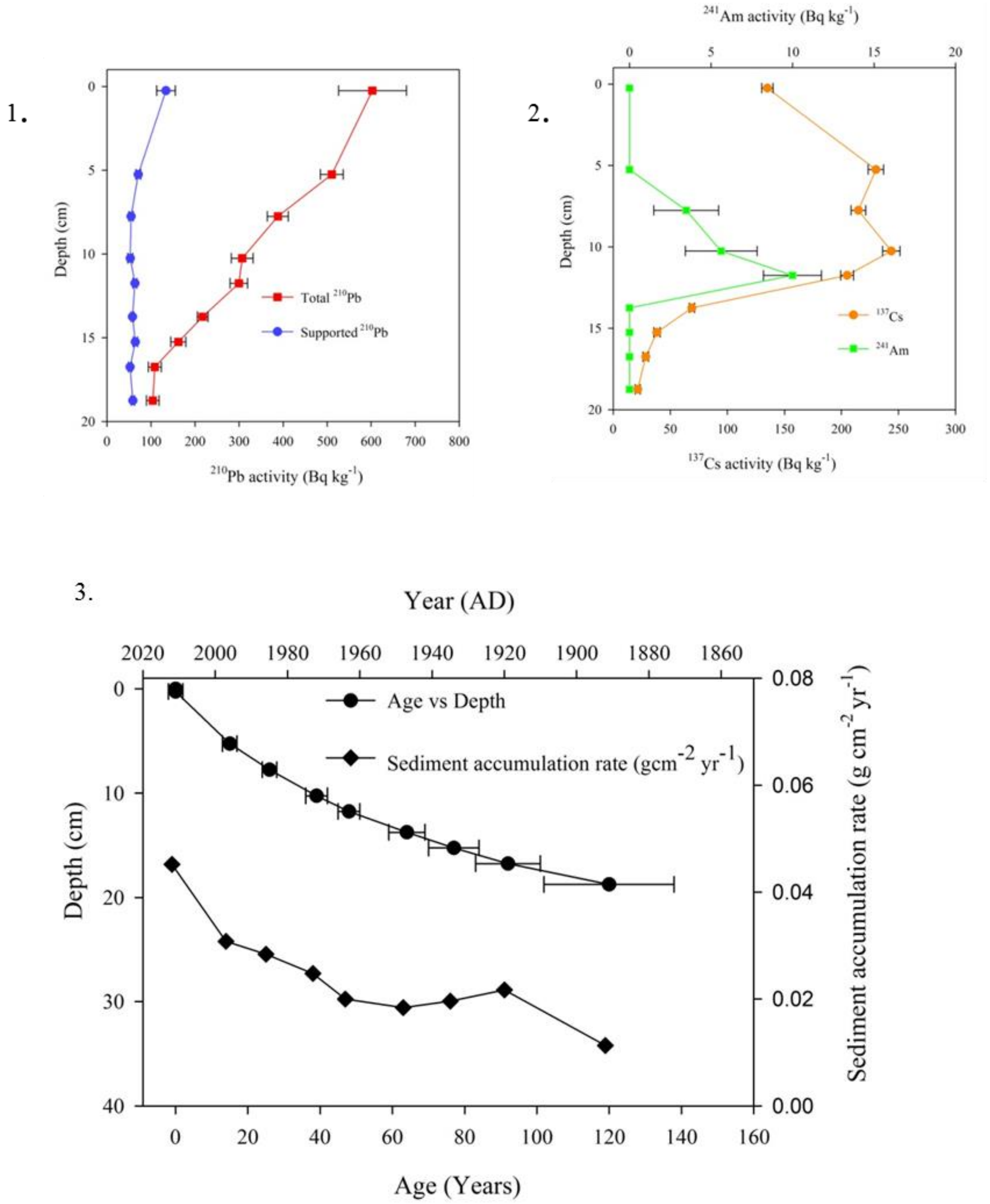


Figure 6.39 Changes in total and supported ^{210}Pb (1), ^{137}Cs and ^{241}Am activity (2), and CRS age-depth model and sediment accumulation rates for RYD$_{core}$ (3).

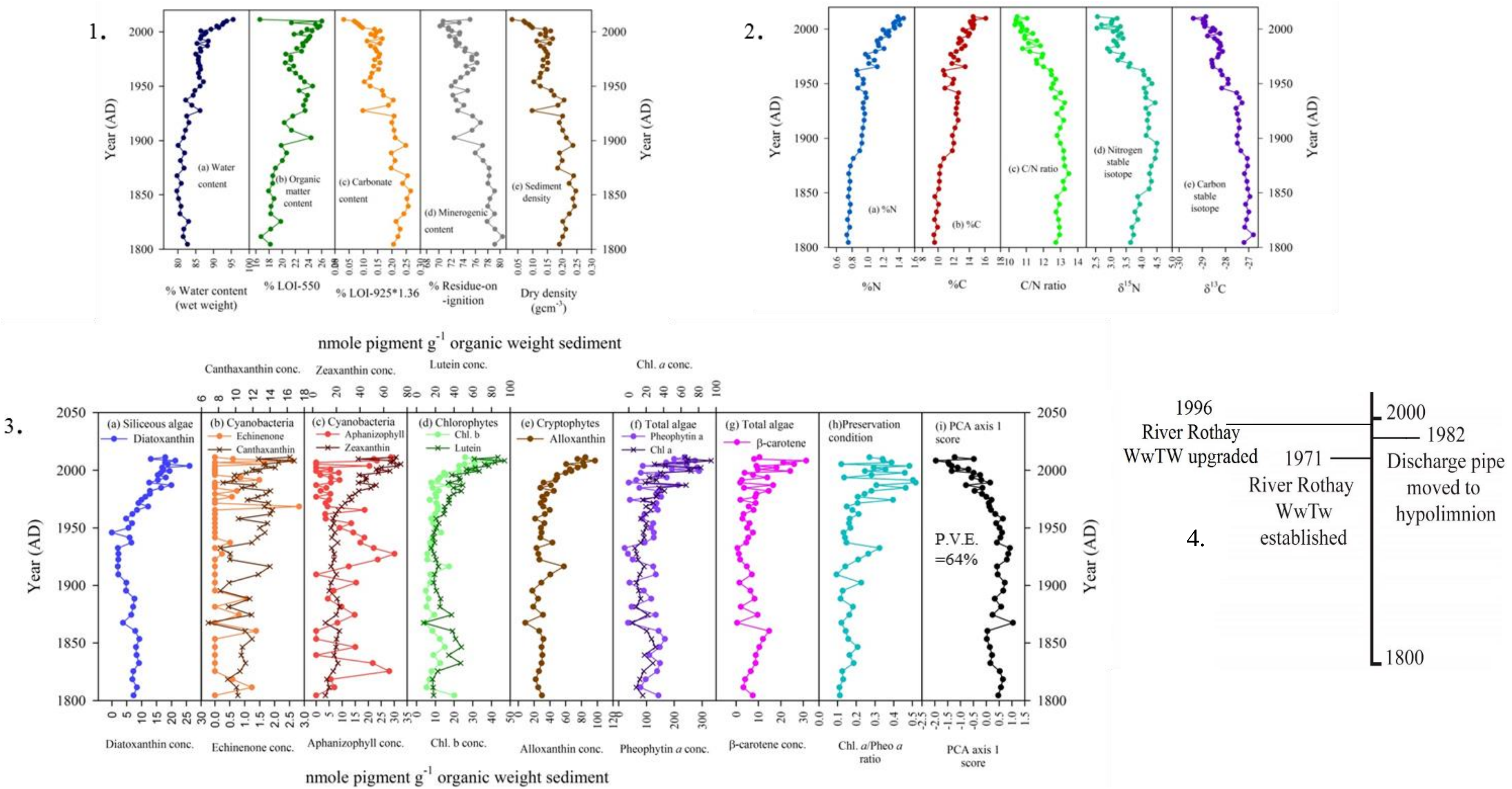


Figure 6.40 Changes in RYD$_{\text{core}}$ sediment lithology (1a-e), bulk organic C and N and their isotopes (2a-e), sedimentary chlorophylls and carotenoids (3a-g), pigment preservation condition (3h) and the PCA axis 1 scores (3i) from 1800 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the RYD$_{\text{site}}$ catchment from 1800 onwards (4).

6.16 Blelham Tarn (BLE$_{site}$). Lowland (42 m.a.s.l.)

Figure 6.41 Blelham Tarn from FBA boathouse, November 2011 (Photo: author), and location in Windermere catchment (red circle).

6.16.1 Field core description

The 77.5cm Mackereth core consisted of brown gyttja from the base to 30cm depth, with abundant macrofossils from 50 to 77.5cm. Above 30cm the sediment was darker brown, finer and more organic. The uppermost 1cm was composed of very floccy biofilm material.

6.16.2 Sediment chronology

Total ^{210}Pb and supported ^{210}Pb activity reached equilibrium at 43cm, and there were some irregular features in the exponential decrease in total ^{210}Pb activity indicating a non-monotonic sedimentation rate (Figure 6.42 (1)). Therefore the CRS model was used to develop the chronology. The 1963 peak of ^{137}Cs and ^{241}Am was identified at 25cm in agreement with the CRS age-depth model, but the depth of the CRS modelled 1986 at 16.5cm which was slightly deeper than the ^{137}Cs 1986 peak at 15cm (Figure 6.42 (2-3)). Mean SAR was the third lowest of all the lowlands in the Windermere catchment (Table 6.1). From 1890 the SAR slowly increased from 0.0275 g cm^{-2} yr^{-1} to a maximum in the 1980s of 0.1340 g cm^{-2} yr^{-1}, followed by a slight decline but maintenance at higher values (0.10-0.078 g cm^{-2} yr^{-1}) (Figure 6.42 (3)).

6.16.3 Sediment lithology

Mean OM content was relatively low, with mean carbonate content being the third lowest compared to other lowland sites in the Windermere catchment (Table 6.1). Water and OM content increased markedly after 1900 and even more so after 1996, reaching maximum values in 2011 (96% water and 37% OM content) (Figure 6-43 (1a-b)). Carbonate, minerogenic content and sediment density values decreased until ~1960, stabilised and then declined again after 1996 (Figure 6-43 (1c-e)).

6.16.4 Sediment C and N mass and stable isotopes

Mean C/N ratios were the highest, mean $\delta^{13}C_{org}$ the lowest and mean $\delta^{15}N_{org}$ the second lowest of all the lowlands in the Windermere catchment (Table 6.1). %N and %C values increased between 1800 to the late 1960s, stabilised until 1992 and then increased further (Figure 6-43 (2a-b)). C/N ratios increased from 13.3 in 1800 to 13.8 in 1900, before decreasing until the late 1960s where values stabilised ~11.9-12.2 (Figure 6-43 (2c)). $\delta^{15}N_{org}$ increased from 3.3‰ in 1800 to reach 4.5‰ in 1965, with values declining afterwards (fluctuating between 3.8-4.2‰) (Figure 6-43 (2d)). $\delta^{13}C_{org}$ steadily decreased from -28.6 to -29.5‰ in the early 1990s, then decreased to -31.5‰ by 2011 (Figure 6-43 (2e)).

6.16.5 Sedimentary pigments

Mean total algal (β-carotene) concentration was the median of all the lowlands in the Windermere catchment (Table 6.1). Most sedimentary pigments increased post-1950 (Figure 6-43 (3)). Clear increases in pigments from diatoms (diatoxanthin), chlorophytes (Chl. b, lutein) and total algae (β-carotene) occurred after 1900, and there was a decline in the water clarity index and PCA axis 1 scores from this time (68% variance explained) (Figure 6-43 (3a-h/j)). After 1963, diatoxanthin concentrations declined and cyanobacterial pigments increased markedly, with echinenone and aphanizophyll concentrations reaching maximum values by the late 1970s (Figure 6-43 (3ac)). Cyanobacterial pigments declined after 1996, whereas all other pigments increased, and the preservation conditions improved (Figure 6-43 (3)).

6.16.6 Historical records

Sewage infrastructure in the catchment consisted of earth closets and cess pits until the early 20th century, when septic tanks were introduced (Haworth, 1984). Piped water was installed at the hamlet of Outgate in 1951, which led to the overflowing of septic tanks and the subsequent nutrient enrichment of Ford Wood Beck, the tarn's main inflow (Figure 6-43 (4)) (Lund, 1972). Effluent was recognised in the watercourses by local residents in the late 1950s (North Lonsdale Rural District Council sewage documents, letters from local residents to council, 1957 and 1958). In 1962, a small sewage plant was installed to process effluent from Outgate, with the outfall directed into Ford Wood Beck (Haworth, 1984). The catchment land use became dominated by permanent grass (72% by 1988), followed by rough grazing (21% by 1988) after the reduction in temporary grassland in 1881 and woodland cover in 1901 (Figure 6.44 (1)). Livestock densities increased most in the latter half of the 20th century, although like EST_{site}, sheep densities were lower than elsewhere in the catchment (Figure 6.27 (2); Figure 6.44 (2)). The resident population of the parishes of Hawkshead and Claife peaked both in 1841 and in 2001 (at 0.39 and 0.47 individuals per ha, respectively) (Figure 6.44 (3)).

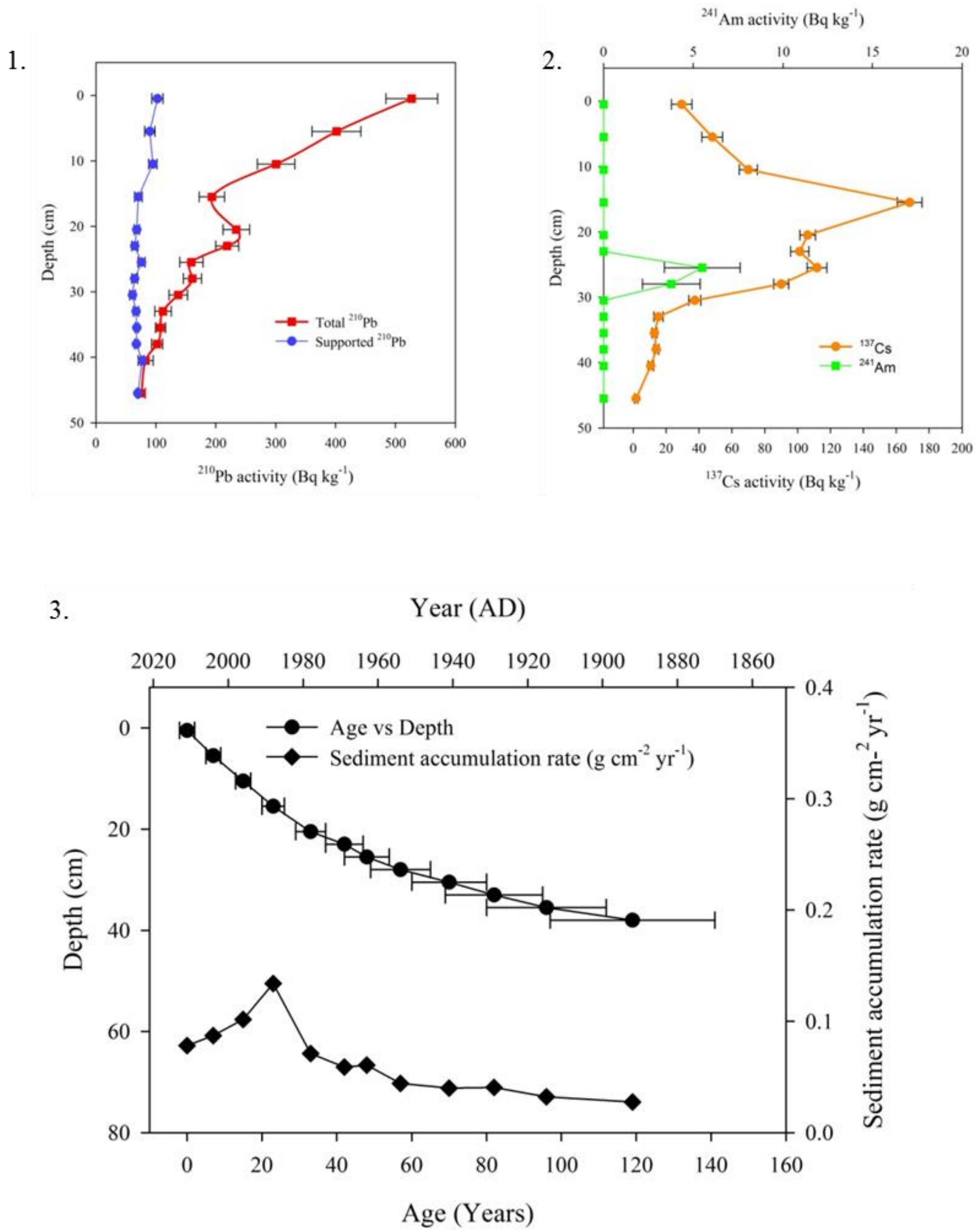


Figure 6.42 Changes in total and supported ^{210}Pb (1), ^{137}Cs and ^{241}Am activity (2) and CRS age-depth model and sediment accumulation rates for BLE$_{core}$ (3).

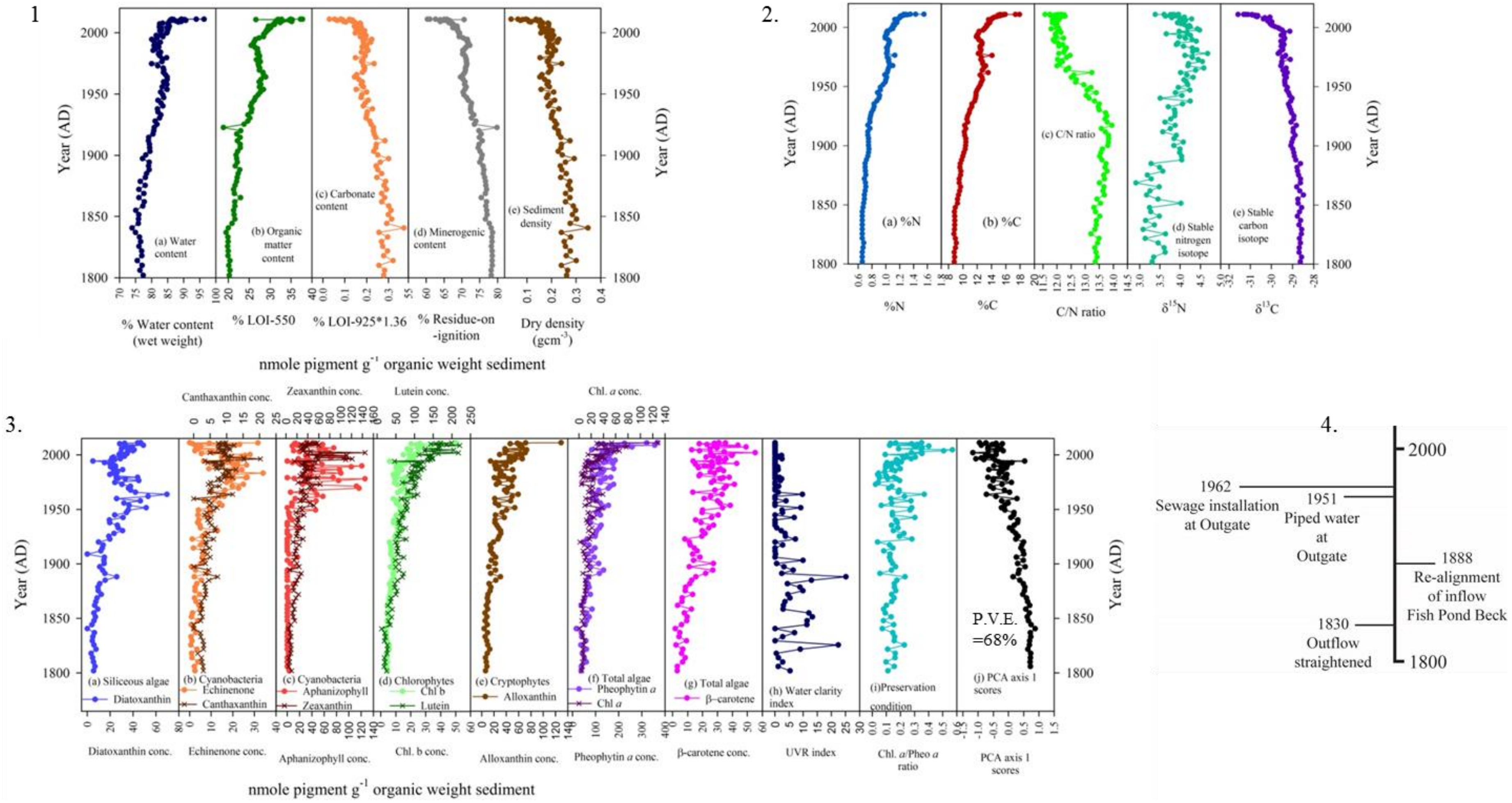


Figure 6-43 Changes in BLE$_{core}$ sediment lithology (1a-e), bulk organic C and N and their isotopes (2a-e), sedimentary chlorophylls and carotenoids (3a-g), water clarity (3h), pigment preservation condition (3i) and the PCA axis 1 scores (3j) from 1800 onwards. Timeline of potential anthropogenic drivers of lake ecosystem change in the BLE$_{site}$ catchment from 1800 onwards (4).

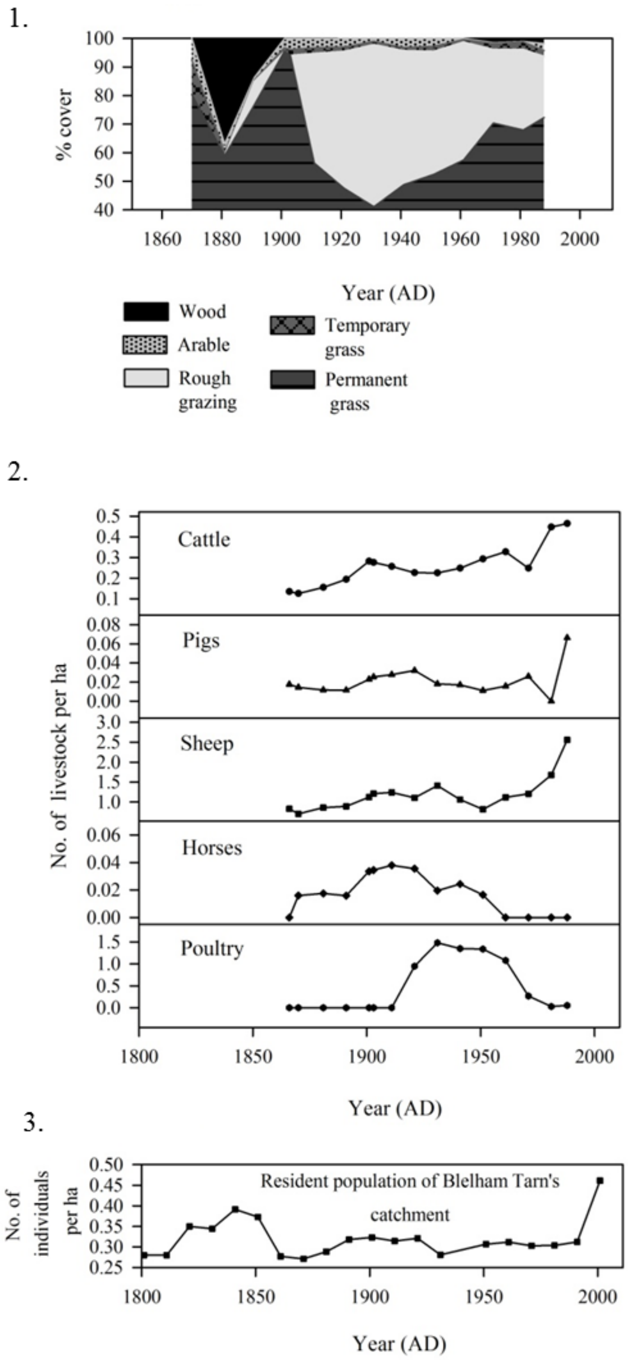


Figure 6.44 Changes in BLE_{site} catchment land use (1), livestock densities (2), and resident human population (3).

6.17 Summary

The results from the thirteen basins showed changes to the sedimentary lithology, isotopes and pigments from 1800 to the present or, where dating was not undertaken (BT_{core}, $ELTMID_{core}$, $ELTOUT_{core}$, LLT_{core}), the full core length. Different averages of sediment variables further documented the unique basin baseline conditions (Table 6.1).

All dated cores required the extrapolation of the chronology from the lowest depth at which $^{210}Pb/^{137}Cs$ was recorded (often just before 1900) to the year 1800, which relied on the assumption of uniform radionuclide supply and sediment accumulation (Battarbee *et al.*, 2002b). Validating ^{210}Pb derived chronologies using ^{137}Cs and ^{241}Am stratigraphic markers helped to reduce the uncertainty of the age-depth models for BLE_{core}, EAS_{core}, EST_{core}, RYD_{core} and STI_{core}. However, the lower sample size and exclusion of ^{241}Am testing for CT_{core} and LOU_{core} have a greater potential error associated with validating the ^{210}Pb chronology with ^{137}Cs activity alone. For $ELTIN_{core}$ and $GRA_{core,}$ the room for error on interpolating dates from ^{137}Cs alone is even greater, but validation of these chronologies using age equivalence techniques found good correspondence and thus, gave greater confidence in the chronologies. In addition, comparison between SARs of this study and those previously published in the region showed good agreement (Table 6.2).

Understanding the nature of temporal and spatial patterns of algal community change across the Windermere catchment required a synthesis of the raw data presented in this chapter and it is this synthesis which is presented in the following chapter.

Table 6.1 Summary of sediment proxies from 1800 onwards or full core length (cm). Upland sites (>100 m.a.s.l) shaded red; lowland sites (<100 m.a.s.l.) shaded blue.

Core	$\bar{x}$ sedimentation rate (gcm^{-2}yr^{-1})	± SE	$\bar{x}$ OM content (%LOI$_{550}$)	± SE	$\bar{x}$ CaCO$_3$ Content (%LOI$_{925}$*1.36)	± SE	$\bar{x}$ C/N ratio	± SE	$\bar{x}$ $\delta^{13}C_{org}$ (‰)	± SE	$\bar{x}$ $\delta^{15}N_{org}$ (‰)	± SE	$\bar{x}$ β-carotene conc. (nmole pigment g^{-1} organic weight sediment)	± SE
STI$_{core}$	0.019	0.002	27.056	0.581	0.213	0.004	21.252	0.440	-27.800	0.065	2.059	0.097	0.062	0.044
CT$_{core}$	0.011	0.008	39.768	0.758	3.966	0.370							3.360	1.166
EAS$_{core}$	0.017	0.002	30.240	0.497	0.179	0.005	17.597	0.145	-27.899	0.061	1.762	0.074	0.960	0.170
BT$_{core}$			36.209	0.614	5.303	0.184							5.662	0.541
LLT$_{core}$			35.493	0.672	2.940	0.127							11.007	0.455
LOU$_{core}$	0.084	0.015	31.349	0.597	5.336	0.143							59.279	3.066
EST$_{core}$	0.122	0.020	23.014	0.235	0.228	0.004	14.114	0.040	-29.117	0.029	4.206	0.026	25.222	0.908
GRA$_{core}$	0.148	0.008	21.816	0.481	4.502	0.097							17.305	2.106
ELTIN$_{core}$	0.156	0.006	31.487	0.708	3.916	0.090							49.231	2.819
ELTMID$_{core}$			35.364	0.491	3.729	0.085							14.052	0.768
ELTOUT$_{core}$			30.025	0.486	4.488	0.157							8.968	0.505
RYD$_{core}$	0.024	0.003	21.206	0.146	0.212	0.004	14.203	0.066	-27.428	0.042	3.252	0.038	5.021	0.345
BLE$_{core}$	0.065	0.009	25.644	0.333	0.278	0.005	15.445	0.093	-29.174	0.057	3.533	0.052	16.524	1.019
WNB$_{core}$	0.124	0.019	14.290	0.208			13.393	0.058	-27.397	0.055	4.954	0.032	12.491	0.695
WSB$_{core}$	0.084	0.007	17.245	0.136			12.835	0.063	-27.145	0.047	5.186	0.039	25.020	1.314

Table 6.2 Comparison of dry bulk sediment accumulation rates (SARs) from this study (shaded grey) and others.

Site	Range of SARs ($g\ cm^{-2}\ yr^{-1}$ unless otherwise documented)	Mean SAR ($g\ cm^{-2}\ yr^{-1}$)	Reference
Upland			
STI	0.01-0.03		
CT	0.002-0.04		
EAS	0.003-0.03		
Burnmoor Tarn		$0.07cm^{-1}\ yr^{-1}$	(Chiverrell, 2006)
Red Tarn		$0.09cm^{-1}\ yr^{-1}$	(Chiverrell, 2006)
Lowland			
LOU	0.02-0.1		
EST	0.03-0.3		
GRA	$0.02\text{-}0.2cm^{-1}\ yr^{-1}$		
ELTIN	$0.09\text{-}0.2cm^{-1}\ yr^{-1}$		
RYD	0.01-0.05		
BLE	0.02-0.1		
EST		0.06	(Dong *et al*., 2011)
GRA		0.04	(Barker *et al*., 2005)
BLE	0.04-0.1		(van der Post *et al*., 1997)
Windermere	0.01-0.05		(Appleby, 2001)
Windermere		0.12	(McGowan *et al*., 2012)
Cumbrian lakes (names not listed)	0.01-0.2		(Appleby, 2001)

CHAPTER 7. THE NATURE AND EXTENT OF ALGAL COMMUNITY CHANGE IN THE WINDERMERE CATCHMENT SINCE THE 19TH CENTURY

This chapter explores changes in the sedimentary algal communities of the Windermere catchment since 1800, and attempts to summarise the degree of change over this period, at both the individual site and the catchment spatial scales.

7.1 Catchment-scale trends in algal pigment concentrations over the last ~200 years

Different algal groups and species within those groups have different tolerances to physical (e.g. temperature) and chemical (e.g. P) variables and so their response to change in environmental conditions can help understand changes in their habitat (Reynolds, 1998). For instance, previous monitoring work in the English Lake District recorded increased cyanobacteria and diatom biomass in response to the same chemical stimuli (P) at BLE_{site}, GRA_{site}, WNB_{site} and $WSB_{site,}$ according to the timings of point nutrient inputs at each site (Reynolds, 1998). However, by investigating longer-term changes to more than one or two algal groups, the relative importance and spatio-temporal effects of multiple environmental drivers can be more easily examined. Therefore centennial-scale trends in pigment concentration are summarized in the following sections (7.1.1-7.1.7), results are given in alphabetical order.

7.1.1 Alloxanthin (cryptophytes)

All lakes (apart from the three highest upland tarns) had significant ($p<0.05$) positive Mann-Kendall trends for alloxanthin, suggesting cryptophyte populations increased in these lakes over the last ~200 years. This is supported by late 20th century monitoring work which found increased cryptophyte populations in Windermere in recent decades (Feuchtmayr *et al*., 2012) (Figure 7.1). Cryptophytes are spring-blooming algae that thrive in low light conditions. Thus, increases in their concentrations point to decreased light conditions perhaps caused by shading of other planktonic, spring-blooming algae such as diatoms, under prolonged growing seasons (Gervais, 1997; Thackeray *et al.*, 2008). In addition, cryptophytes are potentially mixotrophic taxa so are adapted to high nutrient waters due to their ability to feed on particulate matter from autochthonous material or bacteria (Findlay *et al.*, 2001). Increased lake nutrient content and temperatures in the Windermere catchment could have caused the increase in spring-blooming algae such as cryptophytes. This hypothesis is supported by higher algal production as indicated by positive Mann-Kendall trends for β-carotene (total algae) and positive Mann-Kendall trends for spring-blooming diatoms (diatoxanthin) in the lowland lakes, and increased regional temperatures from 1800 (Figure 6.1 (1); Figure 7.3; Figure 7.5).

In the Qu'Appelle lakes, Canada, cryptophytes increased in the latter half of the 20th century due to the prolonged spring growing season caused by increased temperatures, which resulted in decreased ice cover, increased thermal stratification and disequilibrium of herbivore zooplankton population from its algal food source, alongside nutrient enrichment from urban development (George *et al.*, 2000; Patoine and Leavitt, 2006). However, past work found *Cryptomonas* spp. in four lakes in the Windermere catchment responded stochastically to temperature changes and soluble reactive phosphorus (SRP) concentrations, pointing more to zooplankton abundance controlling populations; a factor which has been linked to temperature (George *et al.*, 2010; Feuchtmayr *et al.*, 2012). Short-term climatic variability may have modified seasonal to annual cryptophyte populations, but the longer-term increases in temperature and nutrient enrichment in the lowland lakes could have caused the centennial-scale positive trends of these algae (Winder and Schindler, 2004).

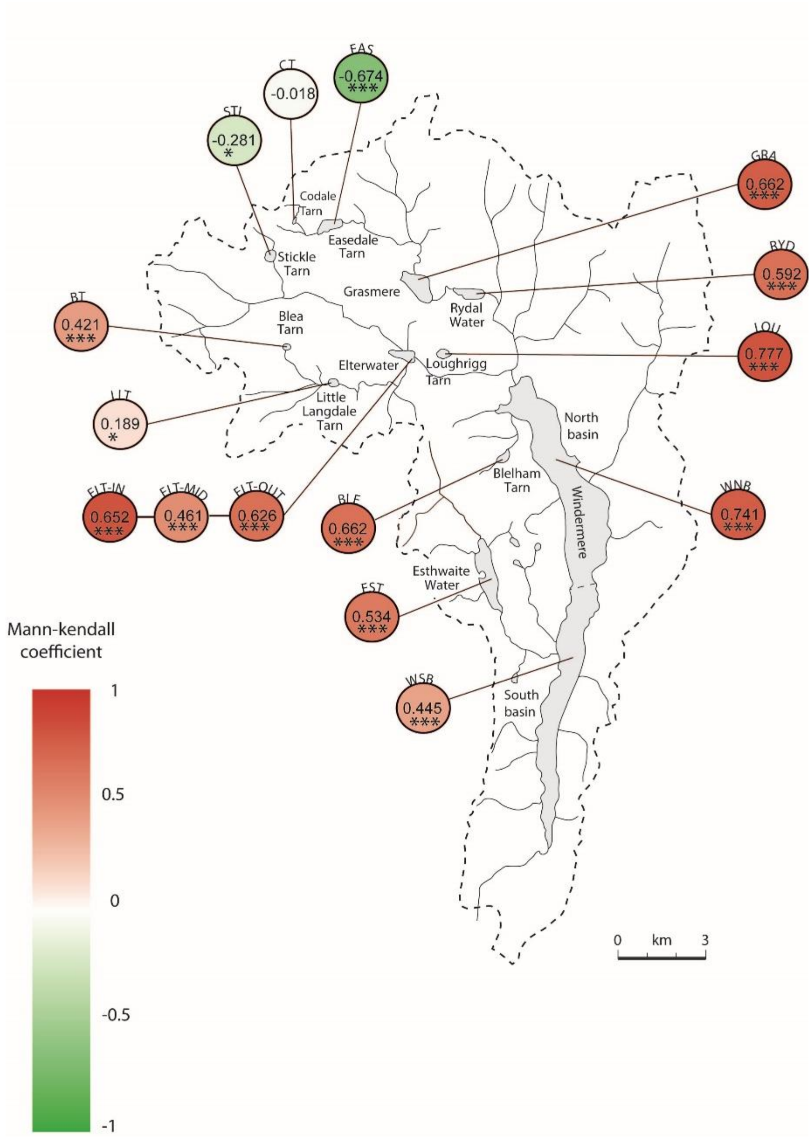


Figure 7.1 Map of lakes in the Windermere catchment and strength of their sedimentary alloxanthin Mann-Kendall trends from 1800 onwards. Gradient of red tones indicates positive trends and green indicates negative. Two sided p-values of Mann-Kendall coefficients indicated by * in the circle as follows: if * absent =p>0.05. *=p<0.05. **=p<0.01. ***=p<0.001.

The significant ($p<0.05$) negative trends in the highest upland tarns, $\mathrm{STI}_{\mathrm{core}}$ and $\mathrm{EAS}_{\mathrm{core}}$, may point to the reversal from acidification in the late 20th century, which would have caused decreased light penetration and higher DOC content as pH increased, and may have reduced the habitat availability or competitive abilities for deeper-blooming cryptophytes (Sutcliffe and Carrick, 1988; George, 1997; Deblois *et al.*, 2013). This is evident by the decreasing alloxanthin pigments in these cores ~1950 onwards (Figure 6.6 (3e); Figure 6.14 (3e)). No direct evidence for the aforementioned mechanism exists however, except that acidified upland lakes across the UK have experienced increased DOC levels and changes in the diatom flora at STI_{site} and EAS_{site} towards more acid-tolerant taxa indicated recovery from acidification, which led to the assumption that DOC levels likely increased at these uplands (Evans and Monteith, 2001; Tipping *et al.*, 2002). Conversely, DOC concentrations have not been quantified at these particular sites and coupled with the observation that DOC levels are low in the Lake District compared to elsewhere in the UK, suggets a certain level of caution be applied to this hypothesis (Tipping *et al.*, 2000b). Elsewhere, in remote mountain lakes in Canada, low DOC from acidification shifted phototrophic community assemblages from planktonic crytophytes to deeper blooming cryptophyte taxa (Vinebrooke and Leavitt, 1999). Thus, even a small change in DOC could have been enough to shift the habitat availability of these taxa. Whereas in the Canadian shield lakes, increased water transparency from low pH led to increased deeper phytoflagellates including cryptophytes, who used their motility to avoid harmful UVB radiation (Vinebrooke *et al.*, 2002). The pH changes recorded in these studies were much lower than those inferred at EAS_{site} and STI_{site} however (Tipping *et al.*, 2002). Notwithstanding, the last few decades of diatom recovery from acidification recorded at these upland sites suggests that the competitive advantage of deeper-blooming cryptophytes was likely reduced, a hypothesis which is supported by the decreasing alloxanthin concentrations from ~1950 at STI_{core} and EAS_{core} and evidence of acidification effects on algal communities elsewhere (Figure 6.6 (3e); Figure 6.14(3e)).

7.1.2 Aphanizophyll (filamentous cyanobacteria)

All but three lakes (EAS_{core}, RYD_{core}, and GRA_{core}) showed significant ($p<0.05$) increased filamentous cyanobacterial (aphanizophyll) population trends over the last ~200 years in the Windermere catchment (Figure 7.2). Filamentous cyanobacteria dominate in turbid, warmer, stable and nutrient enriched conditions (Scheffer *et al.*, 1997). Thus, a shift to these conditions in the Windermere lakes since 1800 would have promoted these taxa. This hypothesis is reinforced by previous research undertaken at WNB_{site}, WSB_{site}, BLE_{site} and $EST_{site,}$ which found increased nutrient enrichment and longer stratification length at these sites had increased filamentous cyanobacterial growth (Foley *et al.*, 2012; Maberly and Elliott, 2012; McGowan *et al.*, 2012; Reynolds *et al.*, 2012). Cyanobacterial carotenoids increased at EST_{site} in the early 20th century and corresponded to increased enrichment (Griffiths, 1978). But in the late 1970s, lower concentrations were found in sediments attributed to other algae outcompeting filamentous cyanobacteria as enrichment progressed. This may explain the low, non-significant ($p>0.05$) trend at EST_{core} and the different Mann-Kendall coefficients of the lowlands according to the difference in scale and timing of cultural eutrophication.

The upland basins BT_{core}, LLT_{core} and STI_{core} show increasing trends similar to the lowland ELT basins and WSB_{core}, albeit STI_{core} was not significant ($p>0.05$). Filamentous cyanobacteria are well-adapted to low light, high N:P ratios and decreased lake turnover from lake warming (Posch *et al*., 2012). High N deposition and increased lake temperatures found in the lowland lakes may also have led to the aforementioned conditions which favour filamentous cyanobacteria in the upland lakes too (McGowan *et al*., 2012; Foley *et al*., 2012).

Interestingly, two lakes (EAS_{core} and GRA_{core}) showed progressively higher, significant ($p<0.05$) negative trends down the hydrological chain, whereas RYD_{core} showed a much lower non-significant negative trend. This could be due to the low WRT (<100 days) of these sites as filamentous cyanobacteria are favoured under stable, stratified conditions (Posch *et al*., 2012). However, negative trends are not seen at other sites with low WRTs such as BLE_{core}. The negative trends may therefore be caused by a complex interaction between thermal stratification, N:P ratios and predation (Posch *et al*., 2012).

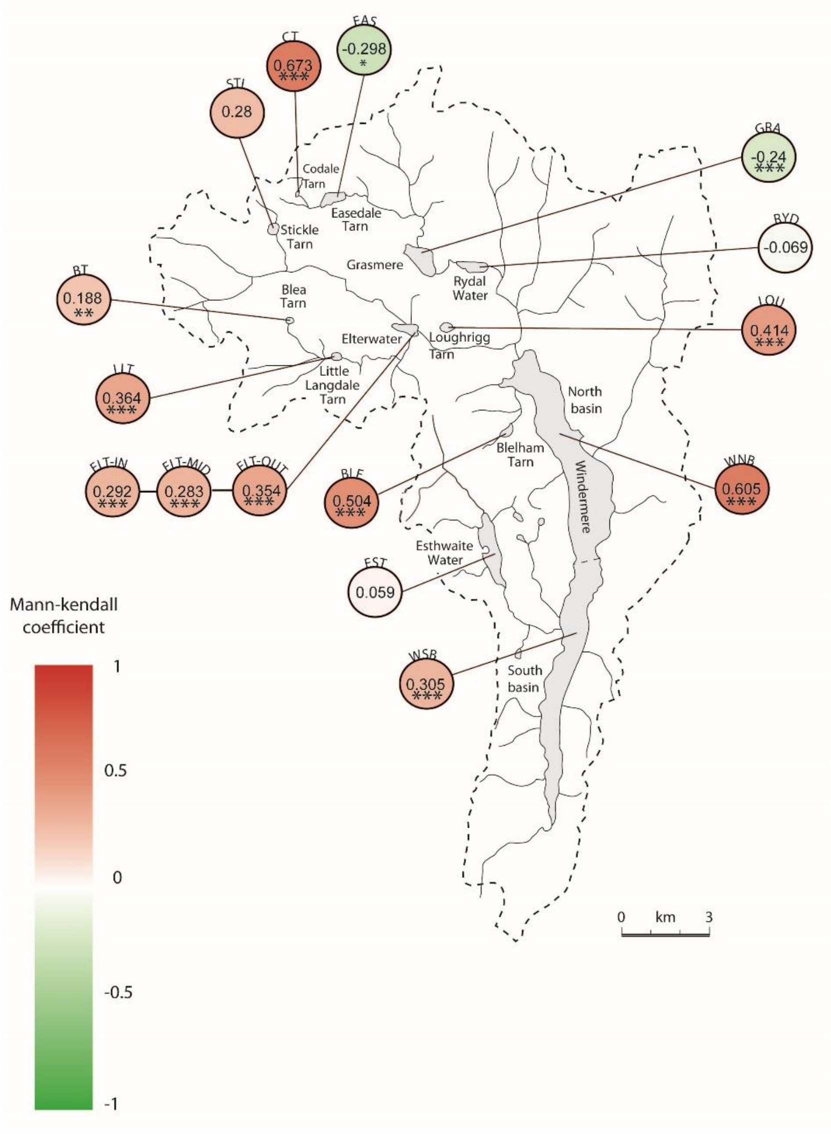


Figure 7.2 Map of lakes in the Windermere catchment and strength of their sedimentary aphanizophyll Mann-Kendall trends from 1800 onwards. Gradient of red tones indicates positive trends and green indicates negative. Two sided p-values of Mann-Kendall coefficients indicated by * in the circle as follows: if * absent =p>0.05. *=p<0.05. **=p<0.01. ***=p<0.001.

7.1.3 β-carotene (total algae)

All lowland lakes apart from ELTMID$_{core}$ and ELTOUT$_{core,}$ had a significant (p<0.05) positive β-carotene trend coefficient, indicating a catchment-wide increase in total algal production since 1800 onwards (Figure 7.3). This was further supported by the declining C/N ratios in lake sediments throughout the catchment, which indicates more autochtonous OM production from 1800 onwards (see chapter 9). Previous work at Windermere attributed increased algal production to cultural eutrophication and increased temperatures (Elliott, 2012; McGowan *et al.*, 2012). These trends may have extended across the catchment, with the different nutrient sources and scales of nutrient-climate interactions causing the different positive Mann-Kendall coefficients for total algal production (β-carotene) at each lake.

There was a difference in the direction of trends between the upland lakes with increasing trends at BT_{core} ($p>0.05$, non-significant), LLT_{core} ($p<0.05$, significant) and CT_{core} ($p<0.05$, significant) but decreasing trends at EAS_{core} ($p<0.05$, significant) and STI_{core} ($p>0.05$, non-significant). This may relate to the difference in spatial recovery from acidification from the late 20th century, which in lakes with decreasing β-carotene trends, would have undergone decreased water transparency from increased DOC influx and surpressed phototrophic production (Vinebrooke *et al*., 2003). It may also relate to subtle differences in productivity at these oligotrophic upland sites. Difference in basin degradation of β-carotene is unlikely as it is the most stable ubiquitous pigment (Leavitt and Carpenter, 1990).

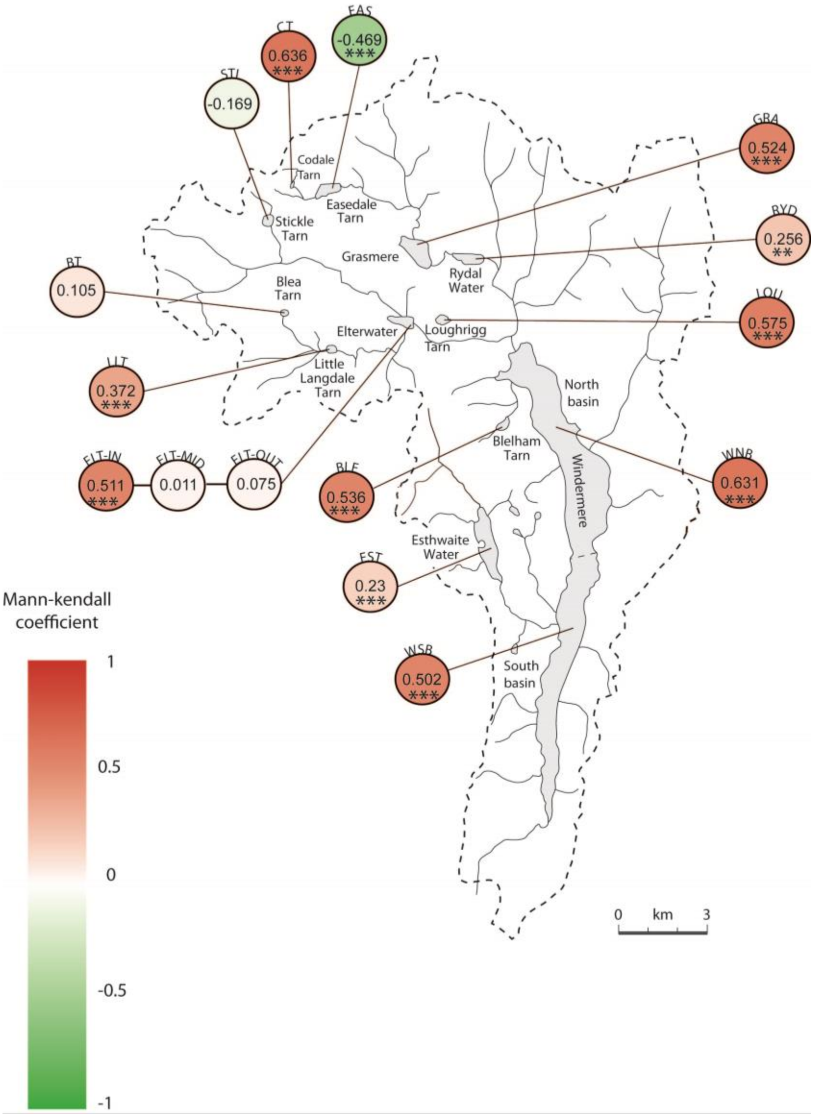


Figure 7.3 Map of lakes in the Windermere catchment and strength of their sedimentary β-carotene Mann-Kendall trends from 1800 onwards. Gradient of red tones indicates positive trends and green indicates negative. Two sided p-values of Mann-Kendall coefficients indicated by * in the circle as follows: if * absent =p>0.05. *=p<0.05. **=p<0.01. ***=p<0.001.

7.1.4 Canthaxanthin (colonial cyanobacteria)

All lakes with significant (p<0.05) trends had positive coefficients, indicating increased concentrations of canthaxanthin and so, populations of colonial cyanobacteria over the last ~200 years in the Windermere catchment (Figure 7.4). Colonial cyanobacteria, much like filamentous forms, dominate in nutrient enriched lakes, and again suggest progressive centennial-scale eutrophication of lakes in the Windermere catchment (Smith, 1983; Reynolds, 1984; Schindler, 1988). Increased colonial cyanobacteria populations such as *Microcystis* spp. were documented in the lowland lakes BLE_{site} and EST_{site} in response to eutrophication and more stable hydrological conditions from increased summer temperatures (Lund, 1972; Lund, 1978).

The non-significant negative trends of BT_{core}, $ELTMID_{core}$ and $ELTOUT_{core,}$ suggest environmental conditions more suitable to cyanobacteria groups of different structures and organisations as shown by the positive trends of filamentous and total cyanobacterial pigments (aphanizophyll, zeaxanthin) at these sites (Figure 7.2; Figure 7.7). Certain colonial species are more susceptible to disturbance from wind-induced turbulence or hydrological flushing which break up the colonies and disrupt their diel migration (Mur *et al*., 1999). For example, $ELTOUT_{site}$ receives 98% of the hydraulic loading of the 3 basins and so, is susceptible to hydraulic flushing which is unfavourable to colonial cyanobacteria (Goldsmith *et al*., 2003).

Alternatively, the different nutrient loading mechanisms of each basin may have selected against different algal groups at BT_{site}, $ELTMID_{site}$ and $ELTOUT_{site}$. For instance, delivery of nutrients to $ELTMID_{site}$ is restricted to sporadic inflow from $ELTIN_{site}$ and nutrient re-release from the sediments (Goldsmith *et al.*, 2003; APEM, 2012). Monitoring undertaken at ELT_{site} found cyanobacteria populations were low at $ELTMID_{site}$ in 2011 due to strong stratification from high summer temperatures (APEM, 2012). This had prevented nutrients being released from the sediments and subsequently mixed within the water column available for algal growth above the thermocline for summer-blooming algae such as colonial cyanobacteria (APEM, 2012). This highlights the complex relationship between climate, timing of lake turnover, hydraulic connectivity, mode of nutrient delivery and its effect on algal group succession even within the same lake, albeit in different basins.

At EAS_{core} however, the non-significant ($p>0.05$) negative trend corresponded to other negative carotenoid trends and again, could point to recovery from acidification and a shift from deeper colonial cyanobacteria to planktonic production (Vinebrooke and Leavitt, 1999).

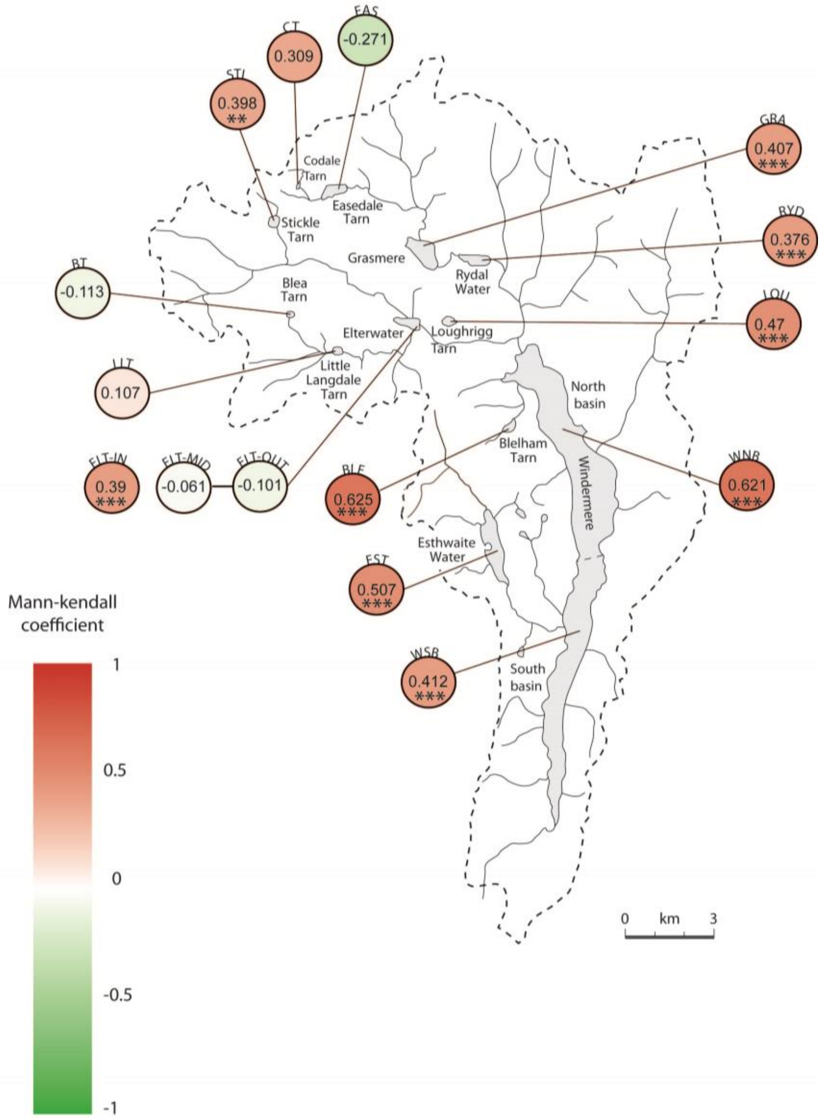


Figure 7.4 Map of lakes in the Windermere catchment and strength of their sedimentary canthaxanthin Mann-Kendall trends from 1800 onwards. Gradient of red tones indicates positive trends and green indicates negative. Two sided p-values of Mann-Kendall coefficients indicated by * in the circle as follows: if * absent =p>0.05. *=p<0.05. **=p<0.01. ***=p<0.001.

7.1.5 Diatoxanthin (siliceous algae)

Significant ($p<0.05$) trends for diatoxanthin were positive in the lowlands and negative in the upland sites, BT_{core}, STI_{core} and EAS_{core}, indicating spatial differences in the diatom trends across the Windermere catchment since 1800 (Figure 7.5).

The complex interaction between flushing rates, nutrient loading from bedrock geology and catchment land use of these basins since 1800 could have caused this spatial difference. Si is an essential ion or nutrient required by all algae but is a major nutrient for diatoms, along with N and P (Officer and Ryther, 1980). Si is often delivered to a water body through land weathering, and thus difference in geology could lead to variation in Si availability (Officer and Ryther, 1980). All upland sites with negative trends overlay BVG bedrock and thus, have naturally lower major ion content and so, Si in their waters. In addition, these upland sites have minimal human catchment land use and so, low Si delivery (Officer and Ryther, 1980). Past work in the lowlands of the catchment documented a relationship between wet winters and low inoculum of the diatom *A. formosa* attributed to high rates of hydrological renewal (Reynolds and Irish, 2000). The low WRTs (<100 days) would mean the effects of flushing and so, Si and other nutrient removal would be more pronounced at these upland sites (Kadiri and Reynolds, 1993).

However, the positive, significant ($p<0.05$) trends of diatoxanthin of the lowland lakes could indicate that high nutrient loadings from sewage and/or agricultural activity in their catchments led to increased diatom production over the last ~200 years despite differences in bedrock geology and WRTs (Table 2.1; Figure 8.3 (a-k)). Si delivered to lakes via point and diffuse sources alongside bedrock weathering has been attributed to enhanced spring diatom growth, and may have occurred in the Windermere lowland lakes (Billen *et al*., 2001).

The Si depletion hypothesis suggests that as P concentrations increase, Si becomes increasingly depleted due to sedimentation of biogenic Si via diatom growth and deposition to the sediments (Schelske *et al*., 1986). However, competition from other algae for nutrients in the spring and flushing in wetter winters could have led to lower short-term annual/seasonal diatom populations and so, made nutrients available for summer-blooming species such as cyanobacteria (which showed positive trends in these lowlands), which would have ensured P remained the limiting nutrient to diatom growth rather than Si (Billen *et al*., 2001). In summary, lake fertilisation from cultural eutrophication increased centennial-scale spring diatom growth in the lowlands, but P-limitation and low WRTs in the oligotrophic upland sites led to decreased diatom abundance.

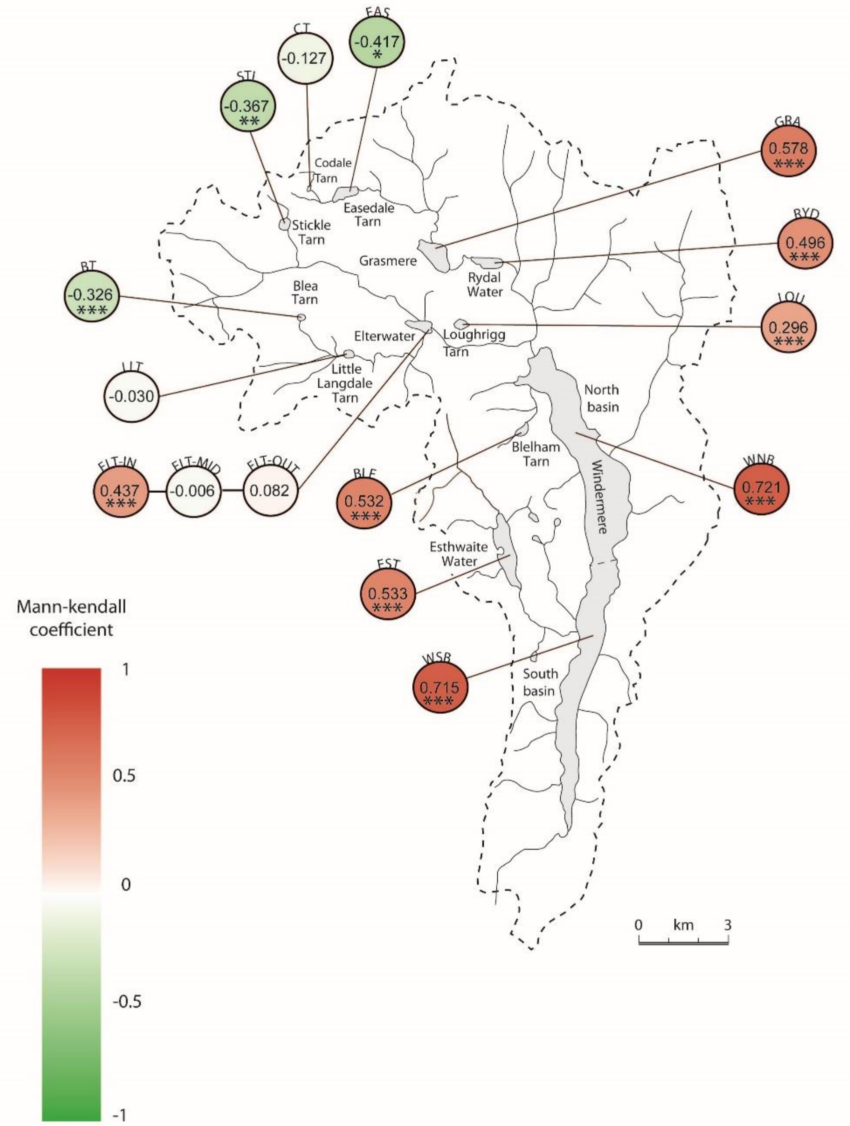


Figure 7.5 Map of lakes in the Windermere catchment and strength of their sedimentary diatoxanthin Mann-Kendall trends from 1800 onwards. Gradient of red tones indicates positive trends and green indicates negative. Two sided p-values of Mann-Kendall coefficients indicated by * in the circle as follows: if * absent =p>0.05. *=p<0.05. **=p<0.01. ***=p<0.001.

7.1.6 Lutein (chlorophytes)

All but four lakes had significant (p<0.05) positive trends in sedimentary lutein indicating increased chlorophyte concentrations in the Windermere catchment over the last ~200 years (Figure 7.6). The upland EAS_{core} was the only site to have a significant ($p<0.05$) negative trend. Chlorophytes, much like cyanobacteria, have a range of physiological traits and environmental tolerances and increased populations are often symptomatic of increased nutrient enrichment (Happey-Wood, 1988; Cottingham and Carpenter, 1998). Thus, the increase in this group across the catchment again points to increased nutrient enrichment from 1800 onwards.

The negative trend of lutein at EAS_{core} could relate to recovery from acidification in the late 20th century. Lower pH in the late 19th and early 20th centuries related to acidification and attendant increased water transparency, could have increased abundances of filamentous green phytobenthos (Vinebrooke *et al*., 2002). The increased pH in the late 20th century would have reduced transparency and so, reduced phytobenthos growth, hence the decreased lutein concentrations from ~1950 onwards (Figure 6.14 (3d)).

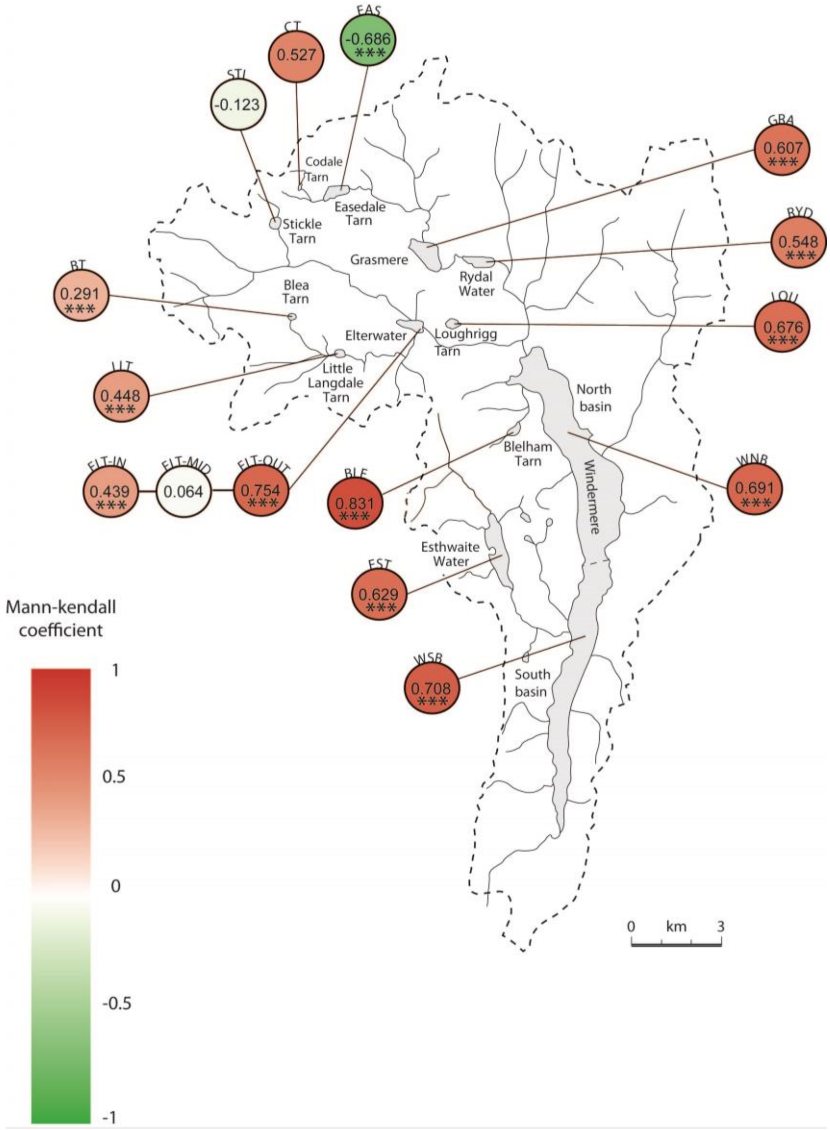


Figure 7.6 Map of lakes in the Windermere catchment and strength of their sedimentary lutein Mann-Kendall trends from 1800 onwards. Gradient of red tones indicates positive trends and green indicates negative. Two sided p-values of Mann-Kendall coefficients indicated by * in the circle as follows: if * absent =p>0.05. *=p<0.05. **=p<0.01. ***=p<0.001.

7.1.7 Zeaxanthin (all cyanobacteria)

Most lakes had significant ($p<0.05$) positive cyanobacterial zeaxanthin trends from 1800 onwards, apart from the two upland sites, STI_{core} and $\text{EAS}_{\text{core},}$ which had significant ($p<0.05$) negative trends (Figure 7.7). This suggests total cyanobacterial production increased across most of the Windermere catchment from 1800 onwards. Increased zeaxanthin concentrations and other cyanobacterial pigments corresponded to nutrient enrichment in recent centuries at Windermere and other temperate lakes, including Lough Neagh (Engstrom *et al.*, 2006; Bunting *et al.*, 2007; McGowan *et al.*, 2012). Furthermore, increased trends in cyanobacterial pigments across northern temperate lakes have been attributed to centennial-scale lake fertilisation over the last ~200 years from human-mediated catchment changes (Taranu *et al.*, 2015).

The significant ($p<0.05$) negative trends of STI_{core} and EAS_{core} could be related to recovery from acidification within the latter half of the 20th century, which corresponded to the timing of declines in zeaxanthin concentrations at both these sites (Figure 6.6 (3c); Figure 6.14 (3c)). Deep-blooming, sediment-dwelling filamentous cyanobacteria are found when pH is low, but as lakes recover from acidity, decreased water transparency reduces the competitive advantages of these taxa, hence their negative trends (Leavitt *et al.*, 1997). Conversely small, non-significant increases in zeaxanthin were recorded in the other upland lakes (CT_{core}, BT_{core} and LLT_{core}) which could point to the role played by physical lake and catchment characteristics in filtering the effects of acidification and/or the influence of another environmental driver.

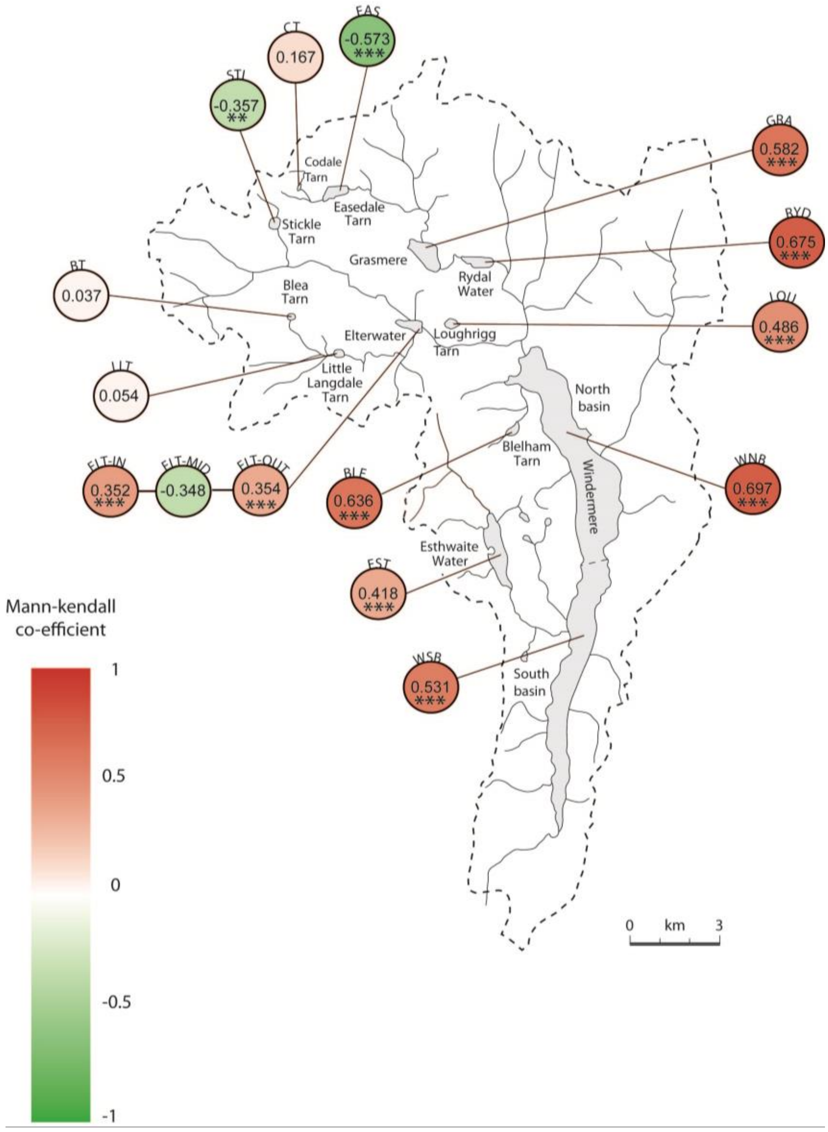


Figure 7.7 Map of lakes in the Windermere catchment and strength of their sedimentary zeaxanthin Mann-Kendall trends from 1800 onwards. Gradient of red tones indicates positive trends and green indicates negative. Two sided p-values of Mann-Kendall coefficients indicated by * in the circle as follows: if * absent =p>0.05. *=p<0.05. **=p<0.01. ***=p<0.001.

7.1.8 Summary

Algal pigment concentrations in lakes of the Windermere catchment had predominantly positive trends over the last ~200 years in most lakes excluding $\mathrm{STI}_{\mathrm{core}}$ and $\mathrm{EAS}_{\mathrm{core}}$ which had mainly negative trends (Table 7.1). Those trend coefficients which were not significant were probably due to co-variance or zero samples (Meals *et al*., 2011).

The dominant positive trends in the lowland lakes indicate regional lacustrine primary production has increased since 1800. Evidence from past work in the catchment suggests nutrient enrichment, climate-mediated changes to temperature, stratification length and grazing populations may have been the driving mechanisms for increased algal production (George *et al.*, 2000; Pickering, 2001; Tipping *et al.*, 2002). The extent to which aforementioned environmental drivers altered algal communities throughout the catchment were identified in the different spatial Mann-Kendall trend coefficients of the pigment concentrations.

In contrast, the upland lakes $\mathrm{STI}_{\mathrm{core}}$ and $\mathrm{EAS}_{\mathrm{core}}$ had mainly negative trends. Evidence from past work indicates this may be an effect of pH changes and climate-driven changes to flushing rates which may have resulted in lowering water transparency, altering nutrient stoichiometry and removing nutrients in these oligotrophic sites, resulting in decreased primary production (Maberly *et al*., 2002; Tipping *et al*., 2002). Drivers of these trends will be investigated in more detail in the following chapter.

Table 7.1 Summary of significant ($p<0.05$) Mann-Kendall trends (+ positive trend and - negative trend) in Windermere catchment lakes.

Lake	**Pigment**						
	alloxanthin	aphanizophyll	β-carotene	canthaxanthin	diatoxanthin	lutein	zeaxanthin
STI	-			+	-		-
CT		+	+				
EAS	-	-	-		-	-	-
BT	+	+			-	+	
LLT	+	+	+			+	
LOU	+	+	+	+	+	+	+
EST	+		+	+	+	+	+
GRA	+	-	+	+	+	+	+
ELTIN	+	+	+	+	+	+	+
ELTMID	+	+					
ELTOUT	+	+				+	+
RYD	+		+	+	+	+	+
BLE	+	+	+	+	+	+	+
WNB	+	+	+	+	+	+	+
WSB	+	+	+	+	+	+	+

7.2 Algal pigment synchrony in the Windermere catchment over the last ~200 years.

Similar year-to-year fluctuations in mean limnological properties, also termed synchrony (S), have been recorded in lakes within the same geographical region (Kratz *et al.*, 1998; Patoine and Leavitt, 2006) (see section 5.6). High degrees of S often relate to regional forcing mechanisms such as climate or widespread land use practices and/or when morphometry or landscape position are similar (Kratz *et al.*, 1998; Patoine and Leavitt, 2006). However, despite biological variables often having lower S on account of lake-specific factors, taxon-specific algal S was identified as a useful tool to assess whether local or regional mechanisms were driving algal community changes in the lakes of the Windermere catchment during different periods (Kratz *et al.*, 1998; Patoine and Leavitt, 2006).

7.2.1 Algal pigment synchrony in the 19th and 20th century

Mean S was highest for all pigments with significant p-values ($p \leq 0.05$) from 1800-2005 ($\bar{x}S=0.22$) compared to 1800-1905 ($\bar{x}S=0.07$), suggesting that 20th rather than 19th century algal community variability was driven by regional forcing mechanisms in the Windermere catchment (Figure 7.8). More specifically, it indicates that in the 19th century, limnological variability was driven by local-scale processes, but by the 20th century regional-scale forcings began to exert a greater effect especially on lakes with similar catchment and hydrological characteristics (Kratz *et al.*, 1998; Patoine and Leavitt, 2006). This can be further seen by the high (>0.5) Pearson's correlation coefficients of most lowland lakes for all but aphanizophyll, compared to the low (<0.2) coefficients of the upland lakes (STI_{core}, CT_{core} and EAS_{core}), particularly for the pigments alloxanthin, diatoxanthin and zeaxanthin (Figure 7.9).

Interestingly, summer taxa cyanobacteria and chlorophytes (canthaxanthin ($S=0.33$, $p \leq 0.05$)), lutein ($S=0.32$, $p \leq 0.05$)) were more synchronous than the spring-blooming diatoms (diatoxanthin ($S=0.15$, $p \leq 0.05$) from 1800-2005 (Figure 7.9 (d-f)). This differs to results found in Canadian lakes of the

Northern Great Plains over the last 15 years, where spring-blooming groups were more synchronous (mean S=0.43) as they were more constrained by regional climatic variability (ice cover length, thermal stratification), alongside increases in zooplankton grazers and thus, had similar fluctuations (Vogt *et al.*, 2011). In the same Canadian lakes, cyanobacteria populations were more asynchronous over the 20th century attributed to lake-specific factors such as nutrient concentrations (Downing *et al.*, 2001), trophic interactions (Elser, 1999) and light regime (Levine and Lewis, 1984; Patoine and Leavitt, 2006). In the Windermere catchment, regional-scale changes must have overridden the importance of local in promoting summer algae. These regional forcings could have been atmospheric N deposition and/or widespread land-use changes which could have resulted in lake fertilisation, or warmer temperatures and reduced summer precipitation, all drivers which have acted across the region (George *et al.*, 2007; McGowan *et al.*, 2012). This hypothesis is supported by work that found accelerated cyanobacterial production relative to vernal algae (diatoms) across the Northern Hemisphere due to lake fertilisation from 1800 (Taranu *et al.*, 2015). On a related note, the S values for Canadian and Windermere catchment lakes for non-labile phytoplankton pigments were comparable overall, although Canadian lakes were slightly higher (S=0-0.42), suggesting S values for Windermere lake pigments are only just lower than the normal range of synchroneity for phytoplankton groups, with the reasoning being discussed in section 7.2.3 (Patoine and Leavitt, 2006; Vogt *et al.*, 2011).

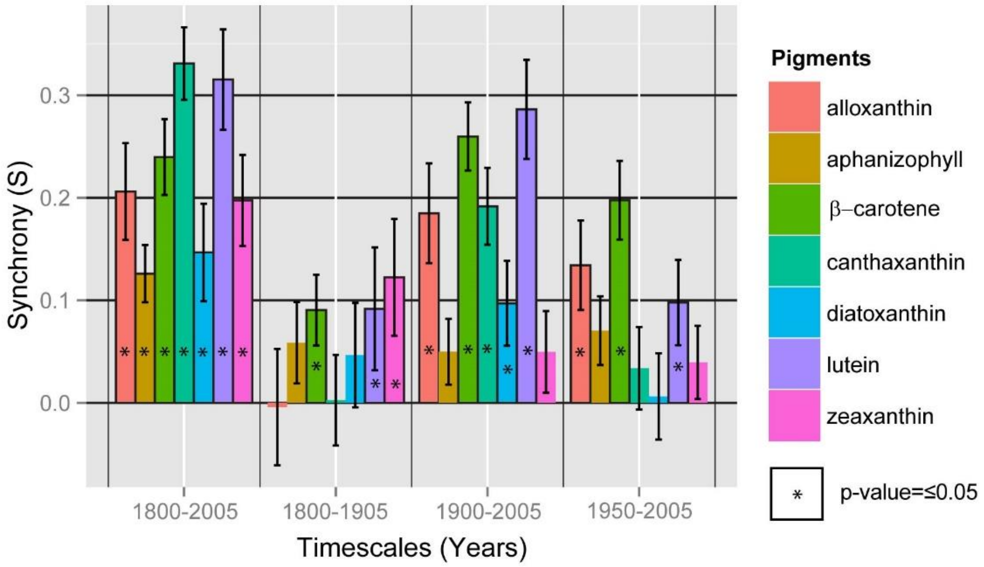
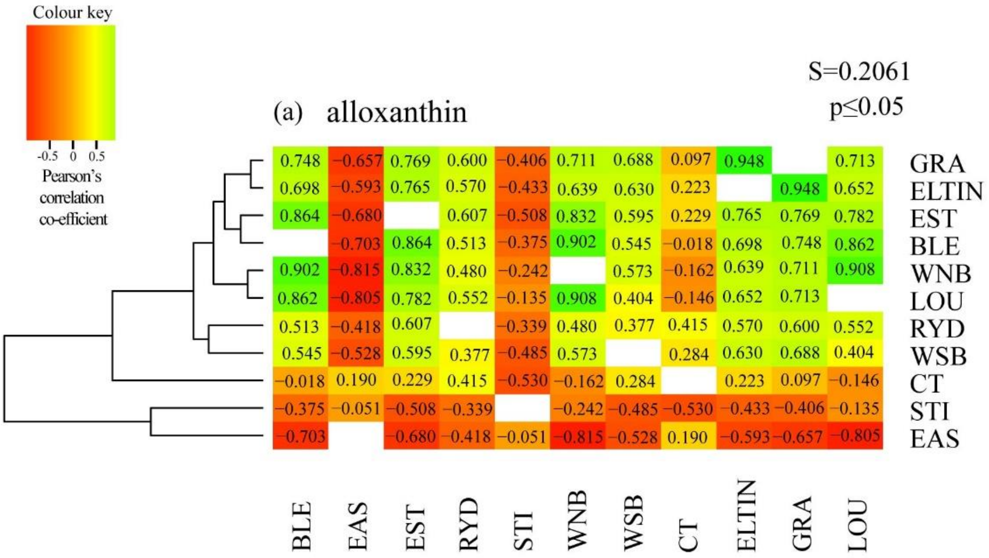
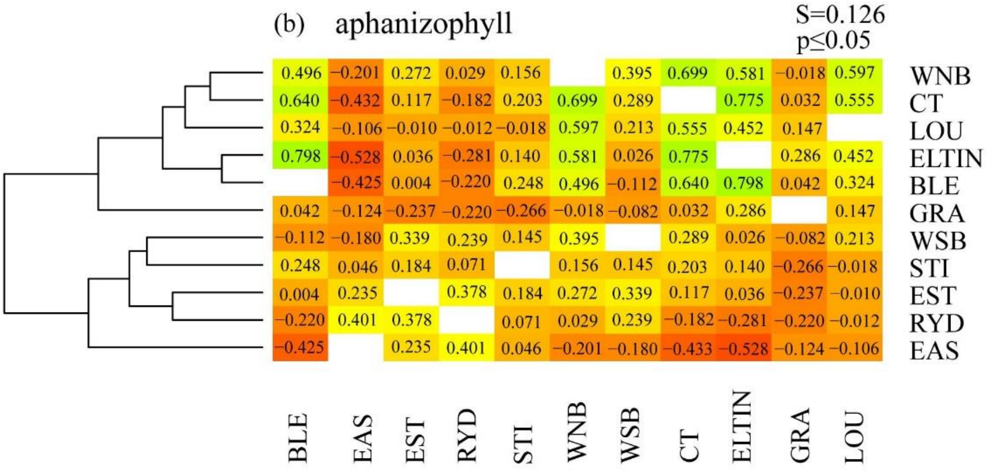


Figure 7.8 Bar chart of synchrony (S) values with SE bars, for seven sedimentary algal pigments for all lakes with chronologies from the Windermere catchment across different timescales. Bars with black outline and * have significant (p≤0.05) S values.

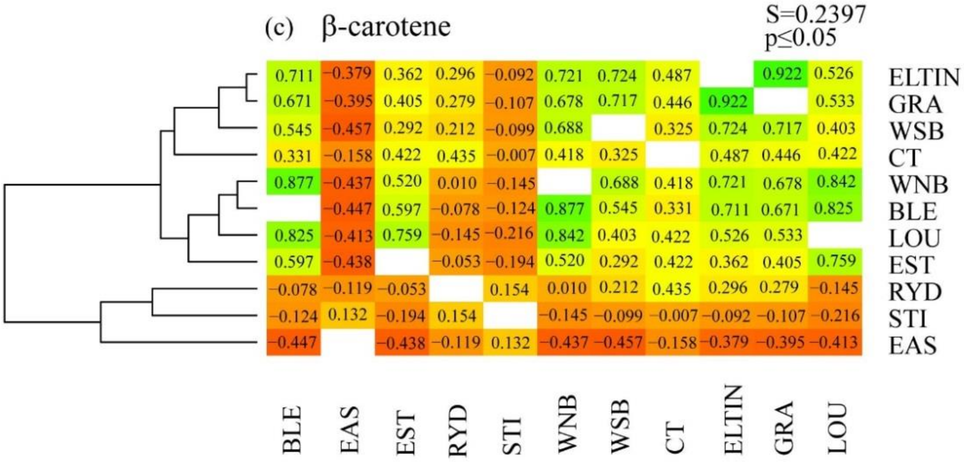


	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
GRA	0.748	−0.657	0.769	0.600	−0.406	0.711	0.688	0.097	0.948		0.713
ELTIN	0.698	−0.593	0.765	0.570	−0.433	0.639	0.630	0.223		0.948	0.652
EST	0.864	−0.680		0.607	−0.508	0.832	0.595	0.229	0.765	0.769	0.782
BLE		−0.703	0.864	0.513	−0.375	0.902	0.545	−0.018	0.698	0.748	0.862
WNB	0.902	−0.815	0.832	0.480	−0.242		0.573	−0.162	0.639	0.711	0.908
LOU	0.862	−0.805	0.782	0.552	−0.135	0.908	0.404	−0.146	0.652	0.713	
RYD	0.513	−0.418	0.607		−0.339	0.480	0.377	0.415	0.570	0.600	0.552
WSB	0.545	−0.528	0.595	0.377	−0.485	0.573		0.284	0.630	0.688	0.404
CT	−0.018	0.190	0.229	0.415	−0.530	−0.162	0.284		0.223	0.097	−0.146
STI	−0.375	−0.051	−0.508	−0.339		−0.242	−0.485	−0.530	−0.433	−0.406	−0.135
EAS	−0.703		−0.680	−0.418	−0.051	−0.815	−0.528	0.190	−0.593	−0.657	−0.805

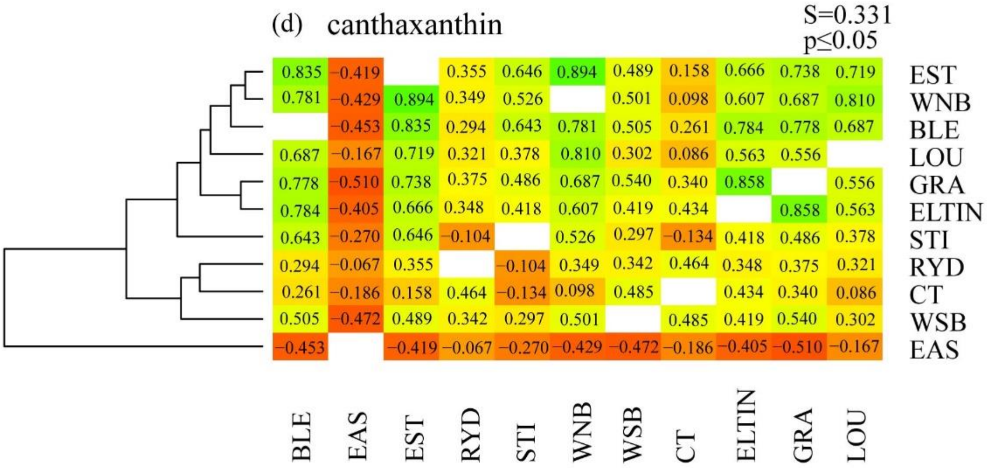
Figure 7.9 (a-g) Heatmaps of Pearson's correlation coefficient matrices for seven stable pigments and all lake pairs (left Y axis arranged in clusters) from 1800 to 2005. S and p-value provided.



	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
WNB	0.496	−0.201	0.272	0.029	0.156		0.395	0.699	0.581	−0.018	0.597
CT	0.640	−0.432	0.117	−0.182	0.203	0.699	0.289		0.775	0.032	0.555
LOU	0.324	−0.106	−0.010	−0.012	−0.018	0.597	0.213	0.555	0.452	0.147	
ELTIN	0.798	−0.528	0.036	−0.281	0.140	0.581	0.026	0.775		0.286	0.452
BLE		−0.425	0.004	−0.220	0.248	0.496	−0.112	0.640	0.798	0.042	0.324
GRA	0.042	−0.124	−0.237	−0.220	−0.266	−0.018	−0.082	0.032	0.286		0.147
WSB	−0.112	−0.180	0.339	0.239	0.145	0.395		0.289	0.026	−0.082	0.213
STI	0.248	0.046	0.184	0.071		0.156	0.145	0.203	0.140	−0.266	−0.018
EST	0.004	0.235		0.378	0.184	0.272	0.339	0.117	0.036	−0.237	−0.010
RYD	−0.220	0.401	0.378		0.071	0.029	0.239	−0.182	−0.281	−0.220	−0.012
EAS	−0.425		0.235	0.401	0.046	−0.201	−0.180	−0.433	−0.528	−0.124	−0.106

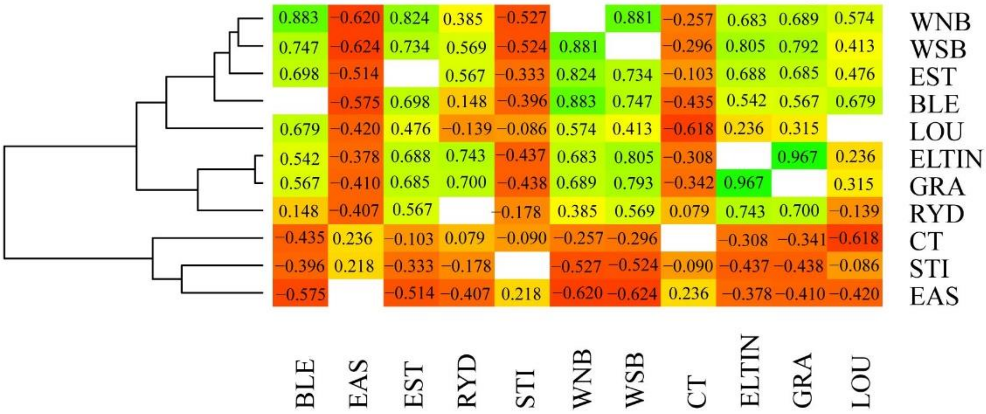


	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
ELTIN	0.711	−0.379	0.362	0.296	−0.092	0.721	0.724	0.487		0.922	0.526
GRA	0.671	−0.395	0.405	0.279	−0.107	0.678	0.717	0.446	0.922		0.533
WSB	0.545	−0.457	0.292	0.212	−0.099	0.688		0.325	0.724	0.717	0.403
CT	0.331	−0.158	0.422	0.435	−0.007	0.418	0.325		0.487	0.446	0.422
WNB	0.877	−0.437	0.520	0.010	−0.145		0.688	0.418	0.721	0.678	0.842
BLE		−0.447	0.597	−0.078	−0.124	0.877	0.545	0.331	0.711	0.671	0.825
LOU	0.825	−0.413	0.759	−0.145	−0.216	0.842	0.403	0.422	0.526	0.533	
EST	0.597	−0.438		−0.053	−0.194	0.520	0.292	0.422	0.362	0.405	0.759
RYD	−0.078	−0.119	−0.053		0.154	0.010	0.212	0.435	0.296	0.279	−0.145
STI	−0.124	0.132	−0.194	0.154		−0.145	−0.099	−0.007	−0.092	−0.107	−0.216
EAS	−0.447		−0.438	−0.119	0.132	−0.437	−0.457	−0.158	−0.379	−0.395	−0.413



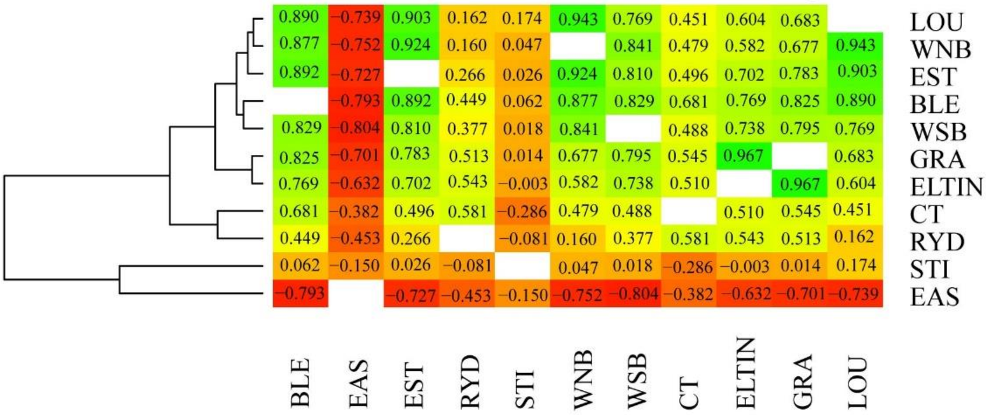
	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
EST	0.835	−0.419		0.355	0.646	0.894	0.489	0.158	0.666	0.738	0.719
WNB	0.781	−0.429	0.894	0.349	0.526		0.501	0.098	0.607	0.687	0.810
BLE		−0.453	0.835	0.294	0.643	0.781	0.505	0.261	0.784	0.778	0.687
LOU	0.687	−0.167	0.719	0.321	0.378	0.810	0.302	0.086	0.563	0.556	
GRA	0.778	−0.510	0.738	0.375	0.486	0.687	0.540	0.340	0.858		0.556
ELTIN	0.784	−0.405	0.666	0.348	0.418	0.607	0.419	0.434		0.858	0.563
STI	0.643	−0.270	0.646	−0.104		0.526	0.297	−0.134	0.418	0.486	0.378
RYD	0.294	−0.067	0.355		−0.104	0.349	0.342	0.464	0.348	0.375	0.321
CT	0.261	−0.186	0.158	0.464	−0.134	0.098	0.485		0.434	0.340	0.086
WSB	0.505	−0.472	0.489	0.342	0.297	0.501		0.485	0.419	0.540	0.302
EAS	−0.453		−0.419	−0.067	−0.270	−0.429	−0.472	−0.186	−0.405	−0.510	−0.167

Figure 7.9 Continued.


(e) diatoxanthin

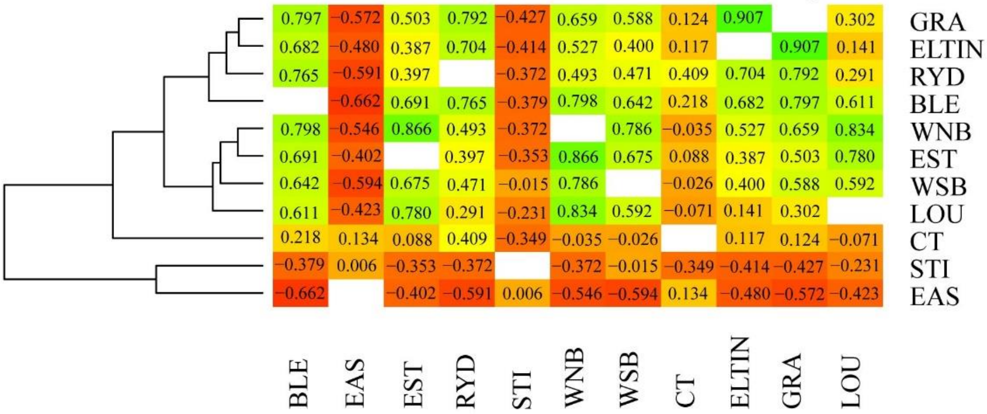
S=0.1467
p≤0.05

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
WNB	0.883	−0.620	0.824	0.385	−0.527		0.881	−0.257	0.683	0.689	0.574
WSB	0.747	−0.624	0.734	0.569	−0.524	0.881		−0.296	0.805	0.792	0.413
EST	0.698	−0.514		0.567	−0.333	0.824	0.734	−0.103	0.688	0.685	0.476
BLE		−0.575	0.698	0.148	−0.396	0.883	0.747	−0.435	0.542	0.567	0.679
LOU	0.679	−0.420	0.476	−0.139	−0.086	0.574	0.413	−0.618	0.236	0.315	
ELTIN	0.542	−0.378	0.688	0.743	−0.437	0.683	0.805	−0.308		0.967	0.236
GRA	0.567	−0.410	0.685	0.700	−0.438	0.689	0.793	−0.342	0.967		0.315
RYD	0.148	−0.407	0.567		−0.178	0.385	0.569	0.079	0.743	0.700	−0.139
CT	−0.435	0.236	−0.103	0.079	−0.090	−0.257	−0.296		−0.308	−0.341	−0.618
STI	−0.396	0.218	−0.333	−0.178		−0.527	−0.524	−0.090	−0.437	−0.438	−0.086
EAS	−0.575		−0.514	−0.407	0.218	−0.620	−0.624	0.236	−0.378	−0.410	−0.420


(f) lutein

S=0.3153
p≤0.05

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
LOU	0.890	−0.739	0.903	0.162	0.174	0.943	0.769	0.451	0.604	0.683	
WNB	0.877	−0.752	0.924	0.160	0.047		0.841	0.479	0.582	0.677	0.943
EST	0.892	−0.727		0.266	0.026	0.924	0.810	0.496	0.702	0.783	0.903
BLE		−0.793	0.892	0.449	0.062	0.877	0.829	0.681	0.769	0.825	0.890
WSB	0.829	−0.804	0.810	0.377	0.018	0.841		0.488	0.738	0.795	0.769
GRA	0.825	−0.701	0.783	0.513	0.014	0.677	0.795	0.545	0.967		0.683
ELTIN	0.769	−0.632	0.702	0.543	−0.003	0.582	0.738	0.510		0.967	0.604
CT	0.681	−0.382	0.496	0.581	−0.286	0.479	0.488		0.510	0.545	0.451
RYD	0.449	−0.453	0.266		−0.081	0.160	0.377	0.581	0.543	0.513	0.162
STI	0.062	−0.150	0.026	−0.081		0.047	0.018	−0.286	−0.003	0.014	0.174
EAS	−0.793		−0.727	−0.453	−0.150	−0.752	−0.804	−0.382	−0.632	−0.701	−0.739


(g) zeaxanthin

S=0.1975
p≤0.05

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
GRA	0.797	−0.572	0.503	0.792	−0.427	0.659	0.588	0.124	0.907		0.302
ELTIN	0.682	−0.480	0.387	0.704	−0.414	0.527	0.400	0.117		0.907	0.141
RYD	0.765	−0.591	0.397		−0.372	0.493	0.471	0.409	0.704	0.792	0.291
BLE		−0.662	0.691	0.765	−0.379	0.798	0.642	0.218	0.682	0.797	0.611
WNB	0.798	−0.546	0.866	0.493	−0.372		0.786	−0.035	0.527	0.659	0.834
EST	0.691	−0.402		0.397	−0.353	0.866	0.675	0.088	0.387	0.503	0.780
WSB	0.642	−0.594	0.675	0.471	−0.015	0.786		−0.026	0.400	0.588	0.592
LOU	0.611	−0.423	0.780	0.291	−0.231	0.834	0.592	−0.071	0.141	0.302	
CT	0.218	0.134	0.088	0.409	−0.349	−0.035	−0.026		0.117	0.124	−0.071
STI	−0.379	0.006	−0.353	−0.372		−0.372	−0.015	−0.349	−0.414	−0.427	−0.231
EAS	−0.662		−0.402	−0.591	0.006	−0.546	−0.594	0.134	−0.480	−0.572	−0.423

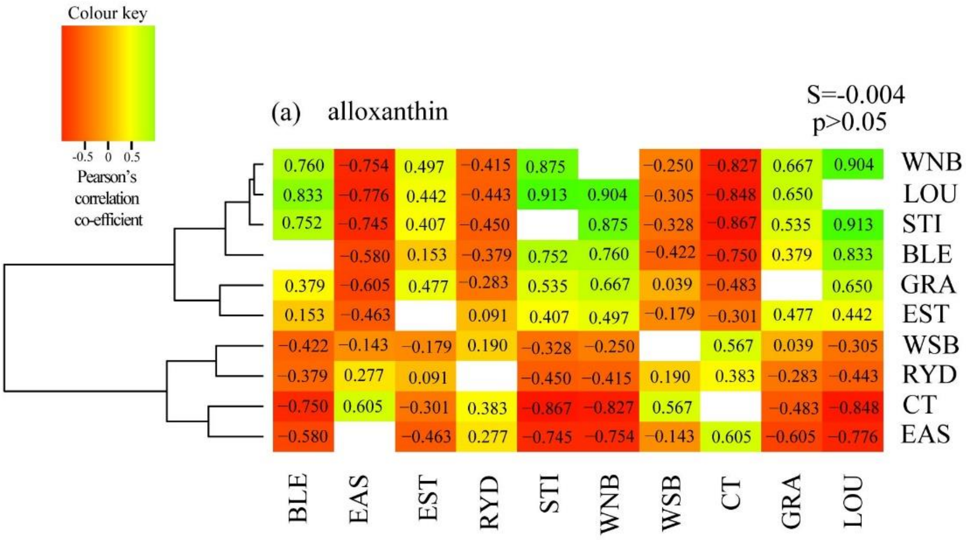
Figure 7.9 Continued.

7.2.2 Algal pigment synchrony in the 19th century

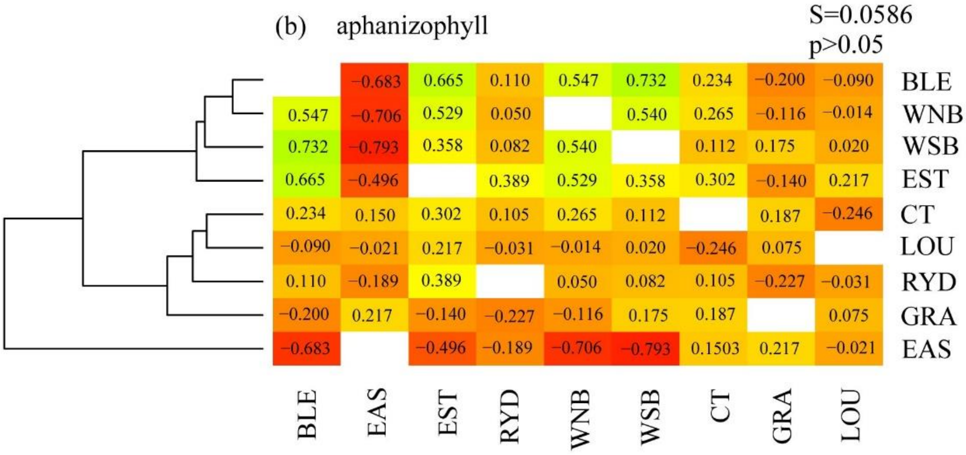
Throughout the 19th century total algae (β-carotene, $S=0.09$, $p\leq0.05$) and summer cyanobacterial (zeaxanthin, $S= 0.12$, $p\leq0.05$) and chlorophyte taxa (lutein, $S=0.09$, $p\leq0.05$) had the highest significant S values, although their 20th and mid-20th century S values were higher (Figure 7.8; Figure 7.10). The Mann-Kendall trends indicate these changes were the increased concentrations or populations of these algal groups (Figure 7.3; Figure 7.6; Figure 7.7). This suggests that compared to the 20th century, local forcings constrained total algae and summer-blooming taxa in the 19th century (Figure 7.8; Figure 7.10). However, the higher S values for summer-blooming taxa compared to other groups in the 19th century, does indicate that these groups were susceptible to regional drivers of change which became more apparent in the 20th century.

Interestingly, the correlation matrices revealed that the lowland lakes had the highest correlation coefficients in the 19th century, particularly WNB_{core} and LOU_{core} for pigments of summer taxa (cyanobacterial canthaxanthin and zeaxanthin, and chlorophyte lutein) (0.8-0.9) (Figure 7.10 (d/f/g)). WNB_{site} and LOU_{site} have very high WRTs (>100 days), which may explain the high correlation of pigments attributed to summer-blooming taxa, as increased nutrient loadings and stable conditions would have promoted algae such as cyanobacteria which dominate in stable, nutrient-rich conditions in summer months (Elliott *et al.*, 2006).

However, correlation coefficients were generally lower overall and unlike the opposing correlations of lowland (generally positive) to upland lakes (generally negative) of 1800-2005, in the 19th century S values were more variable (Figure 7.9 – 7.10). For example, the lowland RYD_{core} and upland lakes CT_{core} and EAS_{core} had negative correlation coefficients to other lakes for all pigments except aphanizophyll and β-carotene (Figure 7.10). On the other hand, the upland lake STI_{core} had a high correlation (0.9) between the lowland lake LOU_{core} for alloxanthin, and between the lowland lake WSB_{core} for zeaxanthin (0.8) (Figure 7.10 (a/g)). The aforementioned lakes differ in landscape position and characteristics (see Table 2.1), thus local factors must have led to the variable spatial synchrony across the catchment. These factors could have been the difference in the chemistry of the lake and its catchment and/or difference in grazing populations (Vogt *et al*., 2011).

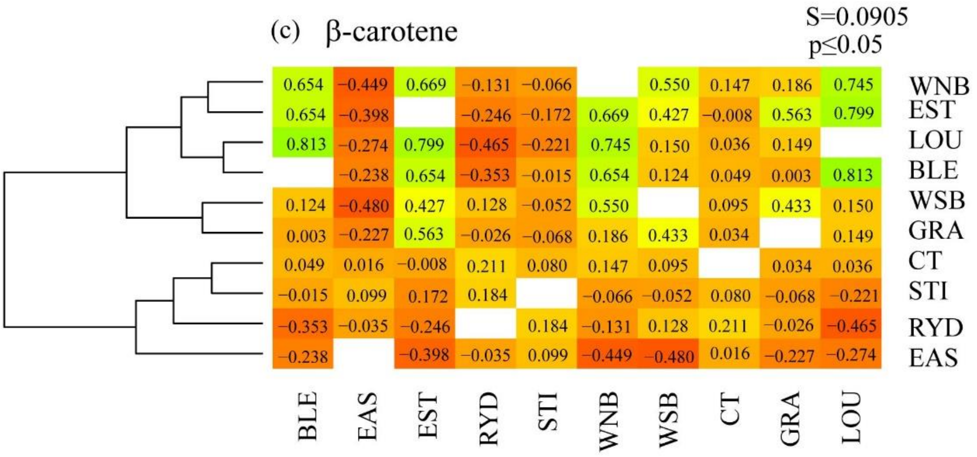


	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	GRA	LOU
WNB	0.760	−0.754	0.497	−0.415	0.875		−0.250	−0.827	0.667	0.904
LOU	0.833	−0.776	0.442	−0.443	0.913	0.904	−0.305	−0.848	0.650	
STI	0.752	−0.745	0.407	−0.450		0.875	−0.328	−0.867	0.535	0.913
BLE		−0.580	0.153	−0.379	0.752	0.760	−0.422	−0.750	0.379	0.833
GRA	0.379	−0.605	0.477	−0.283	0.535	0.667	0.039	−0.483		0.650
EST	0.153	−0.463		0.091	0.407	0.497	−0.179	−0.301	0.477	0.442
WSB	−0.422	−0.143	−0.179	0.190	−0.328	−0.250		0.567	0.039	−0.305
RYD	−0.379	0.277	0.091		−0.450	−0.415	0.190	0.383	−0.283	−0.443
CT	−0.750	0.605	−0.301	0.383	−0.867	−0.827	0.567		−0.483	−0.848
EAS	−0.580		−0.463	0.277	−0.745	−0.754	−0.143	0.605	−0.605	−0.776



	BLE	EAS	EST	RYD	WNB	WSB	CT	GRA	LOU
BLE		−0.683	0.665	0.110	0.547	0.732	0.234	−0.200	−0.090
WNB	0.547	−0.706	0.529	0.050		0.540	0.265	−0.116	−0.014
WSB	0.732	−0.793	0.358	0.082	0.540		0.112	0.175	0.020
EST	0.665	−0.496		0.389	0.529	0.358	0.302	−0.140	0.217
CT	0.234	0.150	0.302	0.105	0.265	0.112		0.187	−0.246
LOU	−0.090	−0.021	0.217	−0.031	−0.014	0.020	−0.246	0.075	
RYD	0.110	−0.189	0.389		0.050	0.082	0.105	−0.227	−0.031
GRA	−0.200	0.217	−0.140	−0.227	−0.116	0.175	0.187		0.075
EAS	−0.683		−0.496	−0.189	−0.706	−0.793	0.1503	0.217	−0.021

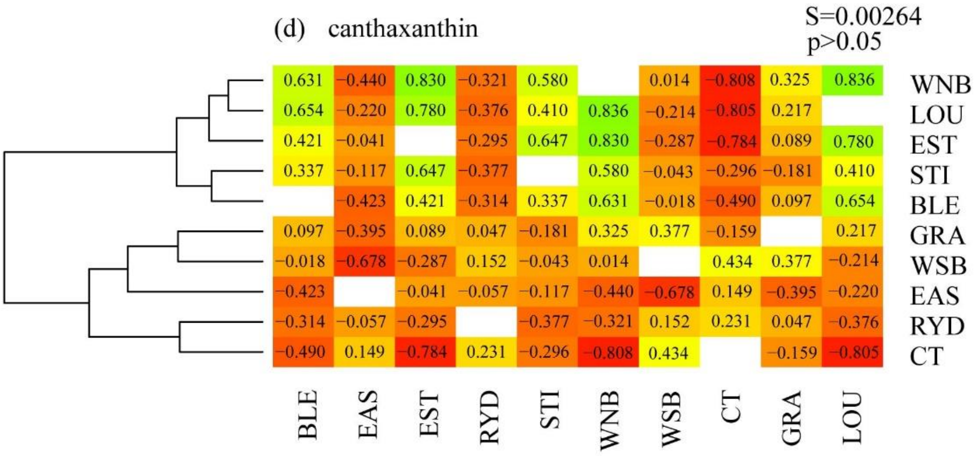
Figure 7.10 (a-g) Heatmaps of Pearson's correlation coefficient matrices with dendrograms for seven stable pigments and all lake pairs (left Y axis arranged in clusters) from 1800 to 1905. S and p-value provided.



(c) β-carotene

S=0.0905
$p \leq 0.05$

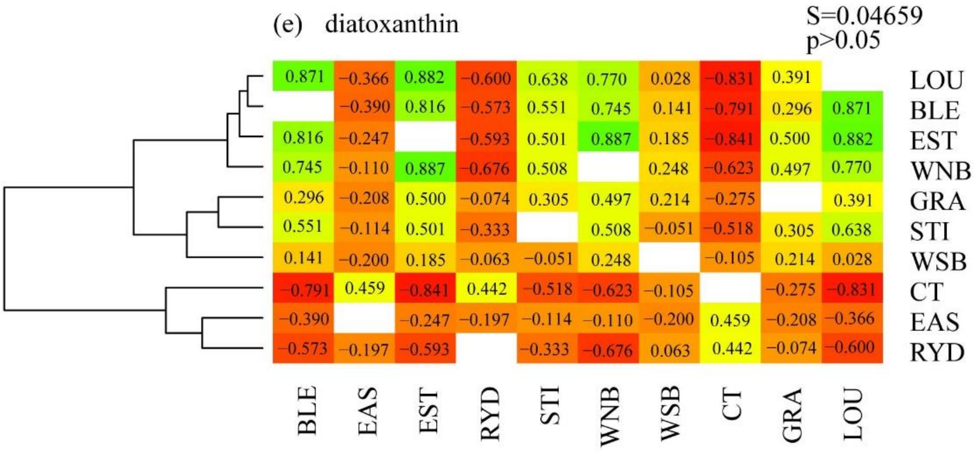
	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	GRA	LOU
WNB	0.654	−0.449	0.669	−0.131	−0.066		0.550	0.147	0.186	0.745
EST	0.654	−0.398		−0.246	−0.172	0.669	0.427	−0.008	0.563	0.799
LOU	0.813	−0.274	0.799	−0.465	−0.221	0.745	0.150	0.036	0.149	
BLE		−0.238	0.654	−0.353	−0.015	0.654	0.124	0.049	0.003	0.813
WSB	0.124	−0.480	0.427	0.128	−0.052	0.550		0.095	0.433	0.150
GRA	0.003	−0.227	0.563	−0.026	−0.068	0.186	0.433	0.034		0.149
CT	0.049	0.016	−0.008	0.211	0.080	0.147	0.095		0.034	0.036
STI	−0.015	0.099	0.172	0.184		−0.066	−0.052	0.080	−0.068	−0.221
RYD	−0.353	−0.035	−0.246		0.184	−0.131	0.128	0.211	−0.026	−0.465
EAS	−0.238		−0.398	−0.035	0.099	−0.449	−0.480	0.016	−0.227	−0.274



(d) canthaxanthin

S=0.00264
$p > 0.05$

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	GRA	LOU
WNB	0.631	−0.440	0.830	−0.321	0.580		0.014	−0.808	0.325	0.836
LOU	0.654	−0.220	0.780	−0.376	0.410	0.836	−0.214	−0.805	0.217	
EST	0.421	−0.041		−0.295	0.647	0.830	−0.287	−0.784	0.089	0.780
STI	0.337	−0.117	0.647	−0.377		0.580	−0.043	−0.296	−0.181	0.410
BLE		−0.423	0.421	−0.314	0.337	0.631	−0.018	−0.490	0.097	0.654
GRA	0.097	−0.395	0.089	0.047	−0.181	0.325	0.377	−0.159		0.217
WSB	−0.018	−0.678	−0.287	0.152	−0.043	0.014		0.434	0.377	−0.214
EAS	−0.423		−0.041	−0.057	−0.117	−0.440	−0.678	0.149	−0.395	−0.220
RYD	−0.314	−0.057	−0.295		−0.377	−0.321	0.152	0.231	0.047	−0.376
CT	−0.490	0.149	−0.784	0.231	−0.296	−0.808	0.434		−0.159	−0.805

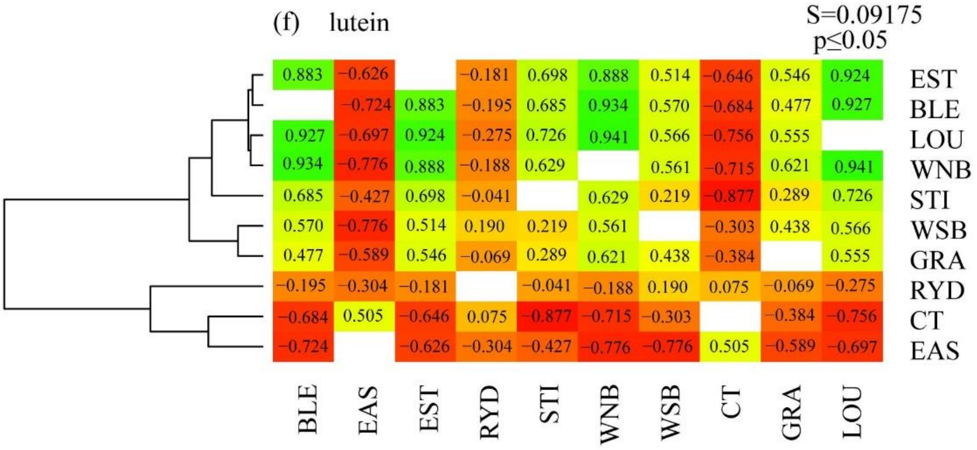


(e) diatoxanthin

S=0.04659
$p > 0.05$

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	GRA	LOU
LOU	0.871	−0.366	0.882	−0.600	0.638	0.770	0.028	−0.831	0.391	
BLE		−0.390	0.816	−0.573	0.551	0.745	0.141	−0.791	0.296	0.871
EST	0.816	−0.247		−0.593	0.501	0.887	0.185	−0.841	0.500	0.882
WNB	0.745	−0.110	0.887	−0.676	0.508		0.248	−0.623	0.497	0.770
GRA	0.296	−0.208	0.500	−0.074	0.305	0.497	0.214	−0.275		0.391
STI	0.551	−0.114	0.501	−0.333		0.508	−0.051	−0.518	0.305	0.638
WSB	0.141	−0.200	0.185	−0.063	−0.051	0.248		−0.105	0.214	0.028
CT	−0.791	0.459	−0.841	0.442	−0.518	−0.623	−0.105		−0.275	−0.831
EAS	−0.390		−0.247	−0.197	−0.114	−0.110	−0.200	0.459	−0.208	−0.366
RYD	−0.573	−0.197	−0.593		−0.333	−0.676	0.063	0.442	−0.074	−0.600

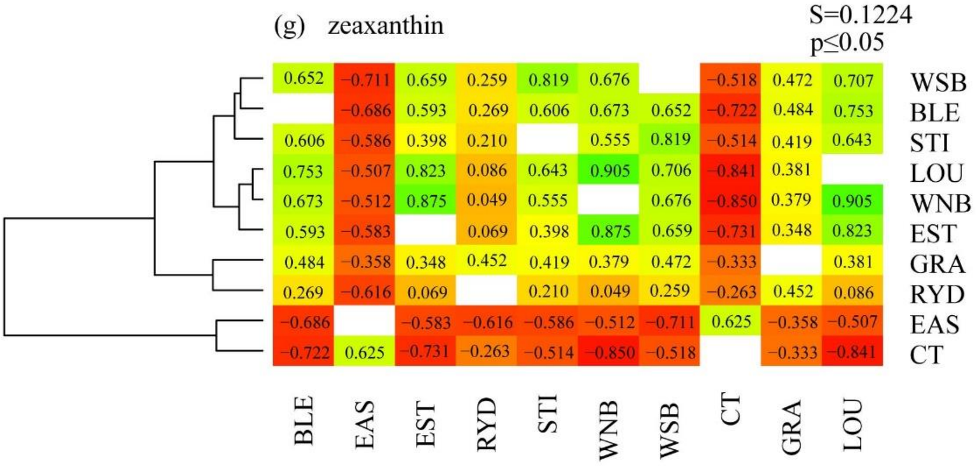
Figure 7.10 Continued.



(f) lutein

S=0.09175
$p \leq 0.05$

BLE	EAS	EST	RYD	STI	WNB	WSB	CT	GRA	LOU	
0.883	−0.626		−0.181	0.698	0.888	0.514	−0.646	0.546	0.924	EST
	−0.724	0.883	−0.195	0.685	0.934	0.570	−0.684	0.477	0.927	BLE
0.927	−0.697	0.924	−0.275	0.726	0.941	0.566	−0.756	0.555		LOU
0.934	−0.776	0.888	−0.188	0.629		0.561	−0.715	0.621	0.941	WNB
0.685	−0.427	0.698	−0.041		0.629	0.219	−0.877	0.289	0.726	STI
0.570	−0.776	0.514	0.190	0.219	0.561		−0.303	0.438	0.566	WSB
0.477	−0.589	0.546	−0.069	0.289	0.621	0.438	−0.384		0.555	GRA
−0.195	−0.304	−0.181		−0.041	−0.188	0.190	0.075	−0.069	−0.275	RYD
−0.684	0.505	−0.646	0.075	−0.877	−0.715	−0.303		−0.384	−0.756	CT
−0.724		−0.626	−0.304	−0.427	−0.776	−0.776	0.505	−0.589	−0.697	EAS



(g) zeaxanthin

S=0.1224
$p \leq 0.05$

BLE	EAS	EST	RYD	STI	WNB	WSB	CT	GRA	LOU	
0.652	−0.711	0.659	0.259	0.819	0.676		−0.518	0.472	0.707	WSB
	−0.686	0.593	0.269	0.606	0.673	0.652	−0.722	0.484	0.753	BLE
0.606	−0.586	0.398	0.210		0.555	0.819	−0.514	0.419	0.643	STI
0.753	−0.507	0.823	0.086	0.643	0.905	0.706	−0.841	0.381		LOU
0.673	−0.512	0.875	0.049	0.555		0.676	−0.850	0.379	0.905	WNB
0.593	−0.583		0.069	0.398	0.875	0.659	−0.731	0.348	0.823	EST
0.484	−0.358	0.348	0.452	0.419	0.379	0.472	−0.333		0.381	GRA
0.269	−0.616	0.069		0.210	0.049	0.259	−0.263	0.452	0.086	RYD
−0.686		−0.583	−0.616	−0.586	−0.512	−0.711	0.625	−0.358	−0.507	EAS
−0.722	0.625	−0.731	−0.263	−0.514	−0.850	−0.518		−0.333	−0.841	CT

Figure 7.10 Continued.

7.2.3 Algal pigment synchrony in the 20th century

The mean significant S value for pigments in the 20th century (1900-2005) ($\bar{x}$S=0.20) was higher compared to the 19th century (1800-1905) ($\bar{x}$S=0.07), supporting the assumption that regional-scale forcings in the 20th century led to more synchronous algal community changes in the Windermere catchment (Figure 7.8; Figure 7.11). Furthermore, total algal production (β-carotene, S=0.26, $p \leq 0.05$) and summer-blooming chlorophytes (lutein, S=0.29, $p \leq 0.05$) had the highest S values (Figure 7.11 (c/f)).

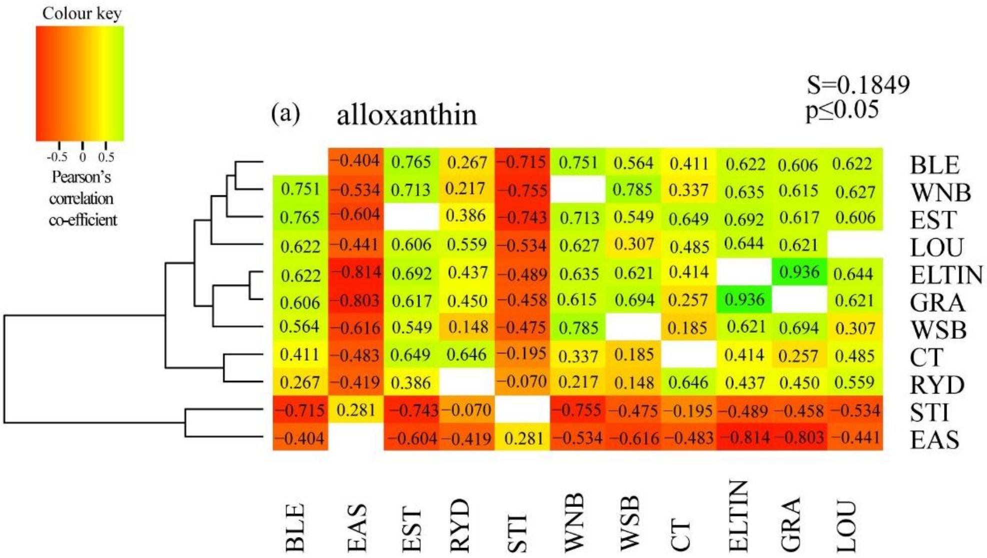
The 20th century S values of the Windermere catchment ($S=0.09-0.28$, $p\leq0.05$) were slightly lower than those of the Northern Great Plains, Canada ($S=0.0-0.42$) (Patoine and Leavitt, 2006). The Canadian lakes had similar morphometry to one another and so, lower spatial heterogeneity (Patoine and Leavitt, 2006). Thus, the slightly lower S values of algal taxa in the Windermere catchment in the 20th century could have been due to the filtering effects of regional drivers such as land-use and climatic changes, by the heterogeneous lake and catchment characteristics.

Notwithstanding these differences, the major contributors to algal community S in the Windermere catchment in the 20th century could be regional land use, climatic changes and/or atmospheric deposition of pollutants. This is supported by the sustained maximum correlation coefficients between the two sites $ELTIN_{core}$ and GRA_{core} from within the 20th century for all pigments (excluding aphanizophyll) and their almost identical land use changes, and increasing agricultural livestock and human population trends within their catchments at this time (Figure 7.11 (a/c-g)); Figure 6.31 (2); Figure 6.34 (2)). This was despite the two lakes having very different lake and catchment morphological features and landscape positions, which could have modified the effects of nutrient influx and climate variables (Table 2.1) (Vogt *et al.*, 2011; Orr *et al.*, 2008). These results imply regional drivers such as nutrient enrichment overrode local-scale influences at these lowland sites.

However, the upland lakes STI_{core} and EAS_{core} had low or negative correlations for the pigments lutein, alloxanthin and zeaxanthin to other lakes in the catchment, and for β-carotene and canthaxanthin for EAS_{core} alone (Figure 7.11 (a/c-d/f-g)). This could imply that in the absence of direct anthropogenic influence, local factors continued to drive and or modify the effects of regional forcings such as climate, resulting in variable algal community changes in these upland lakes.

Considering the wider catchment, livestock and human populations also increased, although to different extents (Figure 6.7 - Figure 6.44). This could explain the high S for total algal production (β-carotene, $S=0.26$, $p\leq0.05$)

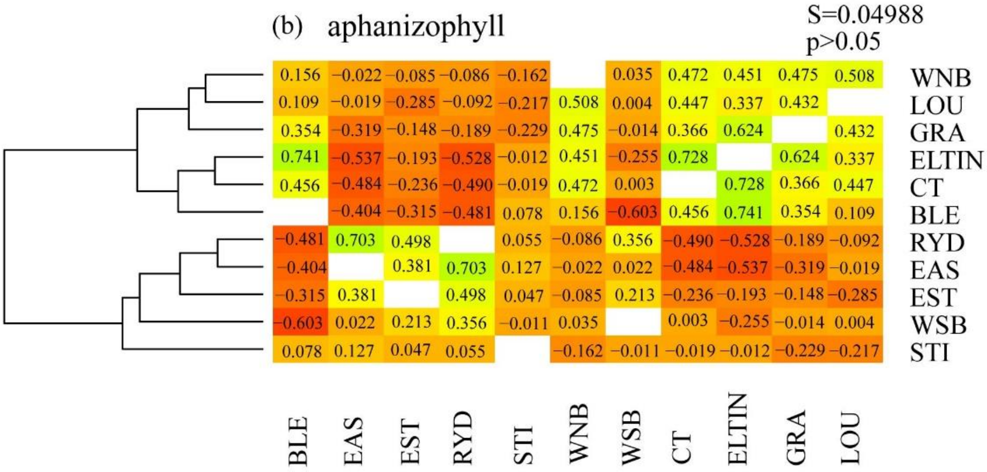
caused by the increased cultural eutrophication throughout the catchment and indeed temperate lakes worldwide in the 20th century (Schindler, 2006). The lower S values for individual taxa compared to total algal production (β-carotene) could indicate greater control by individual driving mechanisms (such as timing and extent of land use change) and the linkages between drivers of change and lakes such as WRTs, which are highly variable in time and space across the Windermere catchment (Vogt *et al*., 2011).



(a) alloxanthin

S=0.1849
$p \leq 0.05$

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
BLE		-0.404	0.765	0.267	-0.715	0.751	0.564	0.411	0.622	0.606	0.622
WNB	0.751	-0.534	0.713	0.217	-0.755		0.785	0.337	0.635	0.615	0.627
EST	0.765	-0.604		0.386	-0.743	0.713	0.549	0.649	0.692	0.617	0.606
LOU	0.622	-0.441	0.606	0.559	-0.534	0.627	0.307	0.485	0.644	0.621	
ELTIN	0.622	-0.814	0.692	0.437	-0.489	0.635	0.621	0.414		0.936	0.644
GRA	0.606	-0.803	0.617	0.450	-0.458	0.615	0.694	0.257	0.936		0.621
WSB	0.564	-0.616	0.549	0.148	-0.475	0.785		0.185	0.621	0.694	0.307
CT	0.411	-0.483	0.649	0.646	-0.195	0.337	0.185		0.414	0.257	0.485
RYD	0.267	-0.419	0.386		-0.070	0.217	0.148	0.646	0.437	0.450	0.559
STI	-0.715	0.281	-0.743	-0.070		-0.755	-0.475	-0.195	-0.489	-0.458	-0.534
EAS	-0.404		-0.604	-0.419	0.281	-0.534	-0.616	-0.483	-0.814	-0.803	-0.441

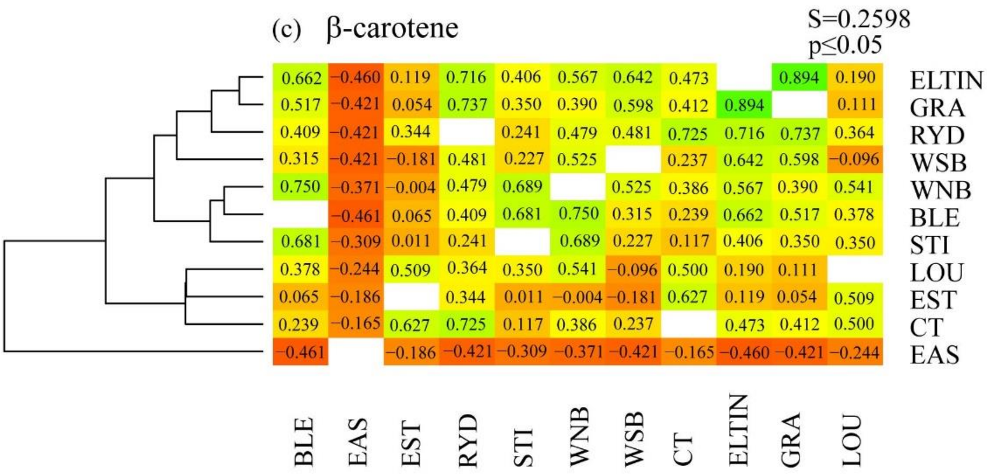


(b) aphanizophyll

S=0.04988
$p > 0.05$

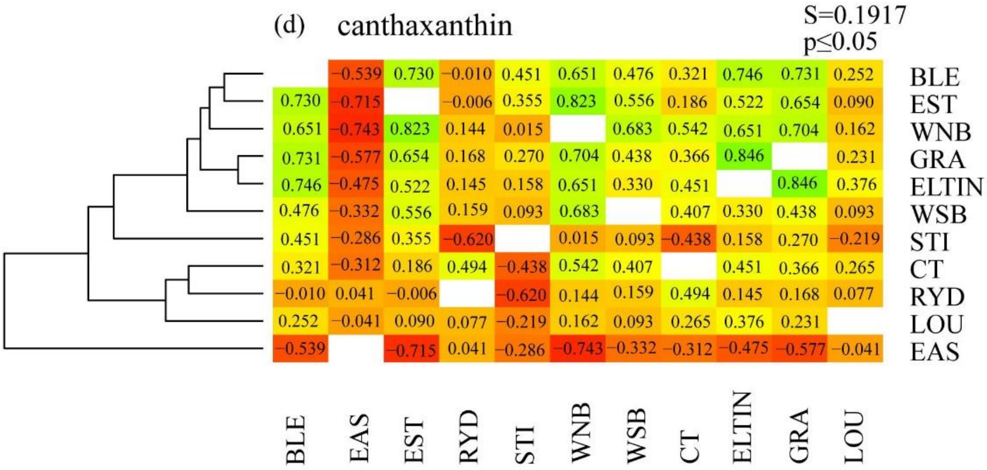
	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
WNB	0.156	-0.022	-0.085	-0.086	-0.162		0.035	0.472	0.451	0.475	0.508
LOU	0.109	-0.019	-0.285	-0.092	-0.217	0.508	0.004	0.447	0.337	0.432	
GRA	0.354	-0.319	-0.148	-0.189	-0.229	0.475	-0.014	0.366	0.624		0.432
ELTIN	0.741	-0.537	-0.193	-0.528	-0.012	0.451	-0.255	0.728		0.624	0.337
CT	0.456	-0.484	-0.236	-0.490	-0.019	0.472	0.003		0.728	0.366	0.447
BLE		-0.404	-0.315	-0.481	0.078	0.156	-0.603	0.456	0.741	0.354	0.109
RYD	-0.481	0.703	0.498		0.055	-0.086	0.356	-0.490	-0.528	-0.189	-0.092
EAS	-0.404		0.381	0.703	0.127	-0.022	0.022	-0.484	-0.537	-0.319	-0.019
EST	-0.315	0.381		0.498	0.047	-0.085	0.213	-0.236	-0.193	-0.148	-0.285
WSB	-0.603	0.022	0.213	0.356	-0.011	0.035		0.003	-0.255	-0.014	0.004
STI	0.078	0.127	0.047	0.055		-0.162	-0.011	-0.019	-0.012	-0.229	-0.217

Figure 7.11 (a-g) Heatmaps of Pearson's correlation coefficient matrices with dendrograms for seven stable pigments and all lake pairs (left Y axis arranged in clusters) from 1900 to 2005. S and p-value provided.


(c) β-carotene

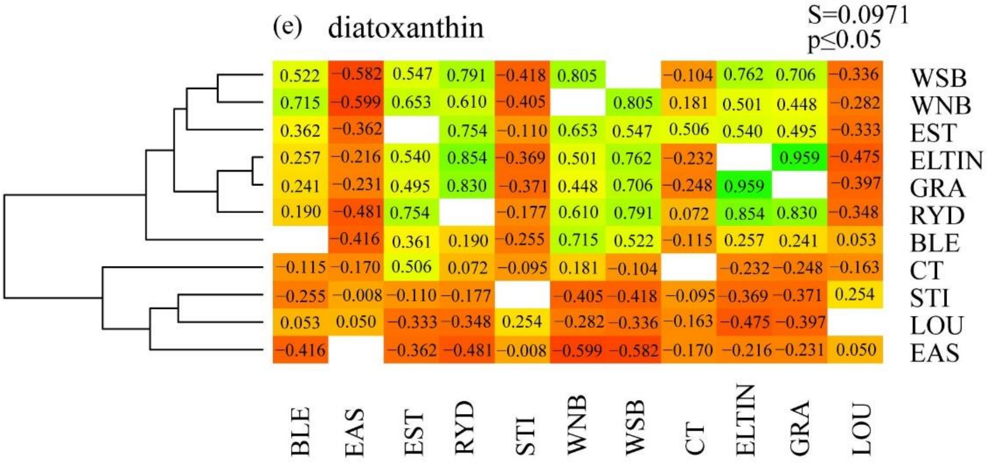
S=0.2598
p≤0.05

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
ELTIN	0.662	−0.460	0.119	0.716	0.406	0.567	0.642	0.473		0.894	0.190
GRA	0.517	−0.421	0.054	0.737	0.350	0.390	0.598	0.412	0.894		0.111
RYD	0.409	−0.421	0.344		0.241	0.479	0.481	0.725	0.716	0.737	0.364
WSB	0.315	−0.421	−0.181	0.481	0.227	0.525		0.237	0.642	0.598	−0.096
WNB	0.750	−0.371	−0.004	0.479	0.689		0.525	0.386	0.567	0.390	0.541
BLE		−0.461	0.065	0.409	0.681	0.750	0.315	0.239	0.662	0.517	0.378
STI	0.681	−0.309	0.011	0.241		0.689	0.227	0.117	0.406	0.350	0.350
LOU	0.378	−0.244	0.509	0.364	0.350	0.541	−0.096	0.500	0.190	0.111	
EST	0.065	−0.186		0.344	0.011	−0.004	−0.181	0.627	0.119	0.054	0.509
CT	0.239	−0.165	0.627	0.725	0.117	0.386	0.237		0.473	0.412	0.500
EAS	−0.461		−0.186	−0.421	−0.309	−0.371	−0.421	−0.165	−0.460	−0.421	−0.244


(d) canthaxanthin

S=0.1917
p≤0.05

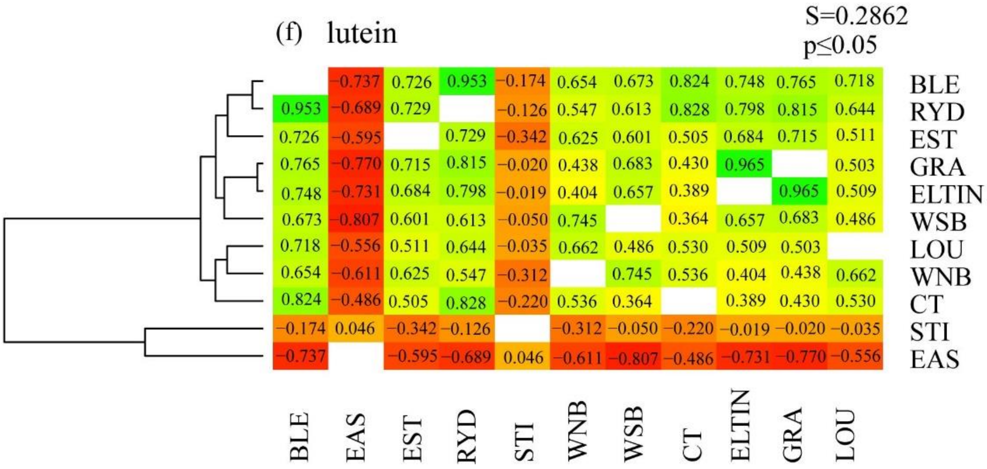
	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
BLE		−0.539	0.730	−0.010	0.451	0.651	0.476	0.321	0.746	0.731	0.252
EST	0.730	−0.715		−0.006	0.355	0.823	0.556	0.186	0.522	0.654	0.090
WNB	0.651	−0.743	0.823	0.144	0.015		0.683	0.542	0.651	0.704	0.162
GRA	0.731	−0.577	0.654	0.168	0.270	0.704	0.438	0.366	0.846		0.231
ELTIN	0.746	−0.475	0.522	0.145	0.158	0.651	0.330	0.451		0.846	0.376
WSB	0.476	−0.332	0.556	0.159	0.093	0.683		0.407	0.330	0.438	0.093
STI	0.451	−0.286	0.355	−0.620		0.015	0.093	−0.438	0.158	0.270	−0.219
CT	0.321	−0.312	0.186	0.494	−0.438	0.542	0.407		0.451	0.366	0.265
RYD	−0.010	0.041	−0.006		−0.620	0.144	0.159	0.494	0.145	0.168	0.077
LOU	0.252	−0.041	0.090	0.077	−0.219	0.162	0.093	0.265	0.376	0.231	
EAS	−0.539		−0.715	0.041	−0.286	−0.743	−0.332	−0.312	−0.475	−0.577	−0.041


(e) diatoxanthin

S=0.0971
p≤0.05

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
WSB	0.522	−0.582	0.547	0.791	−0.418	0.805		−0.104	0.762	0.706	−0.336
WNB	0.715	−0.599	0.653	0.610	−0.405		0.805	0.181	0.501	0.448	−0.282
EST	0.362	−0.362		0.754	−0.110	0.653	0.547	0.506	0.540	0.495	−0.333
ELTIN	0.257	−0.216	0.540	0.854	−0.369	0.501	0.762	−0.232		0.959	−0.475
GRA	0.241	−0.231	0.495	0.830	−0.371	0.448	0.706	−0.248	0.959		−0.397
RYD	0.190	−0.481	0.754		−0.177	0.610	0.791	0.072	0.854	0.830	−0.348
BLE		−0.416	0.361	0.190	−0.255	0.715	0.522	−0.115	0.257	0.241	0.053
CT	−0.115	−0.170	0.506	0.072	−0.095	0.181	−0.104		−0.232	−0.248	−0.163
STI	−0.255	−0.008	−0.110	−0.177		−0.405	−0.418	−0.095	−0.369	−0.371	0.254
LOU	0.053	0.050	−0.333	−0.348	0.254	−0.282	−0.336	−0.163	−0.475	−0.397	
EAS	−0.416		−0.362	−0.481	−0.008	−0.599	−0.582	−0.170	−0.216	−0.231	0.050

Figure 7.11 Continued.



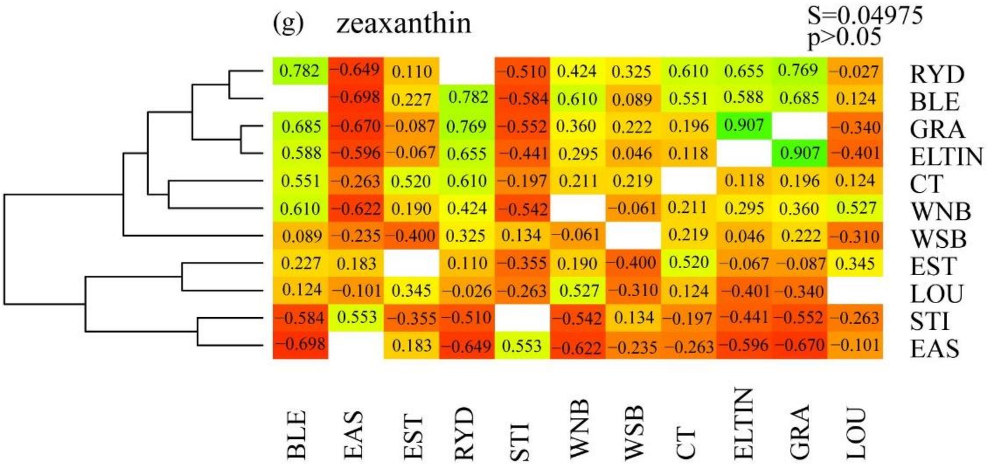


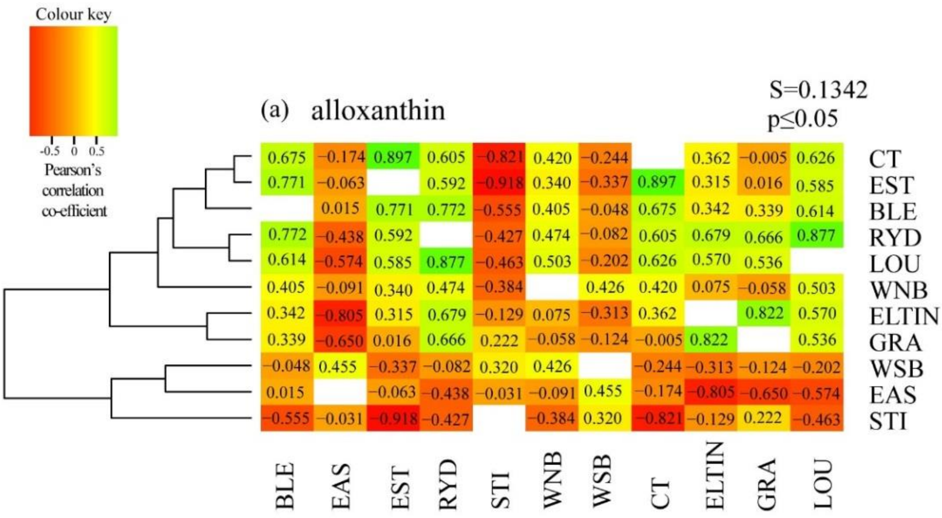
Figure 7.11 Continued.

7.2.4 Algal pigment synchrony since 1950AD

Mean overall significant S values were lower ($\bar{x}$S=0.14, p≤0.05) for all pigments within the latter half of the 20th century (1950-2005) compared to its entirety ($\bar{x}$S=0.20), pointing to a reduction in algal community S post-1950 (Figure 7.8; Figure 7.12). This is further supported by the variable correlation coefficients between upland and lowland lakes for each pigment (Figure 7.12). For example, the upland CT$_{core}$ had a very high correlation coefficient (0.9), with one of either EST$_{core}$, WSB$_{core}$ or BLE$_{core}$ for the pigments alloxanthin, aphanizophyll, β-carotene and diatoxanthin, but very low (<0) coefficients with the other uplands STI$_{core}$ and EAS$_{core}$ (Figure 7.12 (a-c/e)). Interestingly, total algal production (β-carotene, $S=0.20$, $p \leq 0.05$) had the highest S value of the pigments post-1950, which may point to spatial homogeneity in the continued promotion of algal abundance compared to that of the S of constituent taxa throughout the 20th century (Patoine and Leavitt, 2006).

Low S of algal community responses post-1950 could be due to localised environmental perturbations such as point nutrient fertilisation, which have been shown to result in variable site and taxon specific responses (Underwood, 1991; Cottingham *et al.*, 2000). Alternatively, the lack of spatial S across the catchment could be because global change processes such as climate change often incur variable ecological responses particularly when multiple stressors act on a lake (Carpenter *et al.*, 1992; Straile and Adrian, 2000). For example, inconsistent response of phytoplankton to the NAO has been shown in the Windermere catchment, and was attributed to the "filtering" effects of physical lake and catchment characteristics (George *et al.*, 2004). Thus, it is possible that although the Windermere catchment was susceptible to regional-scale drivers of ecological change after 1950, additional local-site drivers and the influence of physical landscape characteristics led to more variable community responses often seen as lake ecosystems are impacted by multiple stressors (Vinebrooke *et al.*, 2004).

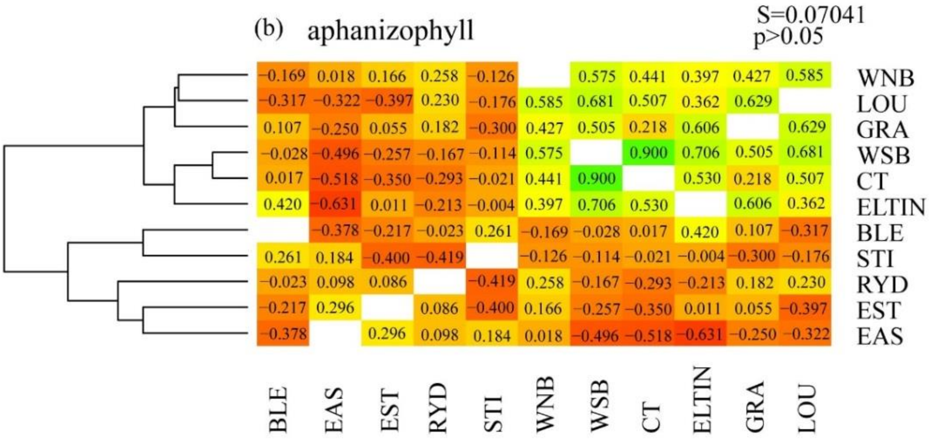
To summarise, algal community S in the Windermere catchment was greatest at centennial timescales, in particular the 20th century. Pigments with the highest S were those of total algae reflecting the high inter-decadal S of summer-blooming chlorophyte and cyanobacterial taxa in the catchment, indicating a regional-control mechanism on these groups. Climate and nutrient loading have been suggested, but drivers of community change will be investigated further in the subsequent chapter.



(a) alloxanthin

S=0.1342
$p \leq 0.05$

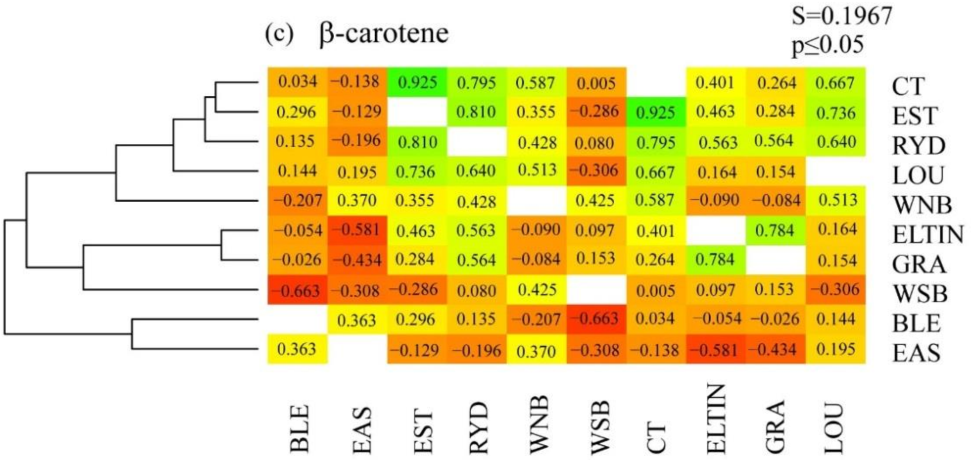
	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
CT	0.675	−0.174	0.897	0.605	−0.821	0.420	−0.244		0.362	−0.005	0.626
EST	0.771	−0.063		0.592	−0.918	0.340	−0.337	0.897	0.315	0.016	0.585
BLE		0.015	0.771	0.772	−0.555	0.405	−0.048	0.675	0.342	0.339	0.614
RYD	0.772	−0.438	0.592		−0.427	0.474	−0.082	0.605	0.679	0.666	0.877
LOU	0.614	−0.574	0.585	0.877	−0.463	0.503	−0.202	0.626	0.570	0.536	
WNB	0.405	−0.091	0.340	0.474	−0.384		0.426	0.420	0.075	−0.058	0.503
ELTIN	0.342	−0.805	0.315	0.679	−0.129	0.075	−0.313	0.362		0.822	0.570
GRA	0.339	−0.650	0.016	0.666	0.222	−0.058	−0.124	−0.005	0.822		0.536
WSB	−0.048	0.455	−0.337	−0.082	0.320	0.426		−0.244	−0.313	−0.124	−0.202
EAS	0.015		−0.063	−0.438	−0.031	−0.091	0.455	−0.174	−0.805	−0.650	−0.574
STI	−0.555	−0.031	−0.918	−0.427		−0.384	0.320	−0.821	−0.129	0.222	−0.463



(b) aphanizophyll

S=0.07041
$p > 0.05$

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
WNB	−0.169	0.018	0.166	0.258	−0.126		0.575	0.441	0.397	0.427	0.585
LOU	−0.317	−0.322	−0.397	0.230	−0.176	0.585	0.681	0.507	0.362	0.629	
GRA	0.107	−0.250	0.055	0.182	−0.300	0.427	0.505	0.218	0.606		0.629
WSB	−0.028	−0.496	−0.257	−0.167	−0.114	0.575		0.900	0.706	0.505	0.681
CT	0.017	−0.518	−0.350	−0.293	−0.021	0.441	0.900		0.530	0.218	0.507
ELTIN	0.420	−0.631	0.011	−0.213	−0.004	0.397	0.706	0.530		0.606	0.362
BLE		−0.378	−0.217	−0.023	0.261	−0.169	−0.028	0.017	0.420	0.107	−0.317
STI	0.261	0.184	−0.400	−0.419		−0.126	−0.114	−0.021	−0.004	−0.300	−0.176
RYD	−0.023	0.098	0.086		−0.419	0.258	−0.167	−0.293	−0.213	0.182	0.230
EST	−0.217	0.296		0.086	−0.400	0.166	−0.257	−0.350	0.011	0.055	−0.397
EAS	−0.378		0.296	0.098	0.184	0.018	−0.496	−0.518	−0.631	−0.250	−0.322

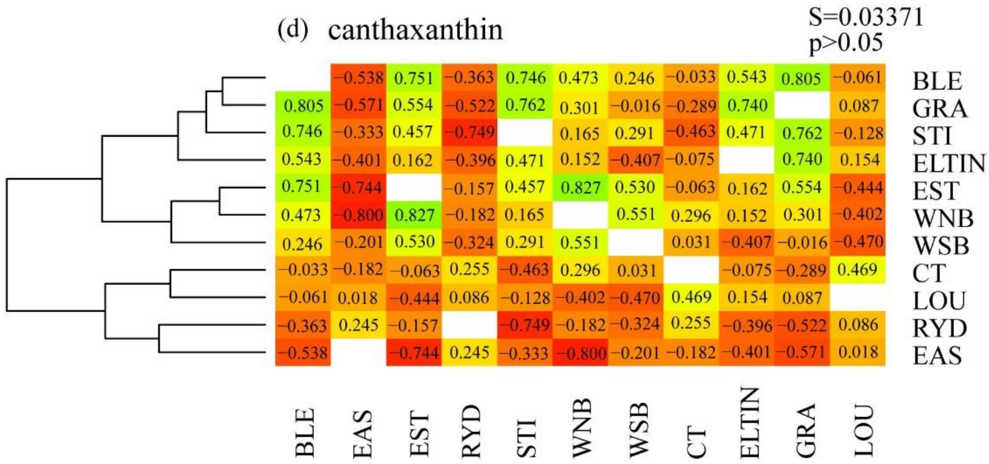


(c) β-carotene

S=0.1967
$p \leq 0.05$

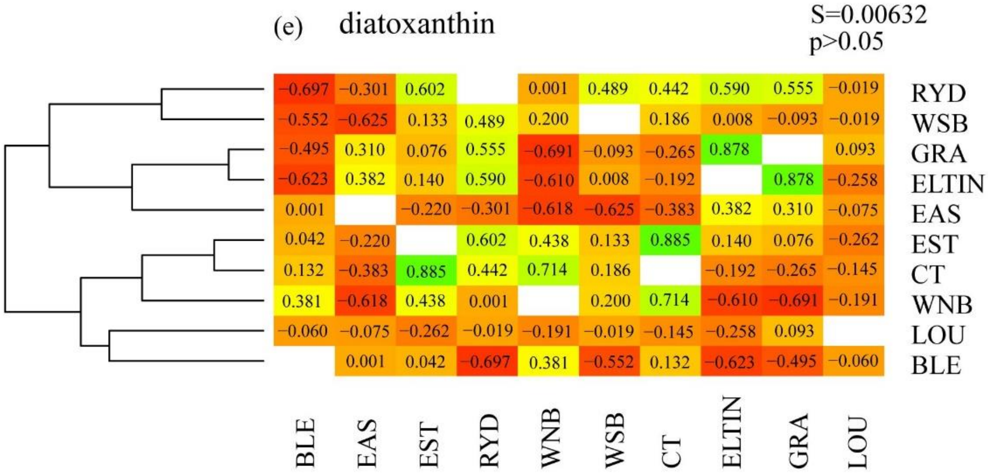
	BLE	EAS	EST	RYD	WNB	WSB	CT	ELTIN	GRA	LOU
CT	0.034	−0.138	0.925	0.795	0.587	0.005		0.401	0.264	0.667
EST	0.296	−0.129		0.810	0.355	−0.286	0.925	0.463	0.284	0.736
RYD	0.135	−0.196	0.810		0.428	0.080	0.795	0.563	0.564	0.640
LOU	0.144	0.195	0.736	0.640	0.513	−0.306	0.667	0.164	0.154	
WNB	−0.207	0.370	0.355	0.428		0.425	0.587	−0.090	−0.084	0.513
ELTIN	−0.054	−0.581	0.463	0.563	−0.090	0.097	0.401		0.784	0.164
GRA	−0.026	−0.434	0.284	0.564	−0.084	0.153	0.264	0.784		0.154
WSB	−0.663	−0.308	−0.286	0.080	0.425		0.005	0.097	0.153	−0.306
BLE		0.363	0.296	0.135	−0.207	−0.663	0.034	−0.054	−0.026	0.144
EAS	0.363		−0.129	−0.196	0.370	−0.308	−0.138	−0.581	−0.434	0.195

Figure 7.12 (a-g) Heatmaps of Pearson's correlation coefficient matrices with dendrograms for seven stable pigments and all lake pairs (left Y axis arranged in clusters) from 1950 to 2005. S and p-value provided.


(d) canthaxanthin

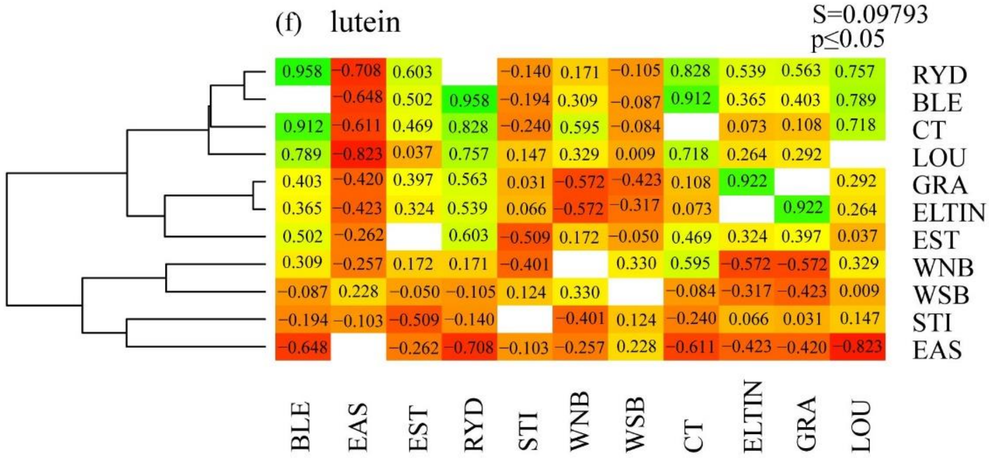
S=0.03371
p>0.05

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
BLE		−0.538	0.751	−0.363	0.746	0.473	0.246	−0.033	0.543	0.805	−0.061
GRA	0.805	−0.571	0.554	−0.522	0.762	0.301	−0.016	−0.289	0.740		0.087
STI	0.746	−0.333	0.457	−0.749		0.165	0.291	−0.463	0.471	0.762	−0.128
ELTIN	0.543	−0.401	0.162	−0.396	0.471	0.152	−0.407	−0.075		0.740	0.154
EST	0.751	−0.744		−0.157	0.457	0.827	0.530	−0.063	0.162	0.554	−0.444
WNB	0.473	−0.800	0.827	−0.182	0.165		0.551	0.296	0.152	0.301	−0.402
WSB	0.246	−0.201	0.530	−0.324	0.291	0.551		0.031	−0.407	−0.016	−0.470
CT	−0.033	−0.182	−0.063	0.255	−0.463	0.296	0.031		−0.075	−0.289	0.469
LOU	−0.061	0.018	−0.444	0.086	−0.128	−0.402	−0.470	0.469	0.154	0.087	
RYD	−0.363	0.245	−0.157		−0.749	−0.182	−0.324	0.255	−0.396	−0.522	0.086
EAS	−0.538		−0.744	0.245	−0.333	−0.800	−0.201	−0.182	−0.401	−0.571	0.018


(e) diatoxanthin

S=0.00632
p>0.05

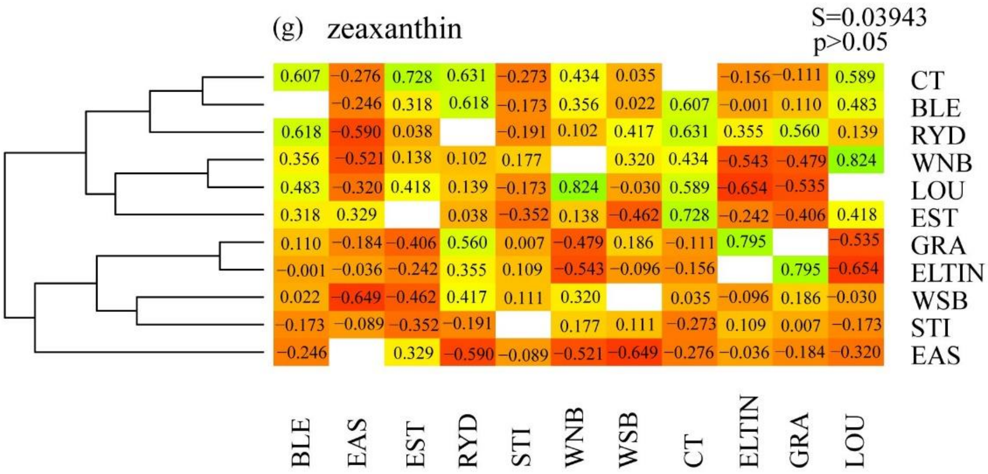
	BLE	EAS	EST	RYD	WNB	WSB	CT	ELTIN	GRA	LOU
RYD	−0.697	−0.301	0.602		0.001	0.489	0.442	0.590	0.555	−0.019
WSB	−0.552	−0.625	0.133	0.489	0.200		0.186	0.008	−0.093	−0.019
GRA	−0.495	0.310	0.076	0.555	−0.691	−0.093	−0.265	0.878		0.093
ELTIN	−0.623	0.382	0.140	0.590	−0.610	0.008	−0.192		0.878	−0.258
EAS	0.001		−0.220	−0.301	−0.618	−0.625	−0.383	0.382	0.310	−0.075
EST	0.042	−0.220		0.602	0.438	0.133	0.885	0.140	0.076	−0.262
CT	0.132	−0.383	0.885	0.442	0.714	0.186		−0.192	−0.265	−0.145
WNB	0.381	−0.618	0.438	0.001		0.200	0.714	−0.610	−0.691	−0.191
LOU	−0.060	−0.075	−0.262	−0.019	−0.191	−0.019	−0.145	−0.258	0.093	
BLE		0.001	0.042	−0.697	0.381	−0.552	0.132	−0.623	−0.495	−0.060


(f) lutein

S=0.09793
p≤0.05

	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
RYD	0.958	−0.708	0.603		−0.140	0.171	−0.105	0.828	0.539	0.563	0.757
BLE		−0.648	0.502	0.958	−0.194	0.309	−0.087	0.912	0.365	0.403	0.789
CT	0.912	−0.611	0.469	0.828	−0.240	0.595	−0.084		0.073	0.108	0.718
LOU	0.789	−0.823	0.037	0.757	0.147	0.329	0.009	0.718	0.264	0.292	
GRA	0.403	−0.420	0.397	0.563	0.031	−0.572	−0.423	0.108	0.922		0.292
ELTIN	0.365	−0.423	0.324	0.539	0.066	−0.572	−0.317	0.073		0.922	0.264
EST	0.502	−0.262		0.603	−0.509	0.172	−0.050	0.469	0.324	0.397	0.037
WNB	0.309	−0.257	0.172	0.171	−0.401		0.330	0.595	−0.572	−0.572	0.329
WSB	−0.087	0.228	−0.050	−0.105	0.124	0.330		−0.084	−0.317	−0.423	0.009
STI	−0.194	−0.103	−0.509	−0.140		−0.401	0.124	−0.240	0.066	0.031	0.147
EAS	−0.648		−0.262	−0.708	−0.103	−0.257	0.228	−0.611	−0.423	−0.420	−0.823

Figure 7.12 Continued.



	BLE	EAS	EST	RYD	STI	WNB	WSB	CT	ELTIN	GRA	LOU
CT	0.607	−0.276	0.728	0.631	−0.273	0.434	0.035		−0.156	−0.111	0.589
BLE		−0.246	0.318	0.618	−0.173	0.356	0.022	0.607	−0.001	0.110	0.483
RYD	0.618	−0.590	0.038		−0.191	0.102	0.417	0.631	0.355	0.560	0.139
WNB	0.356	−0.521	0.138	0.102	0.177		0.320	0.434	−0.543	−0.479	0.824
LOU	0.483	−0.320	0.418	0.139	−0.173	0.824	−0.030	0.589	−0.654	−0.535	
EST	0.318	0.329		0.038	−0.352	0.138	−0.462	0.728	−0.242	−0.406	0.418
GRA	0.110	−0.184	−0.406	0.560	0.007	−0.479	0.186	−0.111	0.795		−0.535
ELTIN	−0.001	−0.036	−0.242	0.355	0.109	−0.543	−0.096	−0.156		0.795	−0.654
WSB	0.022	−0.649	−0.462	0.417	0.111	0.320		0.035	−0.096	0.186	−0.030
STI	−0.173	−0.089	−0.352	−0.191		0.177	0.111	−0.273	0.109	0.007	−0.173
EAS	−0.246		0.329	−0.590	−0.089	−0.521	−0.649	−0.276	−0.036	−0.184	−0.320

Figure 7.12 Continued.

7.2.5 The difference in algal community synchrony between lowland and upland lakes

The difference in sedimentary algal pigment S between lowland and upland lakes was investigated. It was hypothesised that minimal localised land use change in the upland catchments would have led to greater exposure to regional drivers including climatic variation and/or atmospheric deposition on algal communities and so, S values would be higher in the upland sites.

In contrast with this hypothesis, significant S values were higher in algal pigments of the lowland lakes compared to upland for all centennial and inter-decadal timescales since 1800 (Figure 7.13). The low negative S values of the upland sites could have arisen as the pigments varied out of phase (Vogt *et al.*, 2011). The high S values of pigments in the lowlands, particularly in the 20th rather than 19th century could have been due to agricultural and sewage expansion across this time, which increased nutrient addition and promoted both vernal diatoms (diatoxanthin, $S=0.37$, $p \leq 0.05$) and cryptophytes (alloxanthin, $S=0.57$, $p \leq 0.05$) and summer cyanobacterial (canthaxanthin, $S=0.41$, $p \leq 0.05$) and chlorophyte (lutein, $S=0.66$, $p \leq 0.05$) taxa, hence the comparably high S values of these groups (Barker *et al.*, 2005; Dong *et al.*, 2011; McGowan *et al.*, 2012; Moorhouse *et al.*, 2014). This would have resulted in increased autochthonous production as shown by the high S for total algae production in the lowlands (β-carotene, S=0.40, p≤0.05). So, although WwTWs were developed at different times within the 20th century across the catchment, similar increases in human populations (resident and tourist) and sewage processing technologies likely caused this high S of pigments.

The small number of significant (p≤0.05) negative S values for the upland sites suggest localised modifications to regional environmental drivers may have resulted in the different algal community changes since 1800 at these sites (Figure 7.13). Evidence from Mann-Kendall trends point to atmospheric deposition, which can vary both in the magnitude and timing due to differences in terrestrial catchment scavenging of N, buffering of pH and the role of climate and hydrological flushing (Monteith *et al.*, 2000; Evans and Monteith, 2002). These upland sites are oligotrophic, acid-sensitive, and have catchments with relatively little anthropogenic activity. Thus, their chemistry and biology would have been more sensitive to regional forcings such as climate change and atmospheric pollutants which are often registered in upland lakes and which were then modified by lake-specific factors. In contrast, eutrophication

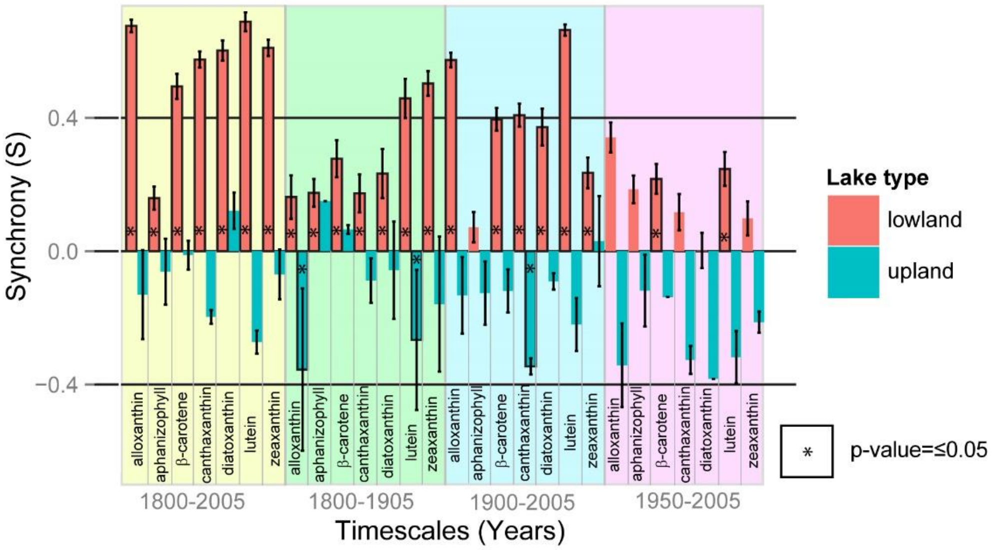


Figure 7.13 Bar chart with SE bars comparing synchrony (S) values of lowland (<100 m.a.s.l.) and upland (>100 m.a.s.l.) lakes with chronologies, from the Windermere catchment, for seven sedimentary algal pigments, across different timescales. Bars with black outline and * have S values with p-values=≤0.05.

often overrides broader-scale longer-term drivers of algal community change such as climate in the lowland lakes (Curtis *et al.*, 2014; Taranu *et al.*, 2015). Both direct climate variability from changes to stratification length and flushing regimes and indirect interactions with atmospheric deposition which alters catchment N and C cycling and attendant NO_3 leaching of catchment soils, have been linked to algal community change in other montane lakes (Wolfe *et al.*, 2001a; Catalan *et al.*, 2002; Bunting *et al.*, 2010). It is likely that differences in catchment vegetation and lake physical characteristics within the Windermere upland sites modified the effects of climate and atmospheric pollutant delivery from the late 19th century onwards, thus causing the asynchronous response of the algal pigments at these sites.

Lowland and upland lakes had no comparable high or low S trends of particular pigments across all timescales (Figure 7.13). Controls of S values of algal communities across lake districts are relatively unknown (Patoine and Leavitt, 2006). Further, little is known about algal succession in the upland sites which makes deciphering patterns of multiple-scale temporal changes even more complex (George, 2010). However, the higher S values of the lowlands compared to the upland sites indicates spatial differences in the control of algal populations in the Windermere catchment since 1800. The close relationship between nutrients and total algal abundance may explain why these lowland lakes, which had similar nutrient fluxes, had relatively high S for most algal pigments (Vogt *et al.*, 2011). Understanding the timings, drivers and landscape controls of algal community change acting on individual lakes can help extricate patterns of catchment-scale S further. This is undertaken in the subsequent chapter.

7.3 Summary: how algal communities have changed in the Windermere catchment since 1800AD

Significant positive monotonic trends and high S values of the total algal carotenoid (β-carotene) are similar to those of summer-blooming cyanobacterial (aphanizophyll, canthaxanthin, zeaxanthin) and chlorophyte (lutein) pigments from 1800, but more notably from 1900 onwards (Figure 7.2

-Figure 7.4; Figure 7.6 - Figure 7.7; Figure 7.8). This suggests increased catchment-wide primary production was dominated by summer- rather than spring-blooming taxa. This trend was identified previously in the Windermere catchment by monitoring work and in other temperate lakes globally (Elliott *et al.*, 2006; Taranu *et al.*, 2015). Prolonged water column stability from climate warming has caused increased summer algal growth and persistence of summer cyanobacterial blooms both in arctic and temperate, oligotrophic and nutrient managed lakes (Kangur *et al.*, 2002; Jeppesen *et al.*, 2005; Smol *et al.*, 2005). A prolonged summer-autumn growing season at BLE_{site} in 1974 was attributed to increased summer temperatures and lower rainfall (Jones and Elliott, 2007). This led to a prolonged WRT and dominance of cyanobacteria as suggested by modelled and observed data (Jones and Elliott, 2007). Thus, it is possible that global climate change has worked synergistically with nutrient enrichment and resulted in prolonged summer algal growing seasons across the Windermere catchment from the 20th century onwards.

However, variable synchrony across algal taxa at centennial and half-centennial timescales and variable Mann-Kendall trend coefficients since 1800 for different pigments at different sites point to other localised control mechanisms of algal community compositions across the catchment (Figure 7.1; Figure 7.13). The difference between lowland and upland S values points to the importance of landscape position on algal community change (Figure 7.13). In the lowlands, the high S values and positive Mann-Kendall trends of nearly all pigments suggest that lowland land use changes led to lake fertilisation and promoted abundance of all taxa from 1800, although more pronounced from 1900 onwards (Figure 7.1; Figure 7.7; Figure 7.13) (McGowan *et al*., 2012). In the upland sites, the predominantly negative Mann-Kendall trends compared to the lowlands and negative S values could be due to the complex interactions between localised catchment and lake characteristics and regional drivers such as acidification and climate variability, at these acid-sensitive, oligotrophic lakes (Figure 7.1; Figure 7.7; Figure 7.13) (Curtis *et al.*, 2014).

The lower S for all pigments post-1950 suggests there was catchment-scale disruption to community succession (Figure 7.8). This again follows an accelerated global pattern of change seen in lentic aquatic systems post-1950 (Catalan *et al.*, 2002; Blenckner *et al.*, 2007; Wolfe *et al.*, 2013). The subsequent chapter attempts to address whether the latter half of the 20th century was indeed a period of extensive environmental change. It also attempts to elucidate the causal mechanisms of algal community changes described in this chapter, and the extent lake and catchment physical characteristics have modified the response of algal communities to drivers of environmental change.

CHAPTER 8. THE KEY TIMINGS AND CAUSES OF ALGAL COMMUNITY CHANGE IN THE WINDERMERE CATCHMENT SINCE THE 19TH CENTURY

8.1 Introduction

This chapter will attempt to address when the major timings of algal community change in the Windermere catchment described in chapter 7 occurred. It will determine and evaluate the relative importance of regional to local environmental drivers of algal community change over the 19th and 20th centuries. It will also investigate to what extent landscape characteristics may have altered community response.

8.2 The key timings of algal community change.

8.2.1 Introduction

Determining the timing of ecosystem change can help to identify major environmental stressors within a region. However, this can be complicated by variability in the timing and nature of human activity and the sensitivity of individual lakes within a region (Bennion *et al*., 2011b). The WFD brought temporally-defined reference conditions to the forefront of lake restoration, commonly using pre-1850 conditions as targets, as this was prior to the onset of rapid industrialisation and population growth (Bennion *et al*., 2011b). But many argue that pre-1945 conditions are more realistic restoration targets, as these pre-dated the growth in use of phosphate-containing detergents and fertiliser applications which elevated atmospheric and fluvial transport of nutrients to surface water bodies (Steffen *et al.*, 2007; Holtgrieve *et al.*, 2011; MacDonald *et al.*, 2011). The following section of this thesis used breakpoint regression (see section 5.5) to help identify when the key timings of algal community change occurred in order to advise appropriate baseline conditions, using 1850 and 1945 as reference points.

8.2.2 Results and interpretation of breakpoint regressions

Synthesis of breakpoint regression results showed that no lakes in the Windermere catchment experienced a break in the slope of algal community change (PCA axis 1 scores) versus time prior to 1850 (Figure 8.1- Figure 8.2). Only STI_{core} had a breakpoint prior to the 20th century (breakpoint=ca. 1880, R^2= 0.64, Figure 8.1). Thus, the 20th rather than the late 19th century was the period of greatest ecological change in the Windermere catchment, as reflected by the lower synchrony of algal groups from this time onwards (Figure 7.8). A reference condition of 1850 for the Windermere catchment lakes would therefore be acceptable as previously recommended for lake Windermere alone (McGowan *et al.*, 2012).

In the 20th century, over half of the lakes had breakpoints in the regression slopes after 1945 (Figure 8.2). This was symptomatic of the "Great Acceleration" (ca.1945), where the rise in detergent and artificial fertilisers led to the eutrophication of lake ecosystems. Lower synchronicity after 1950 of algal groups in the catchment points to increased, localised variability of algal community response, further presented by the different timings of the regression breaks throughout this period (Figure 7.8). Thus, 1945 may well be a useful baseline condition to determine the onset of major ecological change in the Windermere catchment (Bennion *et al.*, 2011b).

However, the four lowland lakes: GRA_{core} (Breakpoint=ca. 1939, R^2=0.74), BLE_{core} (Breakpoint=ca. 1915, R^2=0.76), WNB_{core} (Breakpoint=ca. 1942, R^2=0.83) and WSB_{core} (Breakpoint=ca. 1922, R^2=0.69) had breakpoints in the early half of the 20th century, indicating spatial discrepancy in the timings of change within the lowlands of the catchment (Figure 8.1). The only environmental variable which corresponded to the breakpoints of the four lakes was increases in the individual lake's catchment human resident populations (GRA_{site}=+0.02 individuals per ha. 1931-51, Breakpoint=ca.1939, BLE_{site}=+0.01 individuals per ha. 1911-21, Breakpoint=ca.1915, WNB_{site} and WSB_{site}=+0.004 individuals per ha. 1911-1951, Breakpoints=ca.1942 and

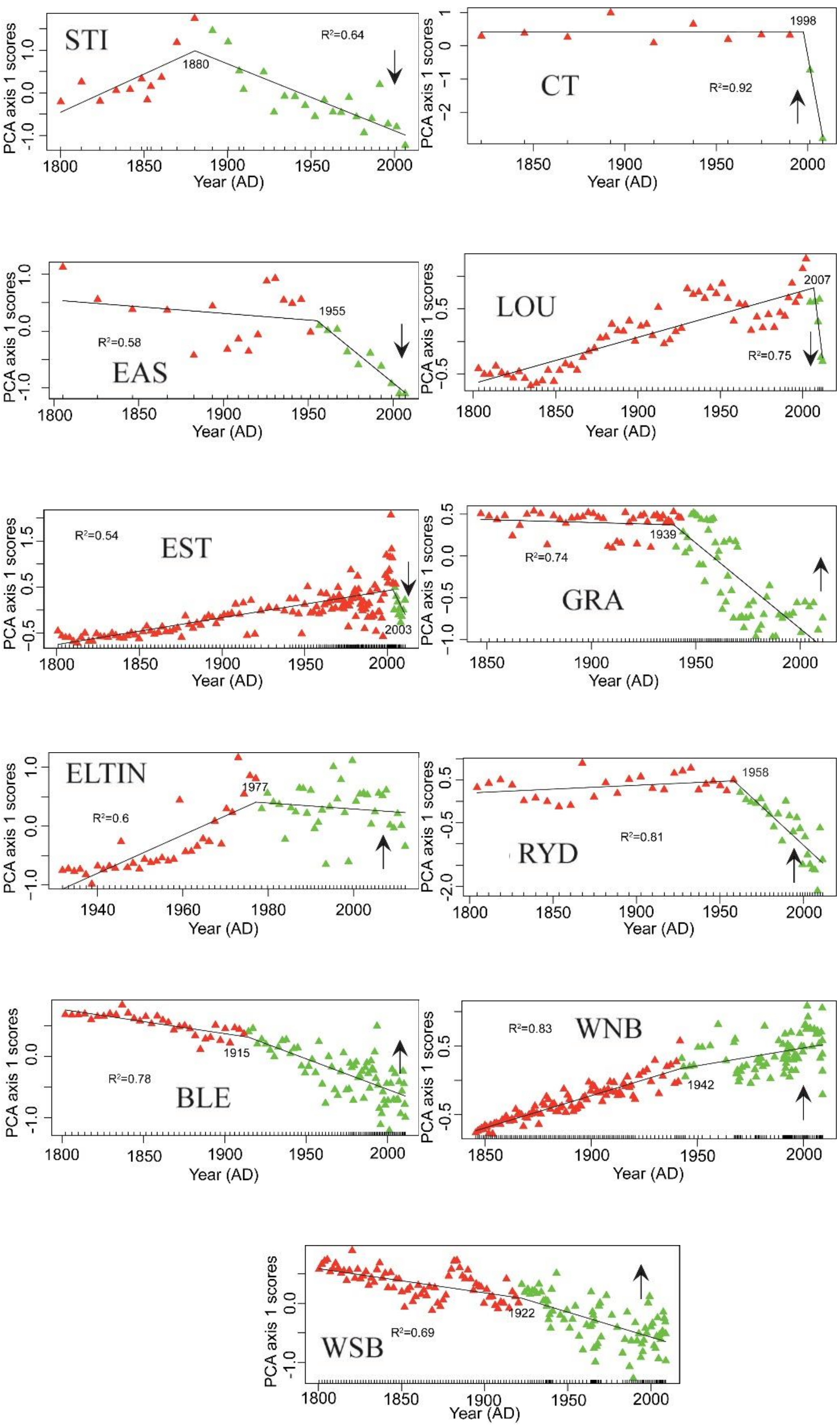


Figure 8.1 Breakpoint graphs of algal community change for dated sediment cores in the Windermere catchment. Red dots indicate PCA axis 1 scores before breakpoint year and green dots after. Black arrow indicates whether most pigments used in the PCA were increasing (up) or decreasing (down) in concentration after the breakpoint. The R^2 value for the regression is also shown.

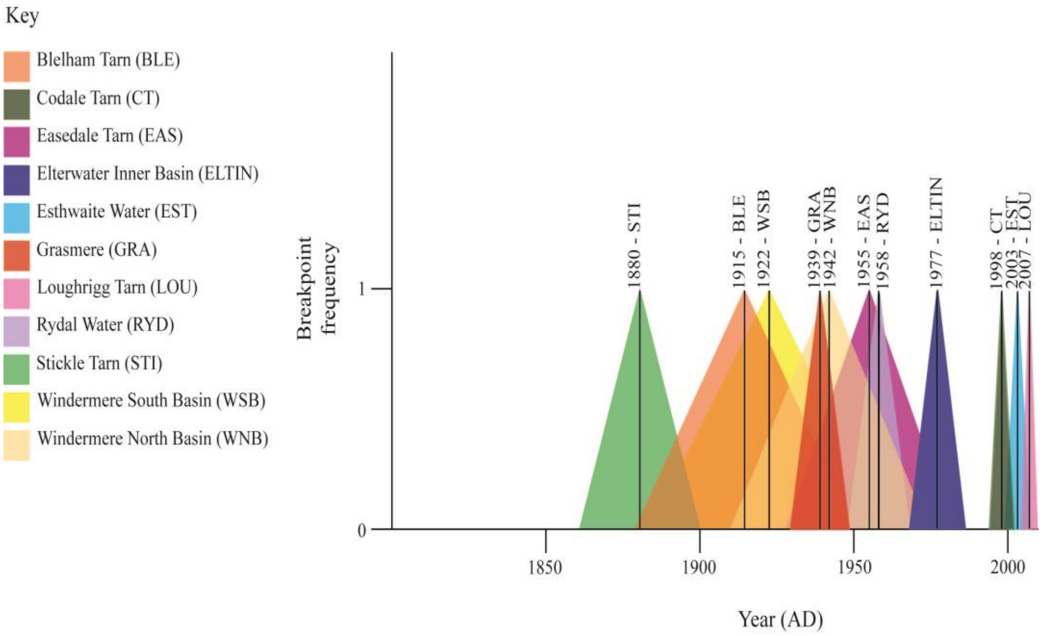


Figure 8.2 Graph showing summary of primary breakpoints of algal community change (PCA axis 1 scores) from dated sediment cores in the Windermere catchment. Base of triangle indicates the 95% confidence interval.

ca.1922 respectively) (Figure 6.31 (3); Figure 6.44 (3)) (McGowan *et al.*, 2012). However, it was unlikely that the rising human populations were ultimately responsible as increased populations were seen before these breakpoints to a greater degree (for example BLE$_{site}$=+0.07 individuals per ha. 1811-21) and were catchment-wide (for example EST$_{site}$=+0.05 individuals per ha. 1811-21, Breakpoint=ca.2003, R^2=0.54).

Another hypothesis is that the human population increases (plus other stressors) acting on these four lakes prior to the breakpoints, made them more sensitive to the later human population changes of the early 20th century. However, agricultural livestock and land use intensification began in the late 19th and early 20th centuries, as did expansion of towns and villages throughout the lowlands of the catchment (McGowan *et al.*, 2012). Specifically, this involved expansion of sewerage systems and housing developments of all lowland lakes including EST$_{site}$ and ELTIN$_{site,}$ where breakpoints occurred much later (Lakes and Grasmere urban district council minutes, 1920-1934, and files relating to sewage, 1969-1972, North Lonsdale urban district council sewerage records letters from local residents to council 1957-1958). In addition, physical characteristics (e.g. CA:LA, WRT or max. depth) of these lakes are markedly different except for altitude (Table 2.1). It was therefore hard to pinpoint why exactly these four lowland lakes had breaks in their slopes in the early 20th century and the other lowland sites did not. However, it highlights the difficulty in using pre-defined spatio-temporal reference conditions beyond the individual lake scale (Bennion *et al.*, 2011b). Lakes within the catchment have responded uniquely in terms of the timings at which algal communities show the greatest change to similar stressors, therefore palaeo records of continuous change are useful (Bennion *et al.*, 2011b).

The lack of spatial trends in breakpoints at finer temporal scales, such as annual to decadal, throughout the Windermere catchment may indicate that localised environmental variables drove the major shifts in algal communities. However, no breaks corresponded with the establishment of point sources or hydromorphological changes in individual catchments (Figure 8.2 ; Figure 8.3). It was therefore more likely that algal communities at each lake responded uniquely to both regional and local stressors from the 19th century onwards. Response to multiple stressors by biological communities can be either threshold changes or gradual and are complicated by the site-specific buffering capacity (Roberts, 1994; Bradshaw *et al.*, 2005). Thus, setting baseline conditions according to threshold changes after 1945 overlooks the gradual change in algal community composition which began after 1850 as shown by the individual pigment stratigraphies in chapter 6.

The use of piecewise regression on PCA axis 1 scores may also help explain the lack of close coherence between breaks and local environmental variables, because some detail is inevitably lost using multivariate analyses to summarise community composition as shown by the PVE scores (Figure 8.1) (Lepš and Šmilauer, 2003). This may explain the discrepancy between the breakpoint dates of c.1922 (R^2=0.69) for $\mathrm{WSB}_{\mathrm{core}}$ and c.1942 (R^2=0.83) for $\mathrm{WNB}_{\mathrm{core}}$ compared to the dates defined by cluster analyses on the individual pigment stratigraphies for these cores (1860, 1945 and 1987 for $\mathrm{WSB}_{\mathrm{core}}$ and 1920 and 1995 for $\mathrm{WNB}_{\mathrm{core}}$). However, community change is a more useful approach to detect ecosystem change as it takes into account group compositional changes and abundance rather than a single diagnostic group which can sometimes be accounted for by changes in only a single stressor such as predation, competition, or a specific environmental condition (Jackson *et al.*, 2001). In such cases, community change summarises the additive or synergistic impacts of multiple anthropogenic stressors affecting lake ecosystems more realistically (Vinebrooke *et al.*, 2004). Because of this a community metric (PCA axis 1 scores) was selected, despite the residual variation (i.e. pigment changes not explained by the PCA axis 1 scores as summarised by the PVE) inherent when using multivariate analyses (Lepš and Šmilauer, 2003). The lack of temporal correlation of the algal communities in the Windermere catchment to a specific local event was therefore unlikely to be a result of the community metric, but more to do with multiple stressors and the breakpoint analysis itself.

Breakpoints look for sharp threshold changes in the changing response variable, but biological responses are often nonlinear and yield no specific threshold change or gradually change over time (Dodds *et al.*, 2010). This raises discussion about defining and measuring threshold changes, which are often inconsistently used when assessing aquatic ecosystem change (Capon *et al.*, 2015). For example, Moorhouse *et al.*, (2014) used cluster analysis which grouped algal pigments into clusters of pigments with similar concentrations and defined 1969 as a period marking an ecosystem state change to dominance of cyanobacteria in $BLE_{core.}$ This year did not correspond to the breakpoint year of ca.1915, which looked for the point at which a threshold change in community composition occurred. It is therefore important from a management perspective to clarify what the analyses are showing. In such cases, most lakes in the Windermere catchment are not showing sudden threshold changes at a certain point in time, but gradual linear change which could make these ecosystems more vulnerable to sudden shifts in states in the future (Folke *et al.*, 2004). However, although the detection and definition of regime shifts continues to be widely debated, it is important managers are made aware of past changes that could indicate future declines in ecosystem condition whether sudden or gradual.

The wide 95% CI's of most of the piecewise regression models could indicate poor fitting of the models and/or lack of a sharp change in the data (Figure 8.2). This indicates that there hasn't been a state change or regime shift, often identified from a sudden change in linear to nonlinear data (Seddon *et al.*, 2014). For example, the wide 95% CI of 71 years at $\mathrm{BLE}_{\mathrm{core}}$ (1879-1950) and the minimal difference in the two regression slopes (despite $p>0.01$) indicates that algal community change was linear (Figure 8.1 – Figure 8.2). Referring to the raw pigment data, the 95% CI represents the period where algae began to increase in abundance and its upper value coincided with large increases in concentrations of all algae in 1950 (Figure 6-43 (3)). Therefore, breakpoints plus their 95% CI's were used to summarise the longer-term trends in algal community change across the catchment rather than detect a single threshold event and attempt to improve the model fit. The use of the 95% CI took into account that some breakpoints occurred at the period marking the beginning of algal community change (i.e. $\mathrm{STI}_{\mathrm{core}}$), whereas others occurred as algae had already changed (i.e. $\mathrm{WNB}_{\mathrm{core}}$). The use of the broader decadel temporal-scale overcame errors associated with the poorly constrained chronologies of $\mathrm{CT}_{\mathrm{core}}$, $\mathrm{LOU}_{\mathrm{core}}$, $\mathrm{GRA}_{\mathrm{core}}$, and $\mathrm{ELTIN}_{\mathrm{core}}$.

The breaks of slopes and small 95% CI's for $\mathrm{CT}_{\mathrm{core}}$ (Breakpoint=ca.1998, $R^2=0.92$, 95% CI=1994-2002), $\mathrm{LOU}_{\mathrm{core}}$ (Breakpoint=ca.2007, $R^2=0.75$, 95% CI=2004-2009) and $\mathrm{EST}_{\mathrm{core}}$ (Breakpoint=ca.2003, $R^2=0.54$, 95% CI=1999-2007) in the early 21st century corresponded to sharp increases and decreases in sedimentary pigments concentrations which suggests threshold changes did occur at these three sites (Figure 6.10 (2); Figure 6.22 (2); Figure 6.26 (3); Figure 8.2). At $\mathrm{EST}_{\mathrm{core}}$ for example, increasing pigment concentrations prior to the breakpoint were parallel with observations of continued nutrient enrichment from the fish farm installation in 1981, catchment runoff and sediment-P release (May *et al.*, 1997; Bennion *et al.*, 2000). This could explain the breakpoint and 95% CI of algal community change in the late 20th and early 21st century (May *et al.*, 1997; Bennion *et al.*, 2000). The reduction in sedimentary pigment concentrations and PCA axis 1 scores from 2003 to 2011 (1 to 0.2) may indicate success of nutrient management strategies such as the removal of the fish farm in 2009, and the lag time between the installation of tertiary treatment at the Hawkshead WwTW in 1986 and response to remediation by the ecology (Figure 6.26 (3)) (CEH, 2015). However, the lower 95% CI year of 1999 occurred well after the 1970s in which increased concentrations of sedimentary pigments and changes to the PCA axis 1 scores ($\bar{x}$PCA axis 1 score=-0.3 from 1800-1970, $\bar{x}$PCA axis 1 score=0.3 from 1970-2011) were found and increased nutrient and phytoplankton biomass was recorded by monitoring (CEH, 2015). Thus, EST$_{core}$ is a useful case to highlight lags in behaviour of biological communities from nutrient enrichment, remediation and complex feedback mechanisms before and after thresholds have been reached (Lau and Lane, 2001). It further highlights that caution is required when setting baseline conditions close to thresholds of community change.

8.2.3 Summary

The result of the breakpoints and 95% CI's provide evidence that a date later than c.1850 such as c.1940 may be more suitable as reference conditions for the Windermere catchment lakes as the majority of lakes had breakpoints and 95% CI's and so, ecological changes in years after 1945.

A baseline of ~1940 is conducive to the definition of land use and agricultural intensification as acknowledged by the WFD, and a more 'realistic' state in which to develop restoration targets (Anderson, 1997). This was evident in the Windermere catchment. For instance, mass tourism began in the mid-19th century with the arrival of the railway to Windermere in 1847, but only in the late 20th century (1960-1980s) did a more extensive growth of the sector and its consequent environmental impact in the Windermere catchment occur (Talling and Heaney, 1988; Bennion *et al.*, 2000). Similarly, a shift from arable to sheep rearing practices in the late 19th century corresponded to changes in the minerogenic and organic composition of lowland lake sediment records. But livestock densities and fertilizer use in the catchment increased in the latter half of the 20th century and led to accelerated soil erosion and nutrient loading and so, changes in the sedimentation rates and algal communities in all lakes (see chapter 6) (Carroll *et al.*, 2004; McGowan *et al.*, 2012; Moorhouse *et al.*, 2014). As such, agricultural intensification often cited as a result of post-war agricultural policy from the mid-20th century onwards results in reference conditions being set c.1945 (Johnes *et al.*, 1994; Robinson and Sutherland, 2002).

Understanding not only when but what caused major shifts in lake ecology is necessary for the success of catchment management. The timings of major algal change in the upland sites (STI_{core}, CT_{core} and EAS_{core}) followed the trend of the lowlands, which began in the late 19th century (STI_{core}), but occurred mainly in the late 20th-early 21st century (CT_{core} and EAS_{core}), despite the differences in localized land use of lowland and upland catchments (Figure 8.2). These similar broader-scale trends could point to the importance of diffuse, regional to semi-regional scale drivers such as agricultural land-use in the lowlands, or climate change and atmospheric N deposition across the region, which although acted at different spatial scales, occurred over similar temporal scales. Such diffuse drivers are often overlooked by studies which focus on lowland lakes influenced by point sources, and induce complex responses at each site in space and time (E.A., 2007).

8.3 The main environmental drivers of algal community change

8.3.1 Introduction

The aim of the Regression Tree (RT) analyses (see section 5.7) was to be able to create a regional long-term synthesis of local and regional environmental stressors that have modified lake ecological communities. This would overcome problems of comparing individual site studies which have used different methodological approaches, whilst also providing the longer-scope and broader perspective required to identify stressors such as climatic variability whose magnitude is often not captured by short-term decadal studies or by individual sites alone (Thies *et al.*, 2012; Tolotti *et al.*, 2012; Taranu *et al.*, 2015).

8.3.2 Results and interpretation of Regression Trees

8.3.3 Wastewater Treatment Works (WwTW) have been the dominant mechanism of algal community change since 1800AD in lowland lakes

RT analyses indicated that the establishment or upgrading of WwTWs in the lowlands lakes of the catchment explained the greatest variation in algal communities over the last ~200 years (Figure 8.3 (a-k); Figure 8-5). This was both in terms of the number of sites at which WwTWs explained the highest amount of variation (n=7), and the amount of variance (34%) explained in relation to other environmental parameters for the whole catchment. Sewage effluent loading likely stimulated algal production at EST_{site}, GRA_{site}, $\text{ELTIN}_{\text{site}}$, BLE_{site}, WNB_{site} and $\text{WSB}_{\text{site.}}$ These lakes had the highest positive Mann-Kendall coefficients of all algal groups, which further suggest that point WwTW treated effluent enhanced algal community abundances. These results were consistent with past studies on Windermere lakes and many other lakes globally, that link point nutrient sources and especially their role in enhanced P delivery to the accelerated eutrophication and increase in algal abundance of lake ecosystems (e.g. Edmondson, 1970; Schindler, 2006; Dong *et al.*, 2012). At WNB_{site} and WSB_{site} efforts to remediate these sources by upgrading in

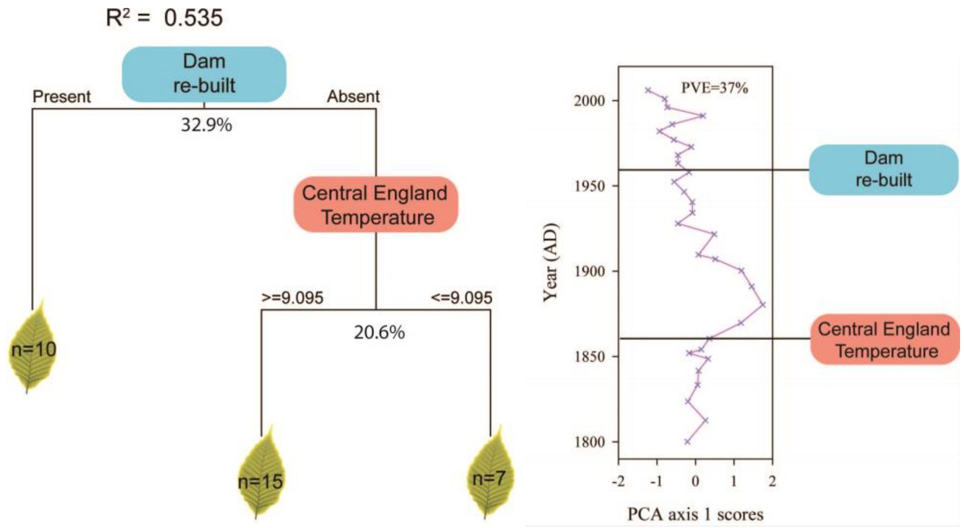
1914 and 1967 respectively, and at $\mathrm{RYD}_{\mathrm{site}}$, the re-location of the discharge pipe to the hypolimnion of its feeder lake $\mathrm{GRA}_{\mathrm{site}}$ in 1982, resulted in the continued modification of their algal communities recorded by the changing PCA axis 1 scores following these years and determined by the RTs (Figure 8.3 (h/j/k)).

Tertiary treatments or P-stripping installed at Hawkshead, Ambleside and TowerWood WwTW at $\mathrm{EST}_{\mathrm{site}}$, $\mathrm{WNB}_{\mathrm{site}}$ and $\mathrm{WSB}_{\mathrm{site}}$ respectively, did not significantly explain any variation in the algal communities (Figure 8.3 (e/j/k)). This suggests these measures were unsuccessful in remediating enrichment. Potential HABs have persisted at these sites, although their prevalence varies from year to year and could be a result of continued nutrient loading from inefficient tertiary treatment, diffuse nutrient sources, inlake recycling and climate warming, which may have confounded these remediation efforts by reducing lake resilience to future change (Pickering, 2001; Folke *et al.*, 2004).

The inconsistency between the breaks in algal community response and the timings of WwTW installation and development throughout the lowland lakes of the catchment was likely related to the linear vs. nonlinear approaches of the statistical analyses. For example, $\mathrm{GRA}_{\mathrm{core}}$ had a breakpoint at ca.1939 (R^2=0.74, 95% CI=1930-1949) but the establishment of the River Rothay WwTW chosen as the best predictor for the sedimentary algal community changes was in 1971. Both analyses detected certain aspects of the algal community change and each approach has its merits. The nonlinear approach of the RT has much more explanatory power than the breakpoint analysis in terms of detecting complex responses to single and multiple stressors (Dent *et al*., 2002). In most cases, community responses to stressors and removal of stressors (such as TP reduction) are nonlinear (Auer and Canale, 1982). In contrast, the linear approach of the breakpoint analysis is useful to detect any sudden changes in the algal communities (Dent *et al*., 2002).

As the breakpoint year at $\mathrm{GRA}_{\mathrm{core}}$ indicated, sedimentary algal pigments had started to show increasing concentrations prior to 1971. For example, fossilised lutein found in chlorophytes often linked to eutrophication increased from 57 to 185 nmole pigment g^{-1} organic weight sediment from 1939 to 1971, but maintained a high mean concentration of 171 nmole pigment g^{-1} organic weight sediment from 1971 to 2013 (Figure 6.30 (2d)). This could suggest that although treated effluent from the River Rothay WwTW significantly modified primary production at GRA_{site}, climate and changes in agriculture, land use and tourism in the catchment much earlier in the 20th century also led to notable changes in the algal communities (Barker *et al.*, 2005). It was therefore more useful to compare the the broader-scale trends identified from the breakpoint analyses to interpret the RT results. In this case, although point source development predicted and explained the greatest amount of algal community change at GRA_{site} and in other lowland lakes, modifications to these communities prior and after indicated by the breaks in slopes vs. time across the 20th century point to additional stressors and/or the gradual response to long-term eutrophication (Davidson and Jeppesen, 2013).

(a) STI



(b) CT

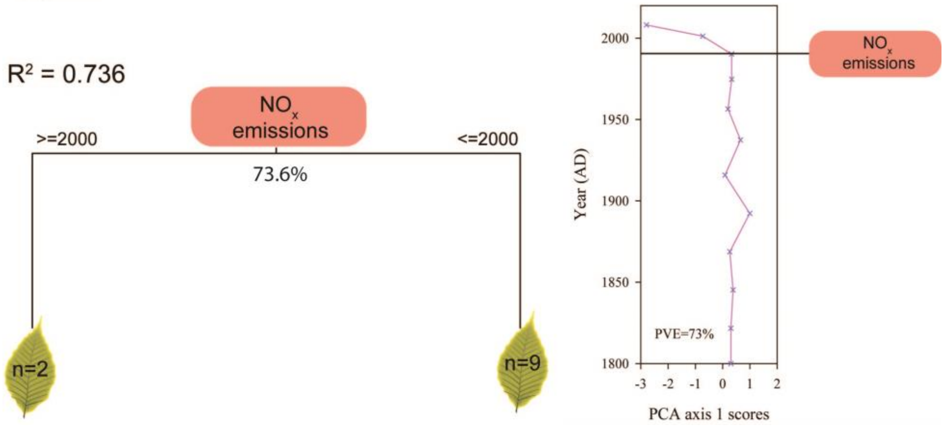
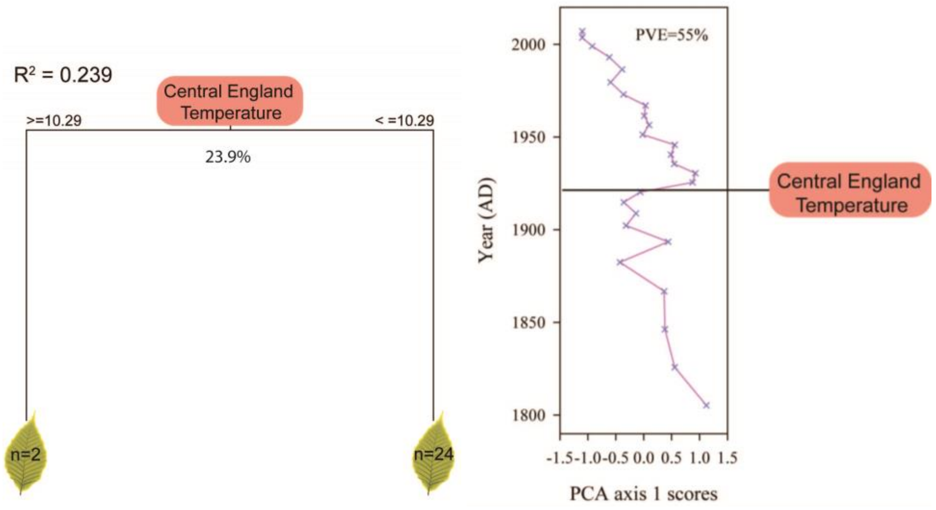


Figure 8.3 (a-k) Regression tree analysis of the relationship between sedimentary algal community change (PCA axis 1 scores) and environmental parameters in the Windermere catchment. Blue environmental variables are related to point sources, red are atmospheric variables, green are agricultural, and yellow are the individual lake catchment human population. R^2 value explains the amount of variation in algal response explained by all nodes, the percentage to which changes in each node or environmental parameter is found below each node. See chapter 5 for details on RT, nodes and leaves. Scatter-line graph beside RT shows PCA axis 1 scores over time and timings of changes in environmental parameters chosen by RT.

(c) EAS



(d) LOU

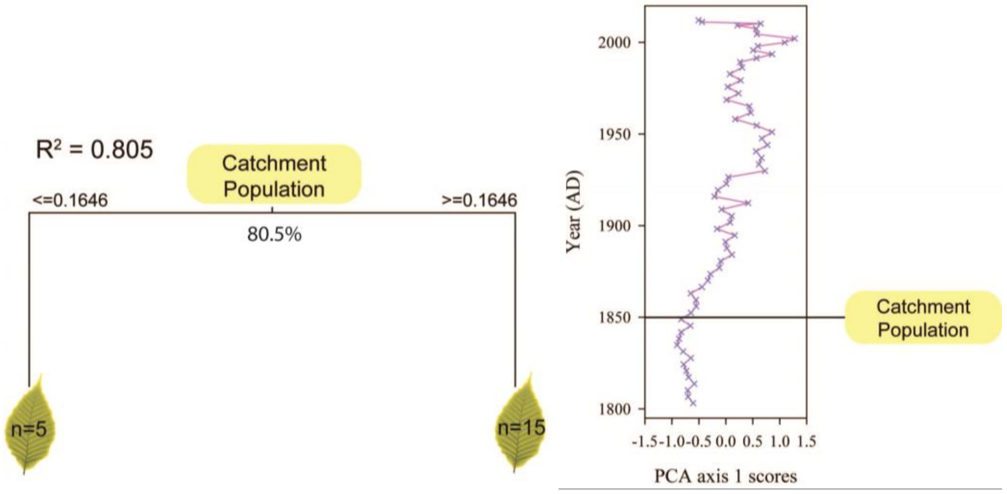
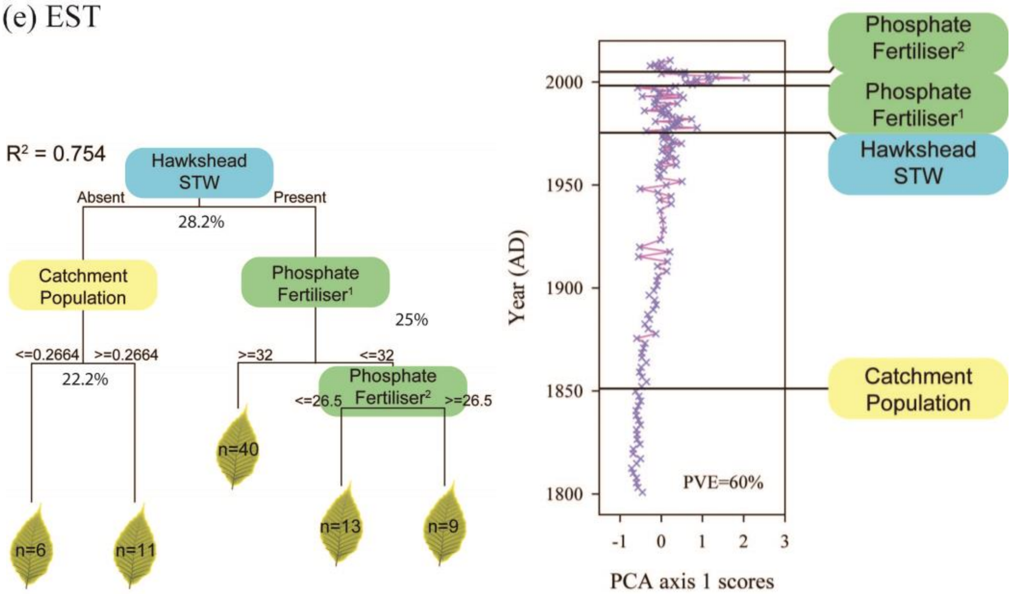


Figure 8.3 Continued

(e) EST



(f) GRA

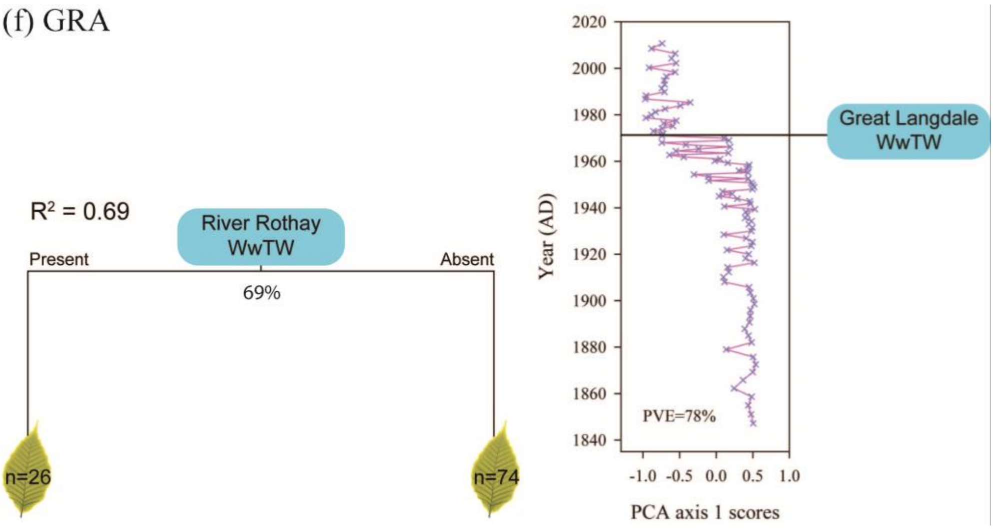
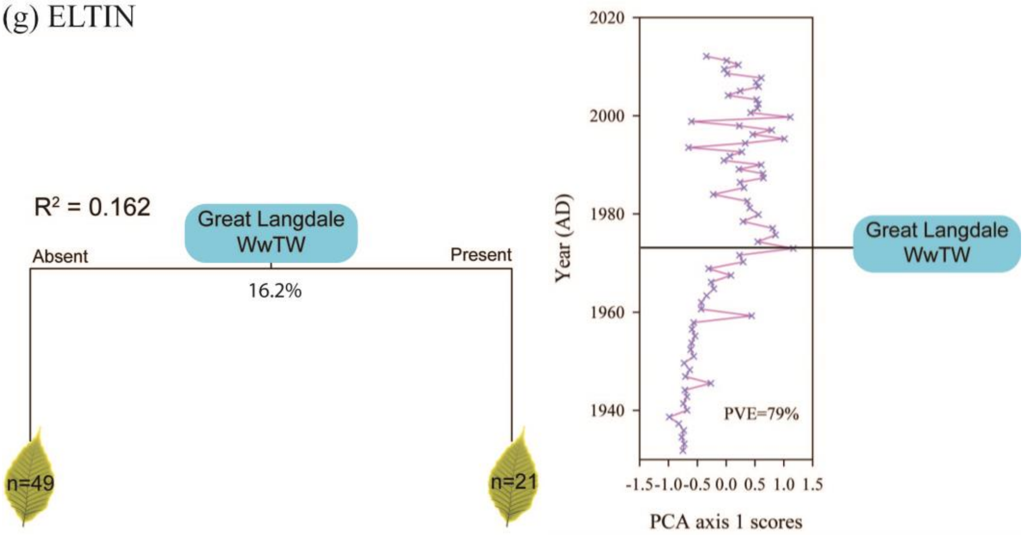


Figure 8.3 Continued

(g) ELTIN



(h) RYD

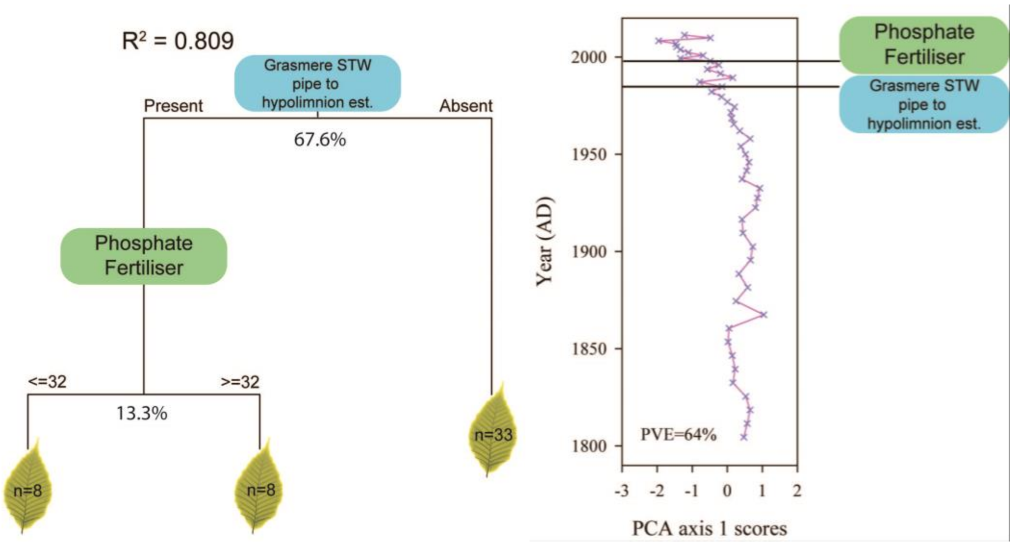
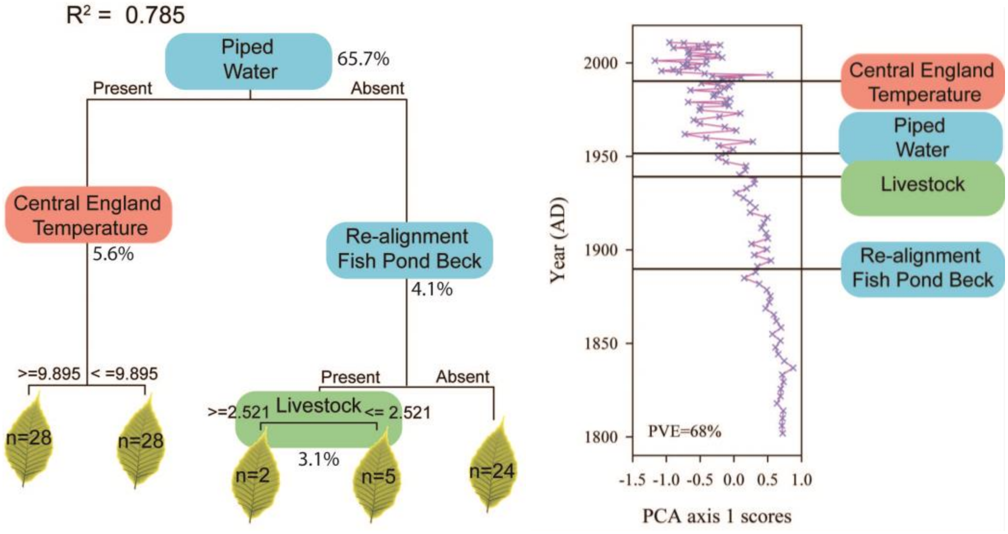


Figure 8.3 Continued

(i) BLE



(j) WNB

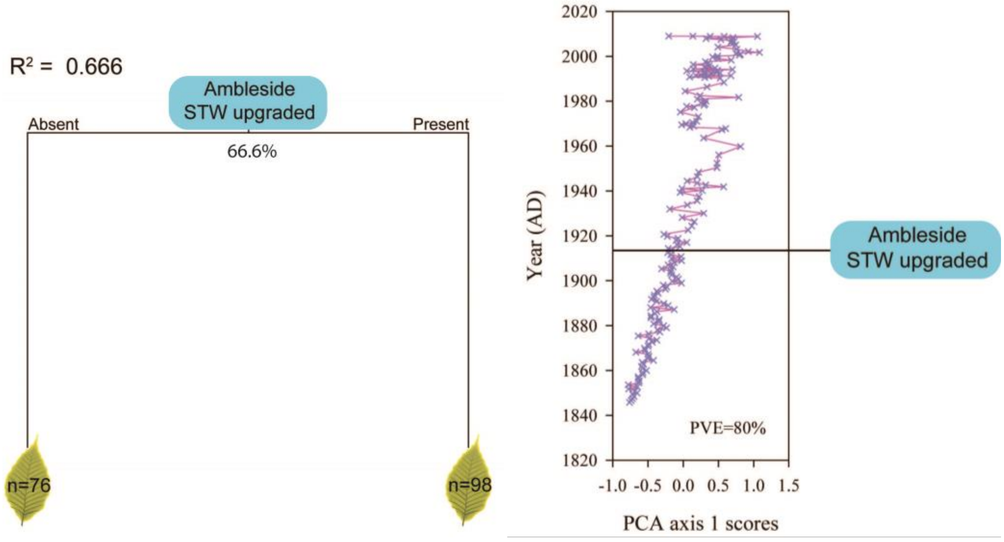


Figure 8.3 Continued

(k) WSB

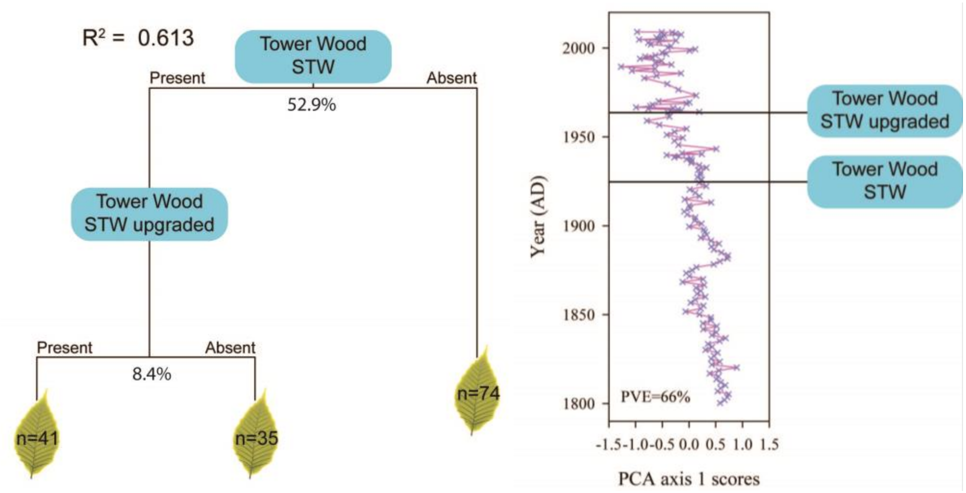


Figure 8.3 Continued

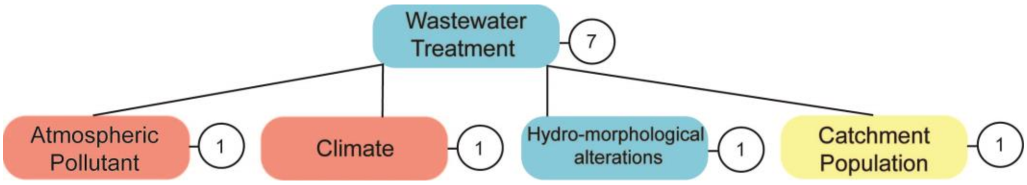


Figure 8.4 Summary of first split nodes and their corresponding environmental parameters. Number of sites occurred in circle.

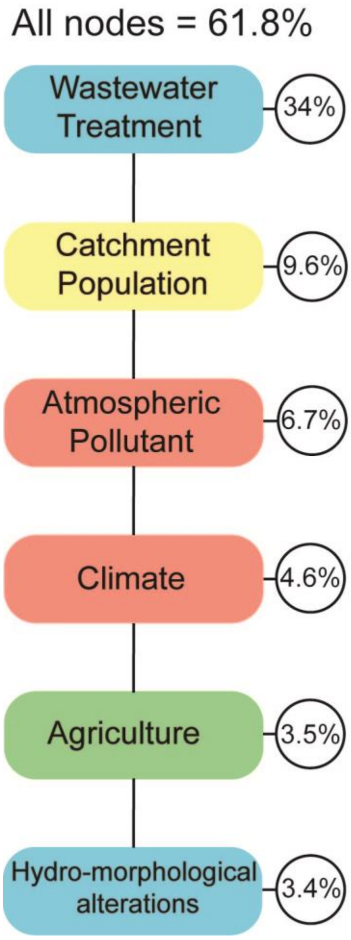


Figure 8-5 Summary of all nodes and their corresponding environmental parameters. The percentage variance explained by the environmental variable is provided in the circle.

The environmental parameters which explained the highest amount of variation at $\mathrm{BLE_{site}}$ and $\mathrm{LOU_{site}}$ (the introduction of piped water (65.7%) and catchment population (80.5%) respectively) were regarded as proxies for sewage loading to these lakes (Figure 8.3(d/i)). At $\mathrm{BLE_{site}}$, the introduction of piped water at Outgate in 1951, led to an overloading of septic tanks and effluent entering the tarn's main inflow Ford Wood Beck (Lund, 1972). From 1957 to 1959, reports of effluent in the Beck continued attributed to poor septic tank construction and maintenance from specified landowners near Outgate (North Lonsdale Rural District Council sewage documents, letters from local residents to council, 1957-59). In 1962, the Outgate sewerage scheme was established to process effluent from Outgate and a small plant and discharge pipe directed treated effluent into Ford Wood Beck (Haworth, 1984). Thus, the installation of piped water marked the beginning of human effluent loading at $\mathrm{BLE_{site}}$, leading to greater algal community change than that of the WwTW installation, likely because the WwTW was installed after pronounced fertilisation. Piped water at Outgate was included as a WwTW parameter in terms of the catchment RT synthesis on account of specific observations of its locality (Figure 8.4-Figure 8-5).

Unlike $\mathrm{BLE_{site}}$, $\mathrm{LOU_{site}}$'s catchment does not contain a small hamlet but several small holdings and a caravan site, all of which are not connected to the mains sewerage (WCRP, 2015a). Cesspools and nuisances with their drainage and reports of overflowing into $\mathrm{GRA_{site}}$ in the late 19th century and early 20th century were documented (Grasmere Urban District Council meeting minutes 1895-1927). It is likely that similar sewage infrastructure at $\mathrm{LOU_{site}}$ nearby to $\mathrm{GRA_{site}}$ was established as the catchment residential and tourist population grew from the mid-19th century in the region, which may have led to nutrient loading at $\mathrm{LOU_{site}}$ (Barker *et al*., 2005). Currently no inventory on the state of septic tanks and cesspools in the Windermere catchment has been undertaken so it is difficult to quantify the extent to which these diffuse point sources contribute to lake fertilisation (WCRP, 2010). Furthermore, increases in catchment populations were concomitant with increases in livestock density throughout the Windermere catchment but censuses of human populations extend further back in time (1801 as opposed to 1866). It could be that in the predominantly agricultural catchment of LOU_{site}, human catchment densities and urban expansion explained the most algal community variation because of its ability to summarise these trends over longer timescales. Further research into the relative importance of these two nutrient sources needs to be undertaken. Therefore, due to its diffuse and unquantified nature, catchment population was kept separate from WwTW despite its links to sewage effluent loading.

8.3.4 Diffuse agricultural inputs

Threshold changes in the agricultural variables P fertiliser and livestock densities, predicted and explained 3.5% of algal community change in some of the lowland lakes (EST_{core}, RYD_{core} and BLE_{core}), which suggest diffuse agricultural nutrients played a minor role compared to point WwTW in modifying algal communities of the lowlands from 1800 onwards. Fertiliser application facilitated the higher livestock densities on the unproductive soils of the catchment lowlands in the latter half of the 20th century, and led to increased sedimentation and nutrient transport to sites such as BLE_{site} (McGowan *et al.,* 2012; Moorhouse *et al.,* 2014). Intensive agriculture was focussed on the fertile catchments of EST_{site} and BLE_{site}, with extensive tracts of improved pasture that led to greater influx of biologically available N and P to these lakes thus enhancing algal production (Heathwaite *et al.*, 1996; George *et al.*, 2000; Donohue *et al.*, 2005).

In contrast, the greater relative effects of agricultural nutrient inputs on algal communities at RYD_{site} compared to GRA_{site} could be attributed to the overarching effect of treated sewage effluent at GRA_{site}. The sewage may have been diluted and/or sequestered by algae and deposited in GRA_{site}'s basin before being transported to RYD_{site}, and hence, could have masked the influence of diffuse agricultural nutrient addition at $\text{GRA}_{\text{site.}}$

Diffuse agricultural pollution is harder to account for as it is dispersed over wider areas and varies according to factors such as weather, slope of the land, topsoil condition, and hydrological pathways (Heathwaite *et al.*, 1996; Carpenter *et al.*, 1998). In the Windermere catchment, agricultural intensification was concomitant with urban sewage development in many of the lakes within the latter half of the 20th century, making it more difficult to extricate the relative influence diffuse agriculture nutrients could have altered algal communities. For example at BLE_{site}, sheep numbers increased 2.5 fold in the 1970s which caused increased poaching and compaction of topsoils and led to enhanced delivery of runoff rich in N to the Tarn, concomitant with the lowest C/N ratios, increased $\delta^{15}N_{org}$ values and a marked increase in fossil cyanobacterial pigments in the sediment record (Figure 6-43 (2c-d/3)) (van der Post *et al.*, 1997; Moorhouse *et al.*, 2014). This followed the expansion of the filamentous cyanobacterial pigment aphanizophyll and the reported appearance of the eutrophic diatom *Fragilaria crotonensis* Kitton (1869) in 1962 in response to the building of the small sewage plant in 1962 (Lund, 1972; Haworth, 1984; Moorhouse *et al.*, 2014). It was therefore likely that both sources worked synergistically in the eutrophication of BLE_{site}.

However, environmental and sedimentary variables changed prior to the latter half of the 20th century at BLE_{site}. Livestock densities began to increase from the 1850s, as did all sedimentary cyanobacterial pigments (echinenone, canthaxanthin, zeaxanthin and aphanizophyll), the chlorophyte pigment lutein, PCA axis 1 scores and lower C/N ratios, albeit not as markedly as those from 1950, suggesting agricultural activity underlies 20th century fertilisation at BLE_{site}. It therefore seems reasonable to assume that highly localised and observable impacts on algal communities from point sources in the lowland lakes acknowledged by the RT results, could have masked the extent of the additive effects of diffuse agricultural nutrients (as previously identified at GRA_{site}) from activity throughout the lowland valleys which are much harder to identify (Carpenter *et al*., 1998).

Changes related to UK P fertiliser trends at EST_{site} (25%) and RYD_{site} (13.3%) showed P rather than N led to the greatest modifications of primary production in the catchment. Artificial P fertilisers contain higher concentrations of soluble and so, biologically available P to that of manure, but inefficient uptake by crops have increased P soil budgets and attendant P losses via runoff and drainage water to aquatic ecosystems (Hart *et al.*, 2004; Johnston and Dawson, 2005). The introduction of artificial fertilisers to the catchment began in the early 1900s and increased in global popularity post-world war II, peaking in the 1980s, which undoubtedly led to increased P loading to the agricultural Windermere lowlands during this period (Bennion *et al.*, 2000; Johnston and Dawson, 2005; Moorhouse *et al.*, 2014). Further, particulate P in surface runoff is facilitated in steep catchments with high rainfall such as the Lake District (Kleinman *et al.*, 2006). High positive Mann-Kendall trend coefficients of the sedimentary colonial cyanobacterial pigment canthaxanthin at EST_{core} ($MK=0.507$, $p<0.005$) and RYD_{core} ($MK=0.376$, $p<0.005$) further suggest that inputs of inorganic P led to the expansion of potentially N_2-fixing cyanobacteria often found in low N but high P waters (Havens *et al.*, 2003). For example, N_2-fixing *Anabaena* spp increased in abundance in years within the 1970s and 1980s when lower dissolved N but high P was recorded in the thermally stratified water column of GRA_{site} (Reynolds *et al.*, 1987).

Several lines of evidence support the hypothesis that agricultural N from both artificial and manure fertilisers acted as significant nutrient sources to these lowland lakes despite not being chosen by the RT analyses. Firstly, several past studies have noted a relationship between increased synthetic N fertiliser use and enhanced primary production in the lowland lakes of the catchment from the 1950s onwards (e.g. Lund, 1972; Sutcliffe *et al.*, 1982; George *et al.*, 2004; Barker *et al.*, 2005; McGowan *et al.*, 2012). Second, high positive Mann-Kendall trends of sedimentary diatoxanthin in the lowland lakes point to enhanced spring diatom growth from 1800 onwards (Figure 7.5). This enhanced spring diatom growth has previously linked to diffuse N from fertiliser application in wet winter months, which increased N leaching and runoff in the catchment (George *et al.*, 2004). Investigating changing $\delta^{15}N_{\text{org}}$ values was undertaken (chapter 9) to investigate this hypothesis further.

8.3.5 Hydromorphological alterations

Hydromorphological changes predicted 4.1% and 32.9% variance in algal community changes at BLE_{core} and STI_{core} respectively, implying increased transport and delivery of nutrients caused algal community changes (Figure 8.3(a/i)). At BLE_{site}, the stream alignment and drainage of Ford Wood Beck (1860-1910) increased the efficiency in the transport of mineralised P-rich effluent from septic tank developments in the hamlet of Outgate from 1900-1950, and N-rich agricultural runoff (Haworth, 1984; Moorhouse *et al.*, 2014). This was marked by a concomitant increase in sedimentary $\delta^{15}N_{org}$ from 2.9 to 3.9‰ from 1860 to 1910 and increased fossil pigment concentrations, both of which suggest enhanced transport alongside increased nutrient loadings at BLE_{site} led to increased primary production (Figure 6-43 (2d/3)) (Moorhouse *et al.*, 2014).

At $STI_{site,}$ the re-building of the outflow dam in 1959, could have led to alterations in the tarn's water level, as experienced with its installation in 1838 (a 2m increase), which would have increased sedimentation of algae as the WRT was lengthened, which would have caused increased pigment deposition. At Red Tarn in the north of the Lake District, and bordering the Windermere catchment, a dam built in 1860 increased the water level to 2.5m and in turn stimulated algal production (Smyntek *et al*., 2014). Increased concentrations of the fossilised pigments lutein (chlorophytes) and alloxanthin (cryptophytes) from the influx of nutrients from terrestrial OM were indicated by increased C/N ratios and decreased $\delta^{13}C_{org}$ values from 1860 onwards (Smyntek *et al.*, 2014). However, similar changes were not seen in the sedimentary pigment and isotope records in 1959 at STI_{core}, as C/N ratios continued to decrease from 20 to 19 implying lower terrestrial inputs, despite decreasing fossil pigment concentrations (Figure 6.6 (2c/3)). In 1838 when the dam was first built at STI_{site}, C/N ratios increased from 22 to 23 but only the sedimentary cyanobacterial pigment zeaxanthin showed corresponding increases from 4 to 6 nmole pigment g^{-1} organic weight sediment from 1833-42. The mismatch between the sediment records and timings of hydromorphological change particularly in the late 20th century may reflect the role of other confounding environmental forcings on centennial-scale algal community change at $\mathrm{STI_{site}}$. Changes in temperature post-1850s was chosen by the model, overruling dam installation as a best predictor of algal community change. This was reflected by the clearer response of the algal community after 1850 with increased concentrations of lutein (chlorophytes) zeaxanthin (cyanobacteria) diatoxanthin (diatoms) and alloxanthin (cryptophytes). This may reflect the low resilience of $\mathrm{STI_{site}}$ and other upland sites to intensified hydrological changes from climate change impacts on already altered hydrological regimes (Smyntek *et al.*, 2014).

8.3.6 Climate

In sites where there were no point nutrient sources such as in the upland tarns, algal community change was best explained by changes in temperature (Figure 8.3-Figure 8-5). This points to the susceptibility of upland systems to climatic variation and/or that climate has been an underlying mechanism in accentuating or magnifying other drivers of change such as atmospheric deposition and eutrophication. Research on alpine and arctic lakes linked changes in water chemistry and primary producers to climate-driven changes in ice cover length and so, growing season duration, as well as changes in catchment vegetation and soils (Anderson, 2000; Sorvari *et al.*, 2002). Such changes may have occurred in the upland sites in accordance with the end of the Little Ice Age from ~1850 onwards and the beginning of global climate change, where warmer temperatures would have reduced ice cover length in the winter and prolonged the growing season (Dokulil, 2013). Minerogenic investigations of sediment at $\mathrm{EAS_{site}}$ found that from 1900 onwards in-wash of catchment material increased related to increased rainfall (Smith, 2014). Although rainfall was not chosen by the RT, soil erosion can be exacerbated by summer drought from increased temperatures if followed by increased winter rainfall and high frequency rainfall events (Engstrom and Rose, 2013).

Similarly, snow-melt duration, not included in the RT analysis due to absence of data, must be considered at these high elevation sites. Early snow melt with higher temperatures corresponded to less NO_3 delivery to surface waters owing to longer terrestrial growing season and less labile N production in catchment soils, however rainfall and atmospheric deposition can override this nutrient reduction (Sickman *et al.*, 2003). The inputs of catchment-derived material from 1900 at $\mathrm{EAS_{site}}$ could have caused an influx of nutrients which alongside increased stratification length from higher temperatures, led to the increased PCA axis 1 scores and cyanobacterial pigments zeaxanthin and aphanizophyll between 1900 to 1950, known to favour nutrient-rich stable conditions (Figure 6.14 (3c/i)) (Paerl and Huisman, 2009; Smith, 2014; Smyntek *et al.*, 2014).

Similarly at $\mathrm{BLE_{site,}}$ temperature changes could have enhanced the effects of eutrophication. A threshold change in CET in the mid-1990s explained 5.6% of algal community change $\mathrm{BLE_{core}}$ (Figure 8.3(i)). Warming temperatures have increased the stratification of $\mathrm{BLE_{site}}$ by 38±8 days since 1968, leading to longer periods of hypolimnetic anoxia and higher spring Chl. *a* concentrations from longer water column stability (Foley *et al.*, 2012). Additionally, these anoxic conditions could have led to the release of P and NH_4 from the sediments, which enhanced eutrophication and promoted summer algal growth as shown by the high concentrations of cyanobacterial (canthaxanthin/echinenone/aphanizophyll) and chlorophyte (lutein) pigments, as well as increasing the potential for enhanced pigment preservation from the mid-1990s onwards (Figure 6-43 (3)) (Nürnberg, 1984; Wetzel, 2001). These results indicate that climate in the late 20th century accentuated and continued symptoms of eutrophication at $\mathrm{BLE_{site}}$, a conclusion which differs from other studies identifying nutrient loading as the major controlling factor on phytoplankton dynamics rather than thermal structure change (Elliott *et al.*, 2006; Foley *et al.*, 2012). The results of this study imply that nutrient loading in the lowland lakes made algal communities more receptive to climate warming and delayed responses to remediation.

8.3.7 Atmospheric deposition: an underlying mechanism of change

Several lines of evidence exist to support the notion that climate change may have enhanced the effects of atmospheric deposition at the upland sites $\mathrm{STI_{core}}$, $\mathrm{CT_{core}}$ and $\mathrm{EAS_{core}}$, and hence why CET was chosen as explaining algal community change in the absence of late 19th to early 20th century acidification monitoring data. First, iron oxide (Fe_2O_3) showed a steady increase at CT_{site} from 1865 and peaked at EAS_{site} between 1900 to the late 1930s, concomitant with increasing PCA axis 1 scores at both sites in the early 20th century (Figure 8.3 (a/c)) (Smith, 2014). Mining and smelting activity in the catchment began in the 16th century and may have been a potential source of Fe_2O_3 to superficial sediments (Marshall and Davies-Shiel, 1969). Under acidified conditions Fe^{3+} in soils is reduced to Fe^{2+}, which may have then been delivered to the lake sediments in the form of Fe_2O_3 via flood-induced inwash along with other acid anions (Tipping *et al.*, 2003; Kabata-Pendias and Mukherjee, 2007; Miller *et al.*, 2014). In addition, wetter and warmer conditions following the end of the Little Ice Age would have enhanced paludification, decreasing the pH of the water percolating through catchment soils and increasing the acidity of the upland sites (Pennington, 1984). Thus, it is possible that acidification and enhanced erosion from high rainfall frequency events were occurring simultaneously in the upland catchments and modifying primary production. For example at EAS_{site}, the increased catchment-derived nutrient delivery shown by peaks in Fe_2O_3 from ~1850 to late 20th century, were parallel to the higher C/N ratios and peaks in deeper-blooming sedimentary cryptophyte (alloxanthin) and cyanobacterial (aphanizophyll) concentrations and PCA axis 1 scores in EAS_{core} (Figure 6.14 (2c/3c-d/3i)). These changes are expected under both enhanced nutrient loading from erosion and habitat expansion from increased water transparency under acidification processes (Whitehead *et al.*, 2009).

Second, acidification from atmospheric deposition of acidic compounds from fossil fuel combustion could have been promoted by increasing temperatures which then altered algal communities at these upland sites (Whitehead *et al.*, 2009). Increased PCA axis 1 scores and deep-blooming cryptophyte (alloxanthin) and cyanobacterial (zeaxanthin, canthaxanthin) sedimentary pigments at STI_{core}, CT_{core} and EAS_{core}, from ~1850 until ~1960, concur with reports of acidification of upland tarns elsewhere in the Lake District attributed to industrialisation and increased artificial N fertiliser use (Haworth and Lishman, 1991; Smyntek *et al.*, 2014). But temperature changes have occurred throughout the 19th to 20th century (Figure 6.1), and so, it was unlikely that small temperature changes could explain the magnitude of algal community response alone detected by the RT (Pla *et al*., 2009). In addition, where longer-term palaeolimnological records in upland lakes exist, no comparable changes in algal communities occurred in recent centuries compared to similar temperature changes of past warmer periods (e.g. Pla and Catalan, 2005). Climate change and recent acidification have both occurred in the last two centuries, with evidence that comparatively small increases in temperature could have enhanced acidification at these upland sites (Pla *et al.*, 2009; Whitehead *et al.*, 2009). Increased temperatures cause lower water tables, leading to enhanced oxidation of sulphur to sulphate in catchment soils, and subsequent rainfall events can transport sulphuric and nitric acids to upland tarns (Dillon *et al.*, 1997; Whitehead *et al.*, 1997; Whitehead *et al.*, 2009). In addition, increased temperatures accelerate snow melt that accumulates dry atmospheric deposition and results in acid shock of surface waters from the sudden decrease in pH in high altitude European lakes (Guilizzoni *et al*., 1992). In the Windermere catchment uplands the effect of snow melt may be comparatively lower than those of the Alps, but high precipitation/flood events common at these sites could still be an important driver of acid shock (Clair and Hindar, 2005; George *et al.*, 2007). This may explain why a single threshold change in CET; a highly variable proxy, explained the most algal community change as shown by the PCA axis 1 scores at STI_{core} and EAS_{core} (Figure 8.3 (a/c)). Finally, the identification of NOx as explaining algal community change at CT_{core} rather than CET, could point to the delayed reversal of past acidification and the complex fertilisation impacts of N deposition on primary production at these remote upland tarns (Figure 8.3 (b)) (Whitehead *et al*., 1997).

8.3.8 Caveats

All the RTs have four or fewer nodes which some may argue result in an oversimplified model of lake ecosystem response to environmental stressors (Figure 8.3 (a-k)) (Van Nes and Scheffer, 2005). This is caused by the pruning procedure by cross-validation that reduces the nodes to obtain the best predictive size tree (Breiman *et al.*, 1984; Ouellette *et al.*, 2012). So, although it could be argued that this oversimplifies complex ecological and environmental relationships, the result is a model which best predicts the response of algal communities to nonlinear threshold changes in environmental variables (Ouellette *et al*., 2012).

Readily interpretable data is paramount to decision makers and hence the use of RT analyses for the Windermere catchment (Orlob, 1992). However, decision makers must be made aware of the limitations to these tools (Orlob, 1992). In which case, although WwTW were the best predictors of algal community change in the Windermere catchment, other variables highlighted by the analyses such as climate and diffuse nutrient sources could have been slightly underestimated by the nature of the RT analysis and the datasets inputted. However, it is unlikely that any other variables would exceed the amount of algal community change explained by the WwTWs due to the number of sites for which it was selected.

Other limitations to the model outputs include exclusion of variables where data did not exist or could not be accessed and the mismatch of sediment records to monitored data from errors with sediment chronologies. In terms of missing explanatory data, sediment-P release has been indicated in many studies in the Windermere catchment including EST_{site} and $ELTIN_{site}$ as an important nutrient source (Bennion *et al.*, 2000; APEM, 2012). External P sources such as WwTW effluent, increased fertiliser and livestock densities have probably been the main sources of P transferred from the water column to the sediment-P pool in the catchment and were included in the model. Thus, because this study was interested in looking for causes of change this was likely not to be too important. However, when considering lake recovery it becomes more important as internal P loading often prevents restoration, and depending on loading history, can continue for several decades (Søndergaard *et al*., 2003). The importance of the internal sediment-P pool in the continued eutrophy of catchment lakes in recent decades was hard to quantify because unlike water column TP and SRP, it has not been monitored (Bennion *et al*., 2005). Although at EST_{site} monitoring work in 2008 and 2009 found hypolimnion SRP concentrations occurred under warmer conditions and increased anoxia, marked differences in inter-annual variation occurred from changes in solar radiation and wind speed (Mackay *et al*., 2014). Increased temperatures at BLE_{site} over several decades (40^+ years) corresponded to lower DO concentrations in the hypolimnion during the extended thermal stratification length and it is likely this increased internal P loads (Nürnberg, 1984; Foley *et al.*, 2012). DO monitoring data could have been used as a proxy for sediment-P release, but this was not pursued as other mechanisms are involved in internal P release such as microbial processes and often lake specific (Søndergaard *et al*., 2003).

Upland acidification in the late 19th to early 20th century was another mechanism of change that was not adequately summarised by the NO_x and SO_2 emissions data for two important reasons. First, substantial non-linearities have been observed between emissions and deposition data (RoTAP, 2012). Although emissions of SO_2 declined by 94%, alongside declines of dry deposition by 93% and wet deposition by 57% from 1970 to 2010, NO_x declined by 50%, but deposition decreased by only 13% from 1988 to 2008 (RoTAP, 2012). The SO_2 emissions and deposition data do follow similar trends, only NO_x emissions were chosen by the RTs at CT_{core}. Unfortunately, deposition data was not readily accessible for this study. Second, the emissions data began in 1970, overlooking most of the period beginning in the Industrial Revolution when acidifying pollutants became abundant. The mismatch between the relatively short-term emissions data to the longer-scale deposition, acidification and reversal processes that have acted alongside other confounding drivers such as climate change at STI_{core}, CT_{core} and EAS_{core} from the late 19th century make it difficult to accurately assess the role air pollutants have shaped algal communities in the Windermere catchment.

The threshold change in NOx was found to be the best predictor of algal communities at CT_{core} (R^2=0.736) (Figure 8.3 (b)) and corresponded to increases in the Chl. *a/* pheophytin *a* ratio from 1996 to 2013 (0.65 to 1.2), alongside other large increases in sedimentary pigments. This suggests that the threshold algal response was a post-depositional degradation curve, rather than a response to the UK NOx emissions decrease to <2,000 10^3 tonnes as implied by the RT after 1996 (Figure 6.10 (2h)) (Moss, 1968). Despite this shortfall, atmospheric deposition (of N) was kept in the regional synthesis because high values in the catchment of 56 kg N km^{-2} yr^{-1} were recorded between 1986-88, and averaged at 3500 N km^{-2} yr^{-1} for the whole lake district indicating this could be a significant source of nutrients to the N and P-limited upland waters and indeed lowlands, despite not been chosen as a predictor of algal communities by the RT analyses elsewhere (Talling and Heaney, 1988; Maberly *et al.*, 2002). Sedimentary $\delta^{15}N_{org}$ isotopes are investigated in chapter 9 to look into the role of N in lake fertilisation in the catchment further.

Detergent-P was not included in the RT analyses due to its presence in sewage effluent, which meant that WwTW installation was a viable proxy for this nutrient source. The rise in phosphate-containing detergents doubled the human P consumption per capita from 1950 to 1970 in the UK, but from 1988 to 1998 detergent-P consumption fell by 25% as the harmful effects on aquatic ecosystems became known (Figure 8.6) (Battarbee, 1978; Foy *et al.*, 2003). P loading in the lowland lakes BLE$_{site}$, EST$_{site}$ and WSB$_{site}$, increased in the 1960s to which P-rich detergents present in sewage effluent were acknowledged as a key source (Lund, 1972; Sutcliffe *et al.*, 1982). Interestingly, no peaks in P from 1945-80 at WNB$_{site}$ were found despite it being a receiving waterbody of treated effluent, which may have been due to its larger upland catchment, basin size and lower population density to that of WSB$_{site}$ (Sutcliffe *et al.*, 1982). Thus, although detergent-P has in the past played a relatively short but important part in lake fertilisation in the catchment and indeed globally, this varied according to the spatial-temporal differences of effluent received and basin and catchment characteristics (Heathwaite *et al.*, 1996). The link between algal community change in the lowlands to WwTW development and more positive Mann-Kendall trends of fossil pigments reflect the role played by detergent-P in the continued eutrophication of these lowlands in recent decades. However, the EU has developed restrictions to phase-out all but trace amounts of P in laundry detergents by 2013 and dishwasher detergents by 2017, which almost removes this as a future management concern.

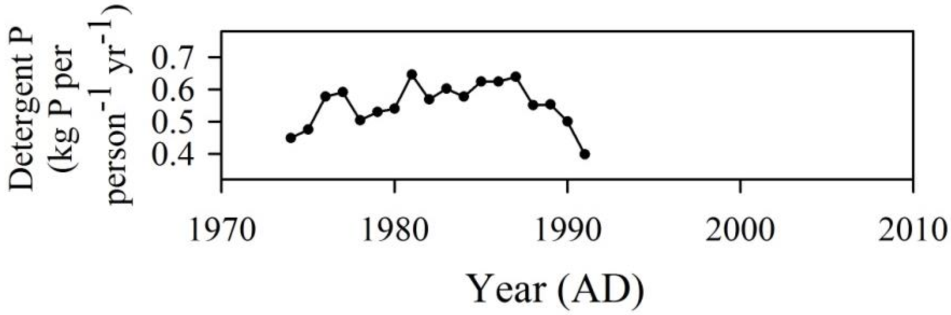


Figure 8.6 UK trends in detergent-P use. Sourced from the Soap and Detergent Industry Association and Patrick (1983). In Foy *et al*. (1995).

A mismatch between environmental monitoring data and sedimentary algal pigment response may stem from errors relating to sediment dating. As previously identified, poorly constrained chronologies from $\mathrm{CT_{core}}$, $\mathrm{ELTIN_{core}}$, $\mathrm{GRA_{core}}$ and $\mathrm{LOU_{core}}$ in particular, could have led to disparity between the timings of environmental threshold changes and sedimentary algal community change, altering the variance explained and even perhaps the environmental variable chosen by the model. However, the input of longer-term monitoring data in the RT analyses and the model's ability to look for nonlinear relationships between explanatory and response variables overcomes finer-temporal scale discrepancies from poorly constrained sediment chronologies (Ouellette *et al*., 2012).

8.3.9 Summary

Like many other historical studies, the regression analyses conclude that point nutrient inputs overwhelmed the effects of noisier background climate and regional drivers in elevating algal community change throughout the Windermere catchment since 1800 (Figure 8.3) (Leavitt *et al.*, 2009; Dong *et al.*, 2011; Taranu *et al.*, 2015). The difference in residual variance of the models identified the individuality of lake algal community response to centennial-scale forcings, and the spatial heterogeneity of the landscape and lakes in the Windermere catchment (Van Nes and Scheffer, 2005). For example, two of the most eutrophic lowland sites: LOU_{core} and $\text{ELTIN}_{\text{core}}$ had starkly different % residual variance: 19.5% and 83.8% respectively. This difference could reflect the role lake and catchment physical characteristics have played in shaping algal community response in the Windermere catchment (Taranu *et al.*, 2015). How landscape heterogeneity may have altered algal community response is investigated in section 8.4 to help explain the residual variance further.

8.4 The relationship between a lake's physical characteristic and algal community change

8.4.1 Introduction

It has long been recognised that ecological phenomena display spatial and temporal patterns, however only relatively recently have limnologists looked at the physical, chemical and biological characteristics of lakes in their landscapes (Soranno *et al.*, 1999; Chase and Leibold, 2002). Lake order or position from headwater seepage to lowland drainage lakes exhibit considerable variation in physical (e.g. CA:LA), chemical (e.g. major ions) and biological variables (Soranno *et al.*, 1999; Quinlan *et al.*, 2003). Landscape position further alters a lake's response to environmental perturbations due to the correlation between physical and chemical variables, and patterns of land use activity (Kratz *et al.*, 1997; Reed-Andersen *et al.*, 2000). However less attention has been paid to biological parameters especially community change in lakes across a landscape (Lewis and Magnuson, 2000). Understanding the role landscape position may have played in shaping community response is paramount when considering baseline conditions and where to prioritise catchment management and hence its undertaking here.

8.4.2 Altitude

It was hypothesised that algal community change would be explained by changing gradients and distinct differences in altitude. This was based on evidence that changes in catchment productivity and human disturbance cause higher trophic status with decreasing altitude (Nõges *et al.*, 2003; Zhang *et al.*, 2010).

In terms of community compositional change, linear regression revealed no significant correlation between lake altitude (m.a.s.l.) and algal community change (Mann-Kendall coefficients of PCA axis 1 scores of seven stable pigments from 1800) (*adj.* R^2=-0.143, p>0.05) across the Windermere catchment (Figure 8.8 (a-b)). Thus, lake order appears to have been unimportant in modifying past algal community change in the Windermere catchment. Other studies found lake order explained sub-fossil algal community compositional changes, but lake-specific environmental variables (e.g. lake chemistry and morphology) explained a much greater proportion (Quinlan *et al*., 2003). In Canadian shallow mountain lakes, algal biomass and community composition showed inverse correlations to lake elevation, but epilithic algae possessed additional positive correlations to DOC and conductivity, and phytoplankton were positively correlated to zooplankton (Vinebrooke and Leavitt, 1999). Therefore, other spatial features which control lake biology, chemistry and physical properties must have played a more dominant role than lake order in the Windermere catchment.

However, a t-test found a significantly higher total algal biomass (mean β-carotene pigment concentrations) and algal community change (Mann-Kendal coefficients of PCA axis 1 scores) over the last ~200 years in lowland than upland lakes ($p \leq 0.05$) (Figure 8.7; Figure 8.8 (c)). This could be due to different trophic statuses; upland lakes are typically oligotrophic and hence have lower algal biomass and community change compared to lowland meso- to eutrophic lakes (Maberly and Elliott, 2012). However, the statistical tests showed that algal biomass was more distinctly different than community compositional changes, implying that different lake physical and morphological controlling factors may better explain algal community shifts.

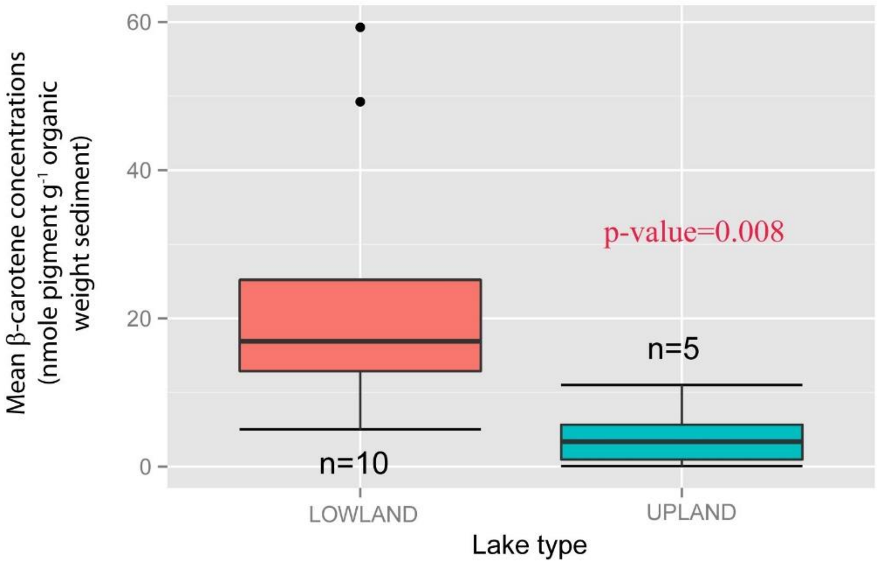


Figure 8.7 Box plot showing mean β-carotene concentrations since 1800 between lowland (<100 m.a.s.l.) and upland (>100 m.a.s.l.) lakes. P-value of t-test shows significant difference between the two lake types with $p \leq 0.05$.

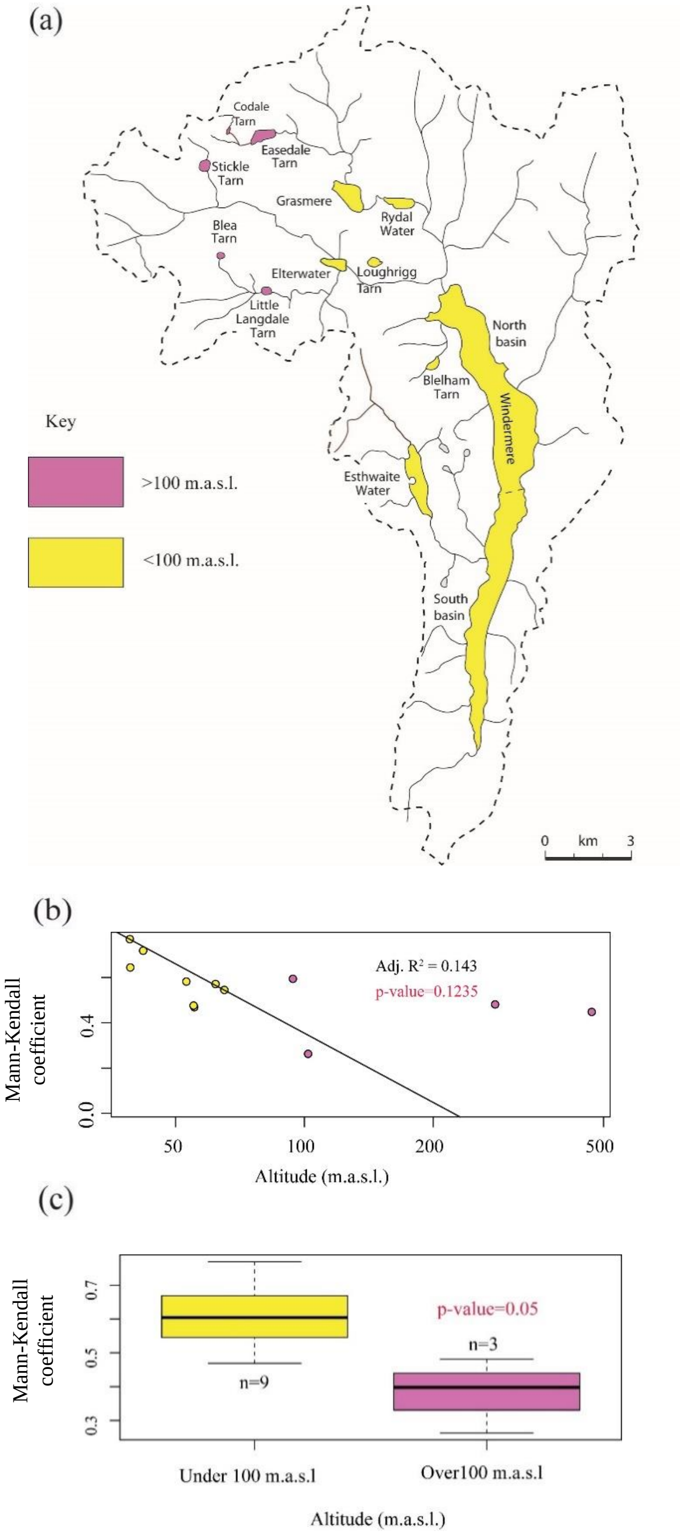


Figure 8.8 (a) Map of Windermere catchment of lakes with altitude >100 m.a.s.l. in pink and <100 m.a.s.l. in yellow. (b) Linear regression showing the relationship between lake Mann-Kendall coefficients of algal community change (PCA axis 1 scores) and altitude. (c) T.test showing difference between Mann-Kendall coefficients of algal community change (PCA axis 1 scores) in lowland (<100 m.a.s.l.) and upland (>100 m.a.s.l.) lakes. P-value of t-test shows significant difference between the two lake types with p≤0.05.

8.4.3 Catchment area: lake area ratio (CA:LA)

Regression analysis revealed a significant relationship (*adj.* R^2=0.258, $p \leq 0.05$) in which algal community change was greatest in lakes with smaller CA:LA ratios, although this gradient was more pronounced with ratios of 40 and above (Figure 8.9). Lakes with larger CA:LA ratios particularly upland sites such as LLT_{site} (CA:LA=184.6), would have experienced greater hydraulic flushing (WRT=3.3 days) due to larger drainage areas (Maberly *et al.*, 2002). This could have diluted nutrients and vernal and summer algal inoculum from increased flushing, hence the lower community change of these lakes (Reynolds and Irish, 2000; Maberly *et al.*, 2002).

The gradient of decreasing algal community change with increasing CA:LA appeared to be driven predominantly by the outlier LLT_{core}, and much greater spatial heterogeneity is apparent. Such spatial differences could have arisen from differences in the level of nutrient management in the catchment, geology and other morphological features that have been linked to lake trophic state and ecological change (George *et al.*, 2000; Maberly and Elliott, 2012).

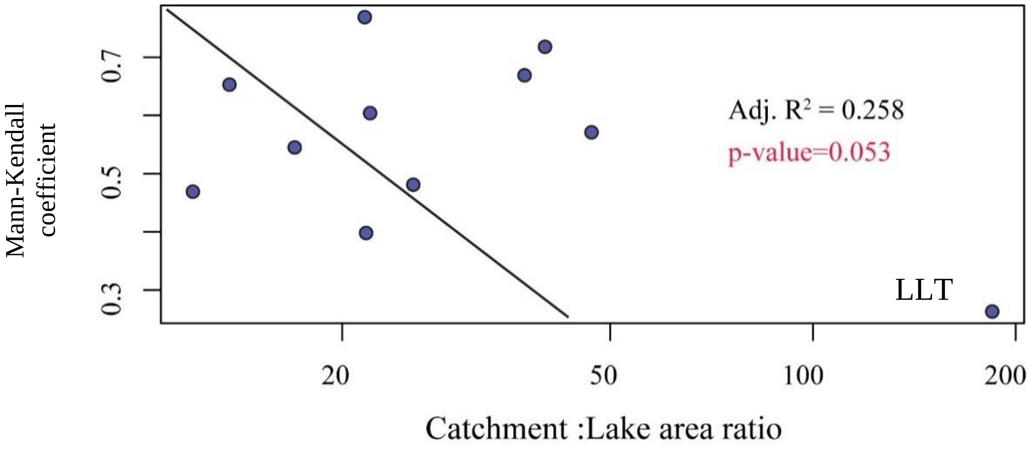


Figure 8.9 Linear regression showing the relationship between lake Mann-Kendall coefficients of algal community change (PCA axis 1 scores) and catchment to lake area ratio (CA:LA).

8.4.4 Geology

Algal community change since 1800 was significantly lower ($p \leq 0.05$) in lakes overlying BVG to those on SIL bedrock (Figure 8.10 (a-b)). This was likely to have been due to the low major ion content of BVG lakes which resembles precipitation (Sutcliffe, 1998). Major ions such as sodium, potassium and chloride are important in regulating plant tissue, and although sulphate is an important component of tissue cells it is more important in maintaining the external lake environment and a balance to H^+ ions (Sutcliffe, 1998). The low content of these solutes have led to BVG waters being historically unproductive and having a low pH from greater acid sensitivity (Sutcliffe *et al.*, 1982; Reynolds *et al.*, 2012).

Human activity within lake catchments could have modified the relative importance of underlying geology. In the lowland BVG lakes such as GRA_{site}, human-mediated catchment changes from the 19th century onwards altered water chemistry and in particular nutrient addition, promoting algal productivity (Reynolds *et al*., 2012). The upland BVG sites are more acid sensitive due to the low ionic content and minimal human catchment activity (Tipping *et al*., 2002). Therefore, atmospheric deposition of N and S from anthropogenic sources, beginning in the Industrial Revolution, had a more pronounced effect on these upland waters, as the lowlands had a greater buffering capacity both naturally (SIL lowlands) and from human catchment inputs (BVG lowlands) (Sutcliffe and Carrick, 1983; Tailing *et al.*, 1986). Acidification in the upland lakes led to increased water transparency and altered algal communities but low nutrient content constrained much higher primary production rates (Maberly *et al*., 2002).

In contrast, the lowland lakes overlying SIL geology were historically more productive on account of higher ionic content from rapid mineral weathering of SIL bedrock and inflows from more fertile, productive catchments (Tailing *et al*., 1986). Increased ion and nutrient content of these waters attributed to atmospheric deposition, sewage, road salt and liming from the 19th century modified the water chemistry further (Tailing *et al*., 1986). This could have led to greater algal community change and enhanced production in SIL lakes relative to the BVG group over the last ~200 years.

The productivity of the catchment may have complicated the relationship between algal community changes since 1800 to lake bedrock geology. In the Windermere catchment, unproductive soils were 'improved' with modern agriculture since ~1850 (Pickering, 2001). Agriculture was less intense in the catchments of BVG lakes where soils consisted of peats and stagnopodzols, bare rock, and unproductive *Sphagnum* mosses and rough grassland (Jarvis *et al.*, 1984; Tipping *et al.*, 2002). Agricultural intensification was most pronounced in the naturally more fertile valley catchments of the SIL lowland lakes BLE_{site} and $EST_{site,}$ which likely enhanced fertilisation and thus, caused the high algal community change at these sites (MK=0.718 at BLE_{site} and MK=0.545 at EST_{site}, $p<0.001$) (Heathwaite *et al.*, 1996; George *et al.*, 2000). The smaller CA:LA particularly at EST_{site} (CA:LA=17) would have further concentrated nutrients in surface runoff and soil leachates entering the lake (Tailing *et al*., 1986).

In contrast at WNB_{site}, its larger unproductive upland catchment could have diluted nutrient inputs and led to the lower total algal production since 1800 to that of the other SIL lakes ($\bar{x}$ β-carotene concentration at WNB_{core}=12.5, WSB_{core}=25, EST_{core}=25.2, BLE_{core}=16.5 nmole pigment g^{-1} organic weight sediment respectively) (Heathwaite *et al*., 1996). Therefore, its highest positive trend (MK=0.769, $p>0.001$) in algal community change must be explained by point nutrient additions from WwTW as shown by the RT, and its high WRT (180 days) which would have magnified algal community compositional change in this historically less productive basin (Heathwaite *et al*., 1996). In contrast, WSB_{site} received runoff from its lower-lying catchment where agriculture and human activity were more extensive, and so, the degree of community change (MK=0.669, $p>0.001$) was less marked at this more productive basin (Heathwaite *et al*., 1996). In conclusion, higher catchment productivity and SIL geology acted synergistically in providing greater baseline trophic conditions, which then amplified point nutrient inputs and led to greater algal community change. Greater magnification of community response was seen at WNB_{core} despite lower catchment productivity, which could be attributed to not only its SIL geology and point nutrient enrichment in the early 20th century, but its long WRT (180 days). Therefore, understanding a lake’s hydrology and fertilisation history is important when interpreting algal community baseline conditions.

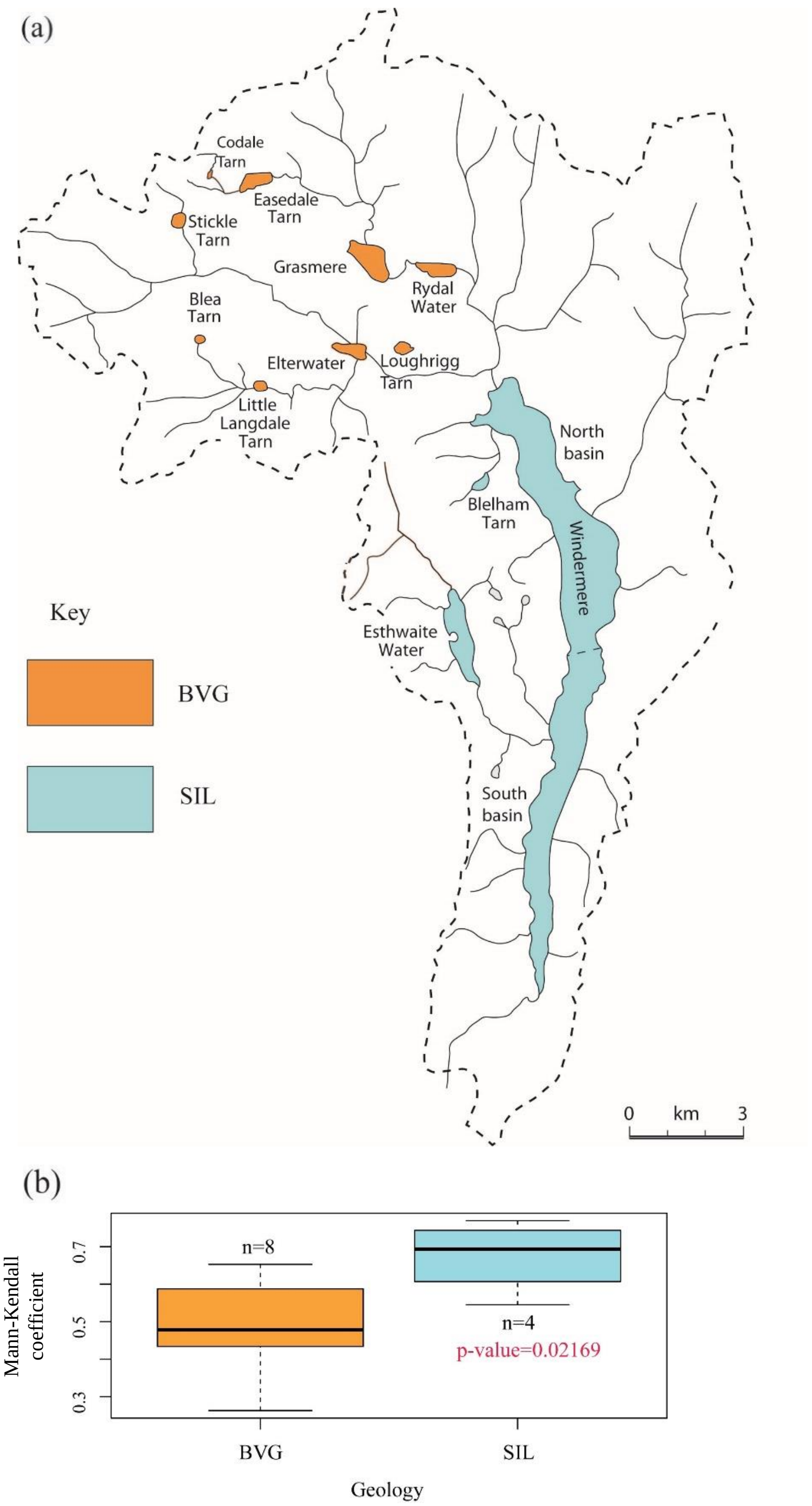


Figure 8.10 (a) Map of Windermere catchment with lakes underlying BVG (Borrowdale Volcanic Group) bedrock in orange and SIL (Silurian Coniston Flags and Slates) in blue. (b) T-test boxplot comparing Mann-Kendall coefficient of algal community change (PCA axis 1 scores) between the two geology types. P-value of t-test shows significant difference between the two lake types with p≤0.05.

8.4.5 Water Retention Time

Regression analysis showed the most pronounced gradient of algal community response was correlated with WRTs, where community change over the last ~200 years was greater the longer the WRT of the lake (*adj.* R^2=0.301, $p<0.05$) (Figure 8.11 (b)). However, there was no significant ($p>0.05$) difference between algal community change in lakes of shorter WRTs (<100 days) compared to longer WRTs (≥100 days) (Figure 8.11(c)). This may be due to the varied effects of WRTs on temperature regimes, supply and cycling of nutrients on the development of algal succession and abundance in different basins, resulting in no distinct pattern (Bailey-Watts *et al.*, 1990).

Although lakes with longer WRTs (≥100 days) were lowland and meso- to eutrophic (EST_{site}, LOU_{site}, $\text{ELTIN}_{\text{site}}$, WNB_{site} and WSB_{site}) and had the highest positive Mann-Kendall trends of all algal groups, suggesting that both centennial-scale fertilisation and WRT worked synergistically to promote high algal production (Figure 7.1 - Figure 7.7). Stronger stratification from reduced flushing would have prolonged hypolimnetic anoxia, and increased sediment-P release, which could have additionally enhanced algal growth in these lakes (Carvalho *et al.*, 2011). Potentially toxic bloom-forming cyanobacteria such as *Anabaena* spp. and *Aphanizomenon* spp. dominated in summer months with lower flushing and higher water temperatures at EST_{site}, with these taxa then modifying phytoplankton community succession further by altering light, nutrients and CO_2 regimes in the water column (Scheffer *et al.*, 1997; Elliott, 2010). Consequently, algae that are physiologically adapted to tolerate substantial shifts in the aforementioned limnological variables became more apparent since the late 1980s, such as *Aphanizomenon* spp. and *F. crotonensis* as found at WNB_{site} (Reynolds, 1998). In contrast, the dominant non-buoyant cyanobacteria *Oscillatoria bourrelleyi* which dominated at WNB_{site} in the 1980s, disappeared from the basin from 1993 (Reynolds, 1998). Thus, increasing temperatures worked synergistically with eutrophication and longer WRTs, and resulted in prolonged stratification and shifted primary producer community structure in these lowland lakes.

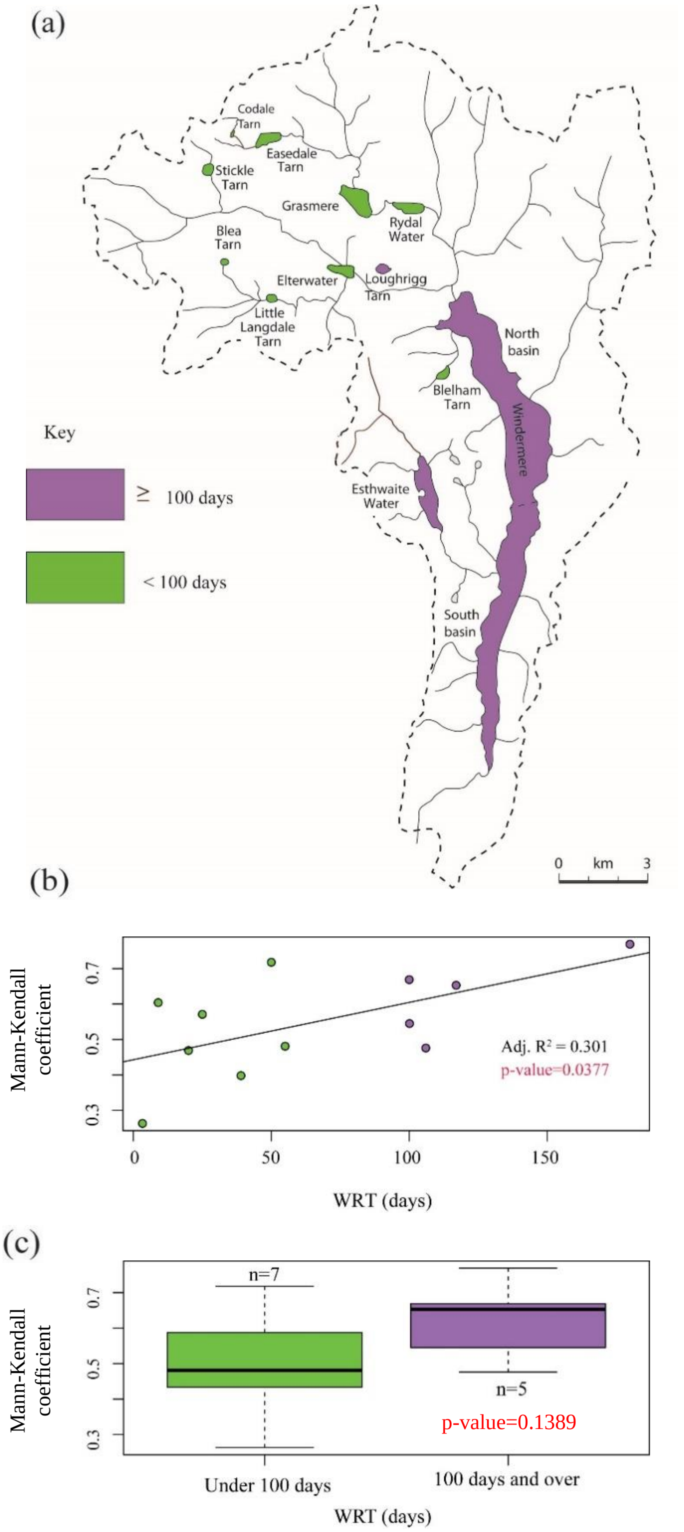


Figure 8.11 (a) Map of Windermere catchment with lakes of WRT ≥100 days in purple and <100 days in green. (b) Linear regression and (c) t-test boxplot of the difference between Mann-Kendall coefficients of algal community change (PCA axis 1 scores) of lakes with of WRT ≥100 days and <100 days. P-value of t-test shows no significant difference between the two lake types with p>0.05.

Low WRTs and random flushing events could have altered grazing regimes, which would have led to further algal community changes. For instance, in the late 1980s, the longer WRT at EST_{site} led to earlier maxima of the cyanobacteria *Aphanizomenon* from reduced overwintering population losses, and subsequently, greater predation by ciliate protozoan *Nassula* spp (Canter *et al.*, 1990). The earlier grazing allowed enough time for regrowth and large populations in subsequent years (Canter *et al.*, 1990). In contrast, at BLE_{site}, greater flushing led to larger losses of overwintering cyanobacterial filaments and shifted ciliate predation in the later summer maxima, which lowered *Aphanizomenon* populations in the subsequent year (Canter *et al.*, 1990). Higher grazing pressure from longer WRTs at EST_{site} might explain its less positive trends in all algal pigments over the last ~200 years to that of BLE_{site} (Figure 7.1 – Figure 7.7).

Changes in grazing pressure by WRTs could have modified algal communities (Obertegger *et al.*, 2007). In lakes elsewhere, WRTs altered zooplankton community biomass and structure, with crustacean biomass and communities correlated to higher WRTs, whereas rotifer biomass was indirectly correlated and determined by competition for edible algae with crustaceans (Obertegger *et al.*, 2007). Thus, shorter WRTs lower the predictive ability of predator-prey relationships, but both low and high WRTs have likely altered both predator zooplankton and algal prey communities in the Windermere catchment. In addition, other climatic factors have been shown to correspond to zooplankton abundances at EST_{site} including winter temperature and wind-induced mixing (George *et al.*, 2000). The resultant effect is a temporal mismatch which is not just simple peaks in seasonal trophic abundance levels but a complicated interaction of dynamic rates and lags between consumer and resource, and is beyond the scope of this study (Thackeray *et al.*, 2012).

The timing and extent of climate-mediated hydraulic flushing would have altered algal communities in the catchment. At WNB_{core}, WSB_{core} and BLE_{core}, lower siliceous algal pigment (diatoxanthin) concentrations were found in years (e.g. 1960-1980) with wetter winters (McGowan *et al.*, 2012; Moorhouse *et al.*, 2014). This was consistent with the observation that *A. formosa*, which became the dominant diatom taxa (~80% at BLE_{site}) from the mid-20th century in these basins, experienced a 10-fold reduction in inoculum availability for spring growth under wet winter conditions (Haworth, 1980; Reynolds and Irish, 2000). At WSB_{core} and BLE_{core}, cyanobacterial pigments were more abundant in years when diatoms were scarce possibly due to higher epilimnetic nutrients not utilised by large diatom blooms (Krivtsov *et al.*, 2000). Lower summer precipitation would have increased water column stability for cyanobacteria such as *Planktothrix* at BLE_{site}, as hydraulic flushing was the dominant mechanism driving population losses (Davis *et al.*, 2003). Furthermore, earlier summer populations of zooplankton would have removed edible vernal algae increasing nutrient availability for summer algal populations (George *et al.*, 2000). These patterns explain why susceptibility to hydraulic renewal at BLE_{site} led to the second highest algal community changes in the catchment (MK=0.718).

Interestingly, algal community change was typically lower in upland well-flushed systems and higher in lowland well-flushed systems, although a t-test revealed no significant difference ($p>0.05$) between the Mann-Kendall trend coefficients of PCA axis 1 scores for these lake types (Figure 8.12). Hydraulic flushing in the lowland lakes with low WRTs could have removed nutrients (and algae) derived from agricultural intensification and urbanisation which was transported via inflows, surface runoff, soil leachate and sedimentary P-release and would have prevented slow-growing cyanobacterial blooms developing (Cross *et al.*, 2014). However, the poor quality of the riverine inflow would have continued to deliver nutrients to these lowland well-flushed lakes and led to more variable seasonal to annual phytoplankton communities and abundances, further modified by the more dynamic flushing regimes as seen at BLE_{site} (Cross *et al.*, 2014). This ultimately led to greater algal community change at lowland lakes such as GRA_{core} (MK=0.571), which was attributed to flushing in the presence of centennial-scale fertilisation from urbanisation since the 19th century and WwTW modifications in the late 20th century (Reynolds *et al.*, 2012). Shifts between eutrophic and oligotrophic phytoplankton taxa continued despite WwTW remediation, indicating the legacy of eutrophication promoted continued algal community changes at

GRA_{site}. In addition, the low WRT prevented slow-growing often bloom-forming cyanobacterial populations from developing and could explain the negative trends of the filamentous often bloom-forming cyanobacterial pigment aphanizophyll at GRA_{core} and downstream at RYD_{core} whose WRT is even lower (9 days) (Figure 7.2) (Reynolds *et al.*, 2012). In summary, dynamic flushing and nutrient fertilisation have worked synergistically in the long-term modification of phytoplankton communities in lowland well-flushed systems. But the lower trophic state and catchment activity in the upland lakes led to the lower Mann-Kendall trends of algal community change (PCA axis 1 scores) in these basins.

The non-significant difference between upland and lowland well-flushed lakes might be because both lake types have experienced changes in nutrient stoichiometry which would have caused less pronounced differences in trends of algal community change since 1800 (Cross *et al.*, 2014). In the lowland well-flushed lakes receiving point sewage effluent, higher NO_3 and Si but lower TP from flushing of particulate and dissolved sediment-P release in flood-dominated years would have favoured small taxa such as green algal *Scenedesmus* spp. and small centric diatoms (Cross *et al.*, 2014). The higher rates of hydrological renewal would have led to a consistent supply of these nutrients and could explain the increasing trends in chlorophyte (lutein) and diatom (diatoxanthin) pigments over the last ~200 years in these basins (GRA_{core}, BLE_{core}) (Figure 7.5 - Figure 7.6). Inputs from agricultural manures and fertilisers, typically rich in N, and untreated sewage effluent with high P and Si concentrations, may again explain why BLE_{core} with its lower CA:LA experienced the most algal community change compared to GRA_{core} over the last ~200 years (Moorhouse *et al.*, 2014). In the upland lakes, atmospheric N and S deposition would have altered seasonal nutrient stoichiometry and promoted community changes (Maberly *et al.*, 2002). Intermittent flushing would have further altered both the renewal and removal of nutrients, and led to algal community turnover from phenological shifts between groups with differential nutrient requirements (Cross *et al.*, 2014).

Certain species in lakes with high WRTs are more sensitive to changing WRT and nutrient content than others. Modelled simulations of phytoplankton communities at EST_{site} which has a high WRT (100 days), found the vernal diatom spp. *Asterionella* showed little annual or seasonal response to changing drivers, but the bloom-forming cyanobacteria *Anabaena* and *Aphanizomenon* spp. dominated under higher nutrient, longer summer WRTs and increased water temperatures (Elliott, 2010; Carvalho *et al.*, 2011). Thus, agricultural and sewage-derived nutrient additions to lake inflows have altered community succession in the lowlands, but potentially toxic bloom-forming cyanobacteria are more likely to develop in eutrophic lakes with longer summer WRTs.

8.4.6 Summary of the role played by lake physical characteristics in modifying algal community change since 1800AD

Linear regression of physical characteristics in the Windermere catchment found that CA:LA (*adj* R^2=0.258, $p \leq 0.05$) and WRT (*adj* R^2=0.367, $p \leq 0.05$) were the only variables that explained a significant correlation to algal community change over the last ~200 years (Figure 8.9-Figure 8.11). WRT had the closest fit and this could be due to the high annual precipitation in the Lake District which would enhance the close coupling of lake and catchment hydrology. The attendant WRT would have had a more direct effect on lake biology, chemistry and physics and so, algal phenology (Maberly *et al.*, 2002). Thus, WRT could arguably be the direct measure of a series of other indirect morphometric variables such as altitude (e.g. Nõges *et al*., 2009).

While nutrient additions to the Windermere catchment lakes were the dominant cause of phytoplankton community change over the last ~200 years, lakes that overlay SIL geology and have longer WRT have a magnified response to fertilisation, and shifted to greater cyanobacterial dominance. Therefore, mitigation measures should be focussed on lakes with longer WRTs such as EST_{site}, which have an increased likelihood of exceeding WHO thresholds of cyanobacterial seasonal means and maximum abundance (10 and 50 mg m^{-3}) (Elliott, 2010). Potentially-toxic bloom-forming algae have been documented at these sites including toxin-containing *Oscillatoria* spp. in Windermere and

LOU$_{\text{site,}}$ and *Microcystis* spp. in EST$_{\text{site}}$ (Griffiths, 1978; Sano and Kaya, 1998). Further, the biomass of cyanobacteria in the water column is considered the best predictor of local algal toxin concentrations, although broader-scale studies suggest cross-scale interactions of environmental gradients (e.g. light, temperature and nutrient availability and stoichiometry) result in greater spatio-temporal variability in cyanotoxins (Dolman *et al.*, 2012; Soranno *et al.*, 2014; Taranu *et al.*, 2015). The increasing trends in cyanobacterial pigments at lowland sites in the Windermere catchment drives the need to further understand spatio-temporal gradients in the production of cyanotoxins in light of the direct and indirect acute health effects and isolation of new ubiquitous toxin strains linked to neuro-generative diseases and cancer (Lévesque *et al.*, 2014; Taranu *et al.*, 2015). Artificial manipulation of the flushing regime could reduce slow-growing bloom-forming cyanobacteria biomass, although this would depend on the water quality of the inflow and the feasibility in lakes of this size (Cross *et al*., 2014).

Centennial-scale fertilisation has led to populations of potentially-toxic bloom-forming algae from the mid-20th century in lowland lakes which overlie BVG geology and have lower WRTs such as BLE$_{\text{site}}$ and GRA$_{\text{site}}$. Lakes with lower WRTs experience modifications to their inter-annual community composition as hydraulic flushing prevents slower-growing cyanobacteria spp. such as *Anabaena* and *Microcystis* from dominating, as well as the eutrophic diatom *A. formosa* and cryptophyte *Cryptomonas* spp. These taxa are more abundant in drier years (Reynolds *et al*., 2012). Ideally, catchment-scale nutrient management should be focussed throughout the lowland lakes where total algal production increased over the last ~200 years from predominantly point-source nutrient enrichment. Lakes with shorter WRTs such as BLE$_{\text{site}}$ and GRA$_{\text{site}}$ rapidly responded to changing fertility in terms of total production but community compositional changes continue to be modified from historical enrichment and flushing (Reynolds *et al*., 2012).

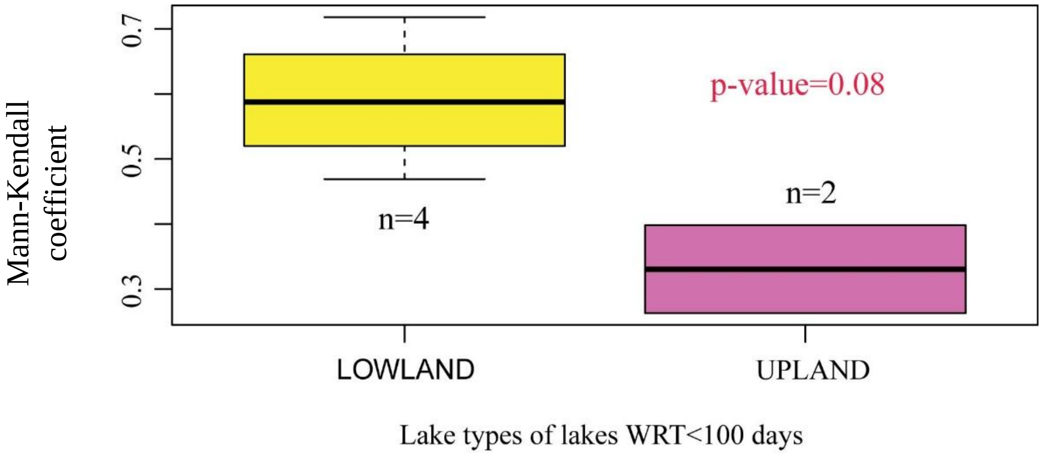


Figure 8.12 T-test boxplot of the difference between Mann-Kendall coefficients of algal community change (PCA axis 1 scores since 1800) between upland lakes (>100 m.a.s.l.) with low WRTs (<100 days) and lowland lakes (<100 m.a.s.l.) with low WRTs (<100 days).

8.5 Summary

The majority of lakes in the Windermere catchment experienced gradual or linear changes in algal community composition in the latter half of the 20th century. The main causes of algal community change have been nutrient enrichment, with additions from point treated and untreated effluent sources overriding the effects of diffuse agricultural sources. The post-world war II era known as the “Great Acceleration” saw a boom in wealth, technology and a tripling of human population, resulting in global eutrophication of aquatic ecosystems (Steffen *et al*., 2007). The increased point-source pollution from urbanisation severely degraded lake ecosystems, as is evident in the sediment records of the Windermere catchment (Grimm *et al*., 2008). Algal community change and production was greatest with proximity to sewage disposal but also agricultural land use, a trend witnessed in other Northern Hemisphere temperate lake districts (Hall *et al*., 1999).

In the upland sites however, the negative trends of major carotenoids point to reversing acidification and suppression of benthic productivity apparent in other upland northern temperate lakes from enhanced DOC loadings (Monteith *et al*., 2007). N deposition and hydromorphological alterations (i.e. the dam at STI_{site}) beginning in the 19th century could have increased the sensitivity of these systems towards climate-driven flow and temperature variations (Smyntek *et al*., 2014). Processes such as denitrification are enhanced under higher temperatures and low flows, and so, could have buffered the effects of atmospheric N loading (Arnell, 1998; Elser *et al.*, 2009). Thus, climate and long-range atmospheric deposition would have worked synergistically in the nonlinear modifications of upland water chemistry, nutrient stoichiometry and attendant algal compositional changes (Maberly *et al*., 2002). These results are indicative of Northern Hemisphere remote upland lakes whose algal communities have been modified by longer-term global drivers in the absence of localised nutrient loadings (e.g. Catalan *et al*., 2009). P-limitation has been found in lakes that have undergone high atmospheric N loading and have led to reduced phytoplankton biodiversity by favouring only a few species adapted to low P (Elser *et al*., 2007).

Since 1800, nutrient enrichment in lowland lakes with long WRTs, overlying SIL geology had the most marked algal production and cyanobacterial increases and community change within the Windermere catchment. This is indicative of other deep lakes with long WRTs and high N and P loads, which are dominated by toxic bloom-forming heterocystous and non-heterocystous cyanobacteria (e.g. Lake Taihu, China) (Jensen *et al.*, 1994; Xu *et al.*, 2010). Although a gradient in CA:LA ratios and community change was detected, the urban and agricultural activity in the catchment outweighed this effect. Lowland lakes, overlaying BVG geology with short WRTs, had modified algal communities from the dynamic relationship between eutrophication and flushing. Remediation in lakes with short WRTs is often harder to govern despite greater removal of nutrients and prevention of slow-growing heterocystous cyanobacteria, due to hydraulic dynamism, poor water quality of inflows and sediment nutrient re-suspension (Reynolds *et al.*, 2012; Cross *et al.*, 2014). This corresponds to work in Danish shallow lakes whose low WRTs and high nutrient loads caused increased dominance of fast-growing bloom-forming chlorophytes (Jensen *et al*., 1994). Because of this close link between lake hydrology, nutrient history and primary producers, it is likely that future climatic changes to temperature and precipitation could continue to disrupt these interactions (Reynolds *et al*., 2012). The subsequent chapter aim investigates the composition of the sedimentary organic matter in order to support the evidence in this chapter and others that autochthonous production has increased in the Windermere catchment since ~1900. It also discusses potential N sources to these lakes, an important nutrient in eutrophication by looking at changing sediment $\delta^{15}N_{org}$ values.

CHAPTER 9. THE KEY TIMINGS AND CAUSES OF BULK SEDIMENTARY C AND N ISOTOPE CHANGES IN THE WINDERMERE CATCHMENT SINCE THE 19TH CENTURY

9.1 Introduction

This chapter will attempt to address when and what caused bulk sediment C and N isotopes to change in the cores collected for this thesis and how this relates to the timings and causes of algal community change described in chapters 7 and 8. It will also investigate the spatial variability of these proxies and to what extent landscape characteristics may have modified the composition of OM.

9.2 Catchment-scale changes in autochthonous and allocthonous organic matter since 1800AD

Lake ecosystems that have undergone continued nutrient loading and increased water temperatures often have increased autochthonous productivity and attendant increased autochthonous OM deposition to lacustrine sediment (Moss *et al.*, 2009). In the lowland lakes of the English Lake District, increased autochthonous OM and pigment concentrations of sediments were documented as beginning ~200 years ago in relation to the addition of sewage discharges, overwhelming the high inputs of allocthonous deciduous leaves (Pennington, 1943; Pearsall and Pennington, 1947; Fogg and Belcher, 1961). However, other palaeolimnological investigations found that after the 1970s allochthonous material at BLE_{site} and LLT_{site} increased, corresponding to increased catchment soil erosion from agricultural land use changes and afforestation respectively (van der Post *et al.*, 1997; Haworth *et al.*, 2011). Changes in the composition of the lacustrine OM in the Windermere catchment was investigated in an attempt to support the causes of algal community change as discussed in chapters 7 and 8.

9.3 C/N ratios and $\delta^{13}C_{org}$

The sediments of the Windermere catchment lakes comprised both autochthonous and allocthonous OM throughout the 19th and 20th centuries (Figure 9.1). The lowland lakes have $\delta^{13}C_{org}$ and C/N ratio values closer to those of algal-dominated OM (see Table II, Meyers and Teranes (2001)) whereas the upland sites EAS_{core} and particularly $STI_{core,}$ had values closer to C_3 terrestrial plants, suggesting allocthonous material dominated the sedimentary OM in these upland sites.

In addition, C/N ratios were significantly ($p \leq 0.05$) higher in upland (C/N=>15) than lowland lakes (C/N=<16) since 1800, which further suggests different lacustrine OM composition of these systems (Figure 9.2). Oligotrophic lakes typically have higher C/N values as observed at EAS_{core} and $STI_{core,}$ which alongside the low pigment concentrations suggest lower autochthonous production, alongside greater in-wash of terrestrial OM at these upland lakes (Figure 6.6 (3); Figure 6.14 (3)) (Meyers and Teranes, 2001). Additionally, the smaller and shallower basins may have concentrated the input of allocthonous OM relative to the larger, deeper terminal Windermere basins where CA:LA ratios are much greater. Specifically, the allocthonous inputs at WNB_{core} and WSB_{core} could have been both diluted in-situ and buffered by basins upstream (Chiverrell, 2006).

The significant difference in C/N ratios could also be attributed to progressive cultural eutrophication down the landscape gradient. Nutrient loadings from WwTWs and agricultural sources stimulated autochthonous production from the 20th century in the lowland lakes and hence, their lower C/N ratios (Figure 8.3; Figure 9.2).

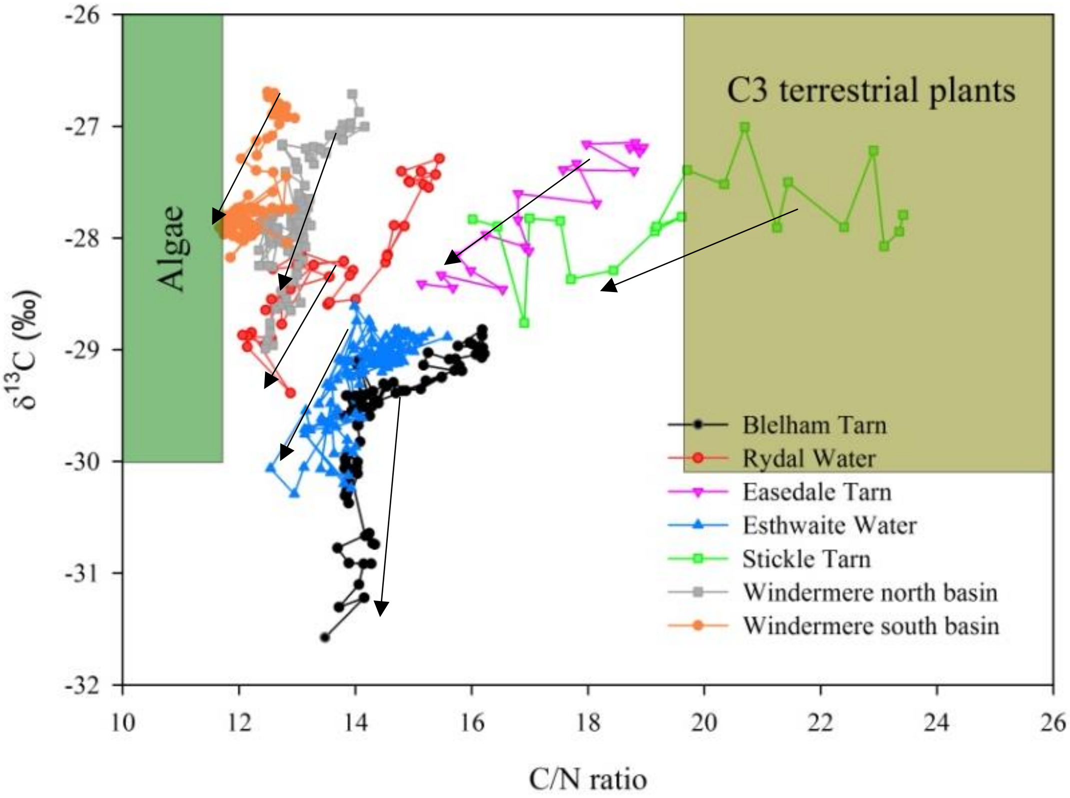


Figure 9.1 Atomic C/N ratios vs. $\delta^{13}C_{org}$ values of lacustrine sediment organic matter from Windermere catchment lakes since 1800 against values of algae and C_3 terrestrial plants taken from Meyers and Teranes (2001). Arrows indicate dominant direction of trends from the oldest to youngest sediment intervals from each core.

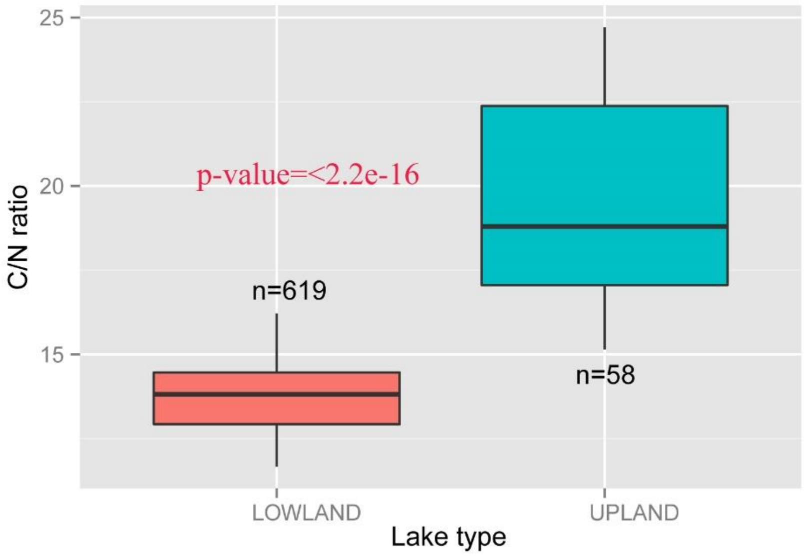


Figure 9.2 Box plot showing C/N ratios from 1800 between lowland (<100 m.a.s.l.) and upland (>100 m.a.s.l.) lakes. P-value of t-test shows significant difference between the two lake types with $p \leq 0.05$.

C/N ratios increased throughout the catchment from 1800 to 1900, which suggest increased allocthonous OM deposition at this time (Figure 9.3). The increased C/N ratios at WNB_{core} and WSB_{core} may have occurred from land disturbance related to increased tourism shoreline development and efficiency of sewers in the transport of terrestrially-derived OM during this period (Westall, 1976). In addition, catchment-wide deforestation and ploughing for increased agricultural land use from 1500 to 1850 may have increased catchment erosion and so, delivery of terrestrial OM throughout the lowlands (Pennington *et al*., 1976). This growing human pressure was concomitant with the Little Ice Age, when increased precipitation increased terrestrial OM delivery to lakes (Noren *et al*., 2002). This points to the difficulty in disentangling the relative importance of climate and human-induced changes to terrestrial OM delivery at this time (Dong *et al*., 2011). Furthermore, the chronologies of the cores were poorly constrained in the early 19th century making it difficult to pinpoint exact timings of land use changes with changes in the sediment record.

Across the catchment there were different timings of C/N ratio declines from the late 19th and 20th centuries, which suggest different timings of increased autochthonous production (Figure 9.3). For $\mathrm{WNB}_{\mathrm{core}}$ and $\mathrm{WSB}_{\mathrm{core}}$ this occurred from the 1890s, whereas at $\mathrm{EST}_{\mathrm{core}}$ and $\mathrm{BLE}_{\mathrm{core}}$ from the 1920s and from all excluding $\mathrm{WNB}_{\mathrm{core}}$ and $\mathrm{WSB}_{\mathrm{core}}$, the major reductions in values were from the 1960-70s onwards. This later period corresponded to sewerage expansion and development as discussed in chapter 8, which began close to Windermere in the late 19th century but developed after World War II throughout the lowlands.

At $\mathrm{STI}_{\mathrm{core}}$ and $\mathrm{EAS}_{\mathrm{core}}$, C/N declines were greater than in the lowlands (reductions of 7 and 4 units respectively) and began ~1900 onwards. Coupled with the increased Chl. *a* concentrations at both sites from 1900, more notable at $\mathrm{STI}_{\mathrm{core}}$, points to increased total algal production, which would have been more apparent at these oligotrophic upland sites compared to the naturally more productive lowlands (Figure 6.6 (3f); Figure 6.14 (3f)) (Gorham *et al.*, 1974).

Sedimentary C/N ratios may have been modified by lake WRTs in the Windermere lakes. Lakes with low WRTs (<100 days) had significantly ($p \leq 0.05$) higher C/N ratios from 1800 onwards than lakes with high WRTs (≥100 days) (Figure 9.4 - Figure 9.5). As for metrics of algal community change, autochthonous OM in lacustrine deposits has been greater in lowlands that had higher nutrient loading and longer WRTs and so, larger populations of potentially bloom-forming algae (Figure 8.12) (Reynolds and Walsby, 1975).

However, autochthonous production was much greater in lowlands with short WRTs ($\mathrm{RYD}_{\mathrm{core}}$ and $\mathrm{BLE}_{\mathrm{core}}$) (C/N=<16) compared to the upland sites as shown by the higher C/N ratios at $\mathrm{STI}_{\mathrm{core}}$ and $\mathrm{EAS}_{\mathrm{core}}$ to all other sites (C/N=>15), and was most likely attributed to increased lake fertilisation in the lowlands throughout the 19th and 20th century (Figure 9.4). This again points to the overriding importance of nutrient loading as a driver of OM production.

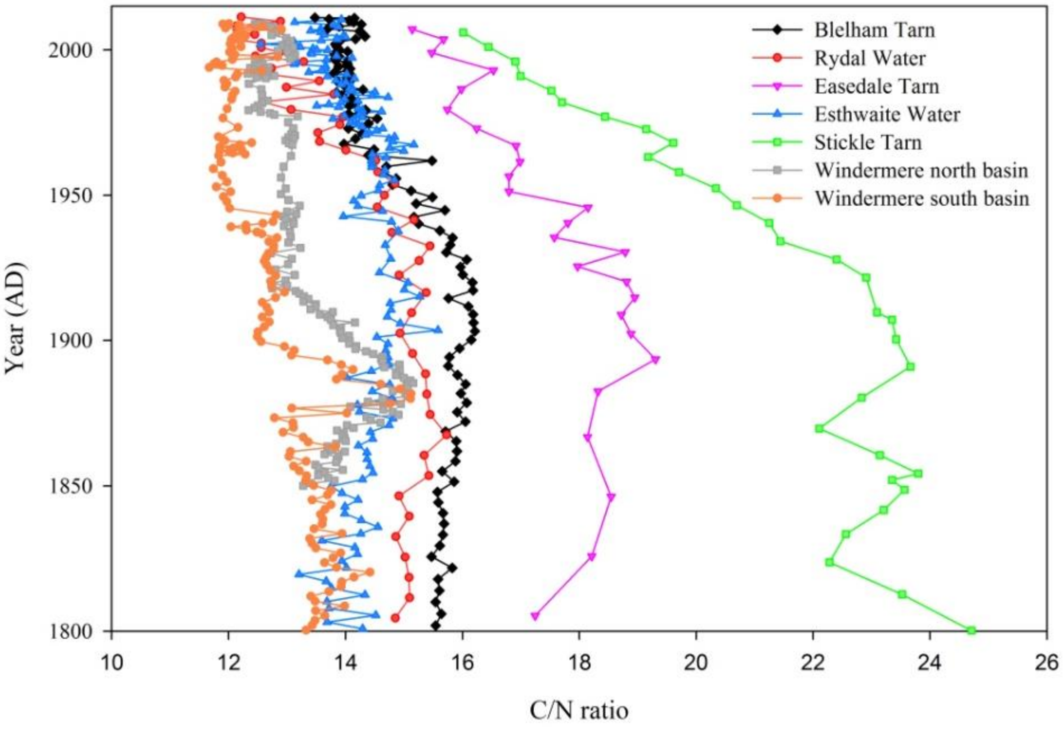


Figure 9.3 C/N ratios of sediment cores in the Windermere catchment lakes from 1800 onwards.

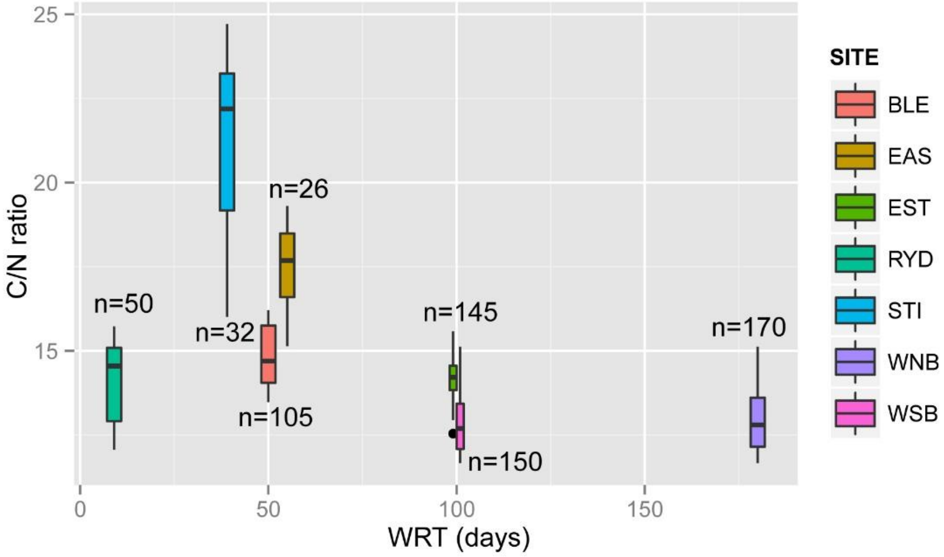


Figure 9.4 Box plot showing C/N ratios from 1800 onwards against the WRT of Windermere catchment lakes.

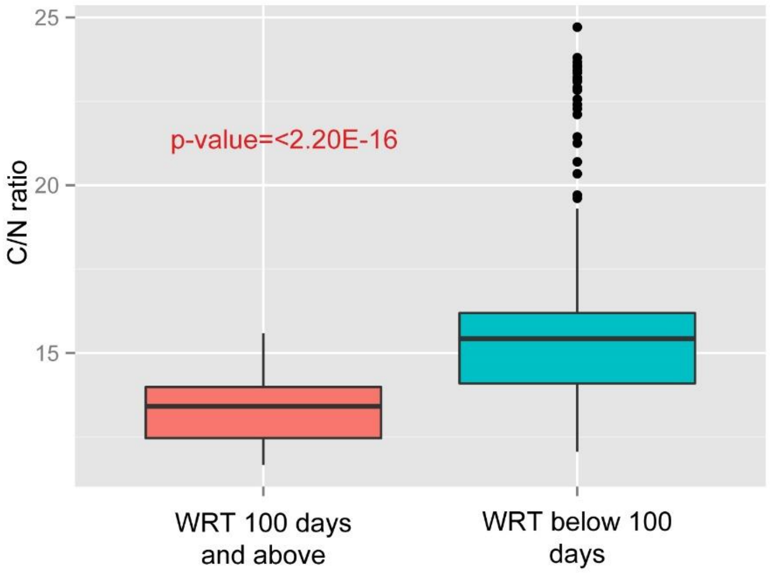


Figure 9.5 Box plot showing C/N ratios from 1800 onwards between lakes with WRTs ≥100 days and those with WRTs <100 days. P-value of t-test shows significant difference between the two lake types with $p \leq 0.05$.

9.4 Sediment stable C isotope indicates changing catchment and lake productivity

$\delta^{13}C_{org}$ values declined in all lakes from 1800 to the top of the core, although the magnitude of this change was relatively small (almost all < 2‰) and occurred at different points in different lakes (Figure 9.6). This disagrees with the well-accepted paradigm that increasing algal production yields less negative values (Meyers and Teranes, 2001). This paradigm is based on the preferential uptake of lighter ^{12}C by algae from the DIC reservoir, which consequently increases the $\delta^{13}C$ of the remaining inorganic C and latterly produced OM (Meyers and Teranes, 2001). The decline in C/N ratios and increased algal pigment concentrations from all cores point to increased algal production. Thus, alternative C fluxes or cycling mechanisms must have occurred in the Windermere catchment. Interestingly, agricultural catchments have been found to yield more negative $\delta^{13}C_{org}$ values in their lacustrine deposits which could explain the $\delta^{13}C_{org}$ fluxes in the agricultural-dominated lowlands of the catchment (Woodward *et al.*, 2012). Further, the $\delta^{13}C_{org}$ values have not been corrected for the Suess effect so, there will be a dilution of the trends after 1950 (Verburg, 2007). However, the different timings to which the cores exhibit declining values and the relatively small change in $\delta^{13}C_{org}$ overall, suggest that the Suess effect is not a dominant process in these lakes. Although the increased primary production as recorded by the pigments in the latter half of the 20th century could have resulted in less negative $\delta^{13}C_{org}$ values and so, masked the importance of the Suess effect. Alternatively, as eutrophication progressed so too did phytoplankton isotopic fractionation which would have yielded more negative $\delta^{13}C_{org}$ values (Goericke and Fry, 1994). In addition, changes in pH, temperature, nutrients and salinity are known to affect $\delta^{13}C_{org}$ (Wolfe *et al*., 2001b). Notwithstanding the potential drivers aforementioned and others discussed hereafter, the small magnitude of change in the $\delta^{13}C_{org}$ and lack of imperical evidence on each process must be noted.

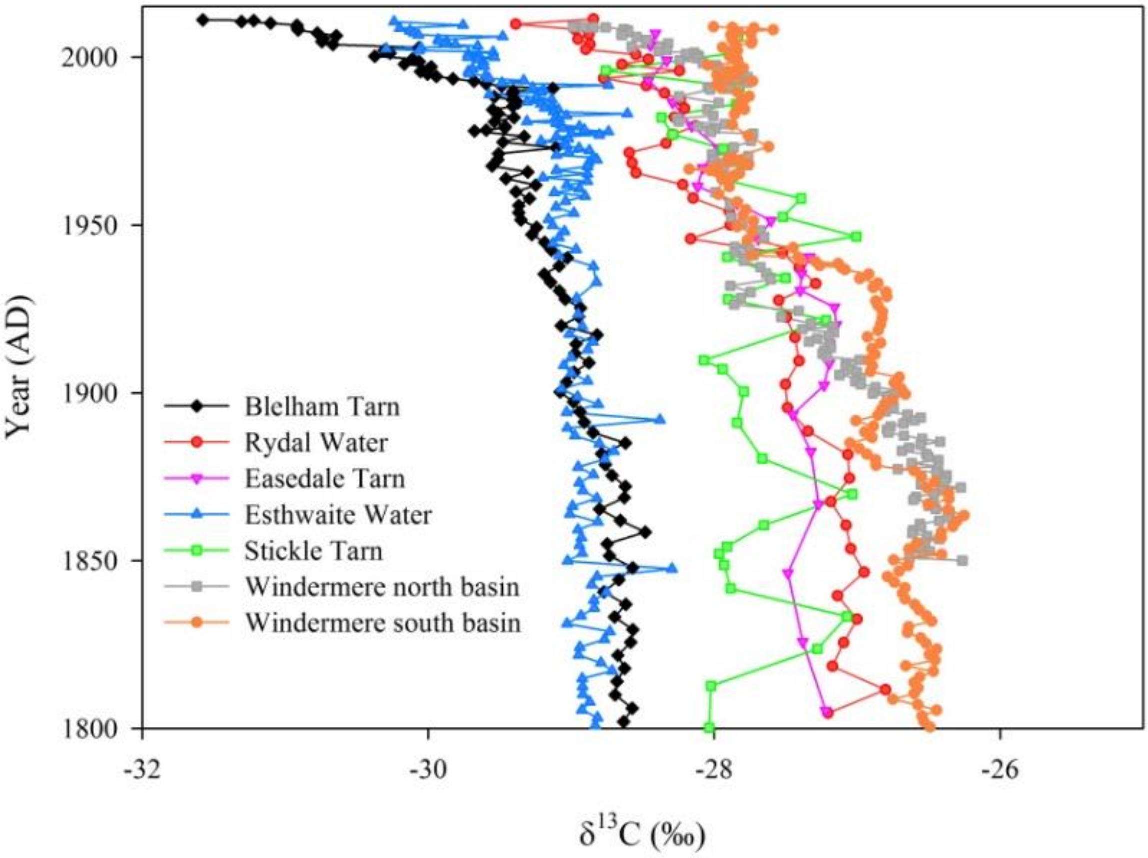


Figure 9.6 $\delta^{13}C_{org}$ values of sediment cores in the Windermere catchment lakes from 1800 onwards.

Two of the most productive and eutrophic sites in the catchment BLE_{core} and EST_{core} showed lower overall $\delta^{13}C_{org}$ values, which until the recent past (~1990) where relatively stable (~-29‰). The overall lower values may be associated with increased catchment productivity which can result in isotopically-lighter DIC being transferred to lake phytoplankton (Maberly *et al.*, 2013; Moorhouse *et al.*, 2014). The other lakes showed more gradual long-term declines, although not to a significant degree. 19th and early 20th century declines in $\delta^{13}C_{org}$ values recorded in WNB_{core} and WSB_{core} were attributed to surface denudation of allocthonous inorganic material by past research (a key C source) (McGowan *et al.*, 2012). After 1945 at WSB_{core} and 1990 at WNB_{core}, isotopically-lighter algal C from increased autochthonous production could have caused a slight increase in $\delta^{13}C_{org}$, although these shifts are not significant enough to be clear but are supported by changes in the algal pigments (Talling and Heaney, 1988; McGowan *et al.*, 2012). The $\delta^{13}C_{org}$ of BLE_{core} declined from -28 to -29‰ in the 1930s and continued to do so along with a concomitant increase in % cover of permanent grass (Figure 6.44 (1)). Furthermore, the sudden $\delta^{13}C_{org}$ decline from 1990 onwards followed an increase to 72% permanent grass cover in BLE_{site}'s catchment, as well as increased arable and woodland cover (Figure 6.44 (1)). This increased conversion to agricultural land and woodland would have increased catchment NPP (Ajtay *et al.*, 1979). These changes were not seen in the catchment of EST_{core} however.

Productive lakes within the English Lake District in productive terrestrial catchments (high NPP) have more negative $\delta^{13}C$ DIC in the water column, and this feature may be transferred to the sediments (Maberly *et al.*, 2013). This was further supported by the significantly ($p \leq 0.05$) less negative $\delta^{13}C_{org}$ values of the upland tarns EAS_{core} and STI_{core} (-27 to -29‰), than the lowlands (-26 to -32‰) (Figure 9.7). These tarns have moorland catchments and minimal agricultural land use thus, a lower NPP (Maberly *et al.*, 2013). This indicates that the lower terrestrial productivity of their catchments despite the higher allocthonous inputs at these sites as indicated by their higher C/N ratios (Figure 9.3) may have led to the less negative $\delta^{13}C_{org}$ in their sediments. However, there is overlap between the $\delta^{13}C_{org}$ values of the uplands and lowlands, perhaps a result of the mixed land-cover at some lowland sites or the lack of significant changes to the $\delta^{13}C_{org}$ values across the catchment.

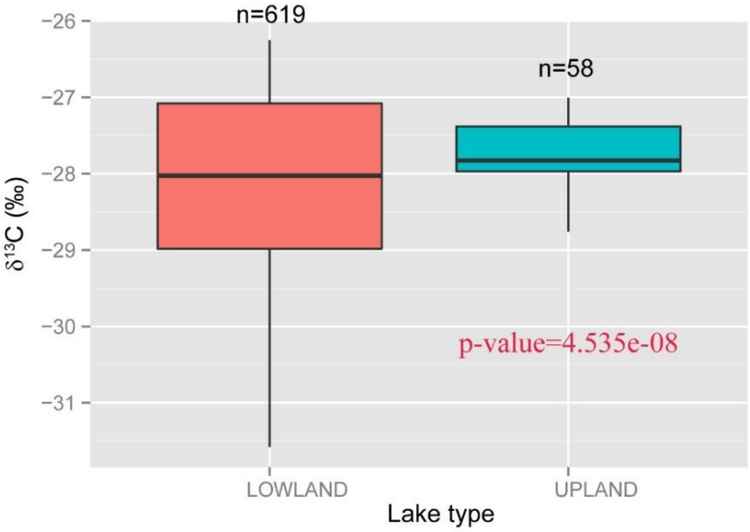


Figure 9.7 Box plot showing $\delta^{13}C_{org}$ values from 1800 onwards between lowland (<100 m.a.s.l.) and upland (>100 m.a.s.l.) lakes. P-value of t-test shows significant difference between the two lake types with $p \leq 0.05$.

CH_4 produced in the anoxic bottom waters of the larger, deeper lowland lakes which undergo thermal stratification and hypolimnion anoxia such as BLE_{site}, WNB_{site} and WSB_{site} could have further depleted the $\delta^{13}C_{org}$ values (Jones and Grey, 2011). At EST_{site}, increased CH_4 production occurred in years with higher temperatures and corresponded to depleted ^{13}C larval chironomid biomass from the consumption of methanotrophic bacteria (Deines and Grey, 2006). However, biogenic CH_4 in sediments is typically much more depleted ($\delta^{13}C_{org}$ = -60 to -80‰) and isotopic fractionation of CH_4 uptake by microbes can further deplete the values (Jones and Grey, 2011). But it is likely that different metabolic pathways of CH_4 and consumption of methanotrophic bacteria, alongside enrichment from primary production would have masked the more depleted values of biogenic CH_4, suggesting it could be an important C source in the lowland Windermere lakes (Deines and Grey, 2006). Notwithstanding, it is very difficult to attribute such processes to the small shifts in $\delta^{13}C_{org}$ and the difference between the timings of change at these lowland lakes.

9.4.1 Summary

Lakes within the Windermere catchment have shown increased autochthonous production in the last 200 years. This has occurred alongside increasing terrestrial catchment productivity more notable in the agricultural dominated lowlands, which alongside increased catchment-wide algal productivity have altered C delivery to the deposits of these lakes. However, the complexity of processes which alter the isotopic composition of OM reaching the lacustrine deposits (Li *et al.*, 2008), and the small magnitude of change in the $\delta^{13}C_{org}$ values makes it difficult to effectively interpret these results.

9.5 Sedimentary stable N isotope indicates different N sources

9.5.1 Introduction

Sedimentary $\delta^{15}N_{org}$ values varied both temporally and spatially throughout the Windermere catchment since 1800 (Figure 9.8). The upland tarns EAS_{core} and STI_{core}, showed similar stable trends with distinct declines in values after 1950, whereas the lowland site's (EST_{core} and BLE_{core}) values increased around 1950, and RYD_{core} and the terminal basins WNB_{core} and WSB_{core} decreased. The lowlands had less synchronous sedimentary $\delta^{15}N_{org}$ trends than the upland sites throughout the 19th and 20th centuries, attributed to the confounding N-enriched and N-depleted anthropogenic sources in the catchments of these lakes (Leavitt *et al*., 2006). The trends in sediment $\delta^{15}N_{org}$ in the Windermere catchment lakes reflect work elsewhere in the Northern Hemisphere which found distinct changes in lacustrine sediment $\delta^{15}N_{org}$ during the Anthropocene, but in particular the latter half of the 20th century (Leavitt *et al.*, 2006; Holmgren *et al.*, 2010).

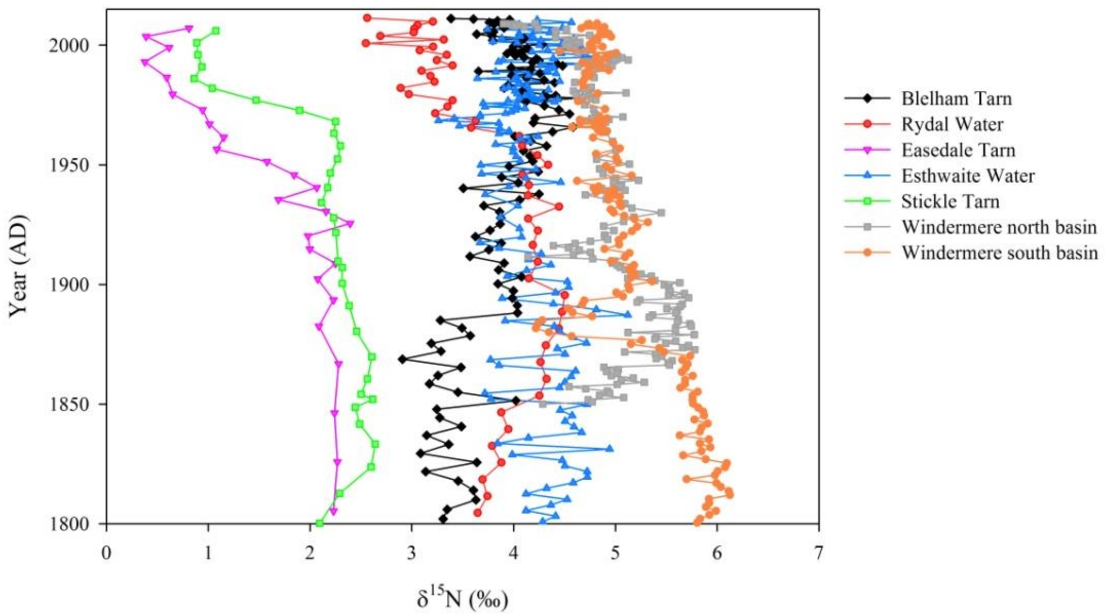


Figure 9.8 $\delta^{15}N_{org}$ values of sediment cores in Windermere catchment lakes from 1800 onwards.

9.5.2 Landscape controls on N cycling

Landscape position altered N acquisition in lake sediments from 1800 onwards as shown by the significant difference ($p \leq 0.05$) between the $\delta^{15}N_{org}$-depleted ($\delta^{15}N_{org}$=<3‰) upland lakes and $\delta^{15}N_{org}$-enriched ($\delta^{15}N_{org}$=>3‰) sedimentary values of the lowlands (Figure 9.10). This may be attributed to the difference in trophic conditions of these systems and/or the relative influence of anthropogenic N loading. Sedimentary $\delta^{15}N_{org}$ in upland lakes is often regulated by influx of allocthonous DOM rather than inorganic N (Bunting *et al*., 2010). Thus, the lower overall $\delta^{15}N_{org}$ records at STI_{core} and EAS_{core} could be attributed to the less productive terrestrial catchments where they are found, and so, lower DOM delivery to the sediments (Bunting *et al*., 2010). In contrast, the more productive terrestrial catchments of the lowlands had higher DOM delivery and was identified by the difference in sedimentary $\delta^{15}N_{org}$ values between lowland and upland lakes pre-1800, a period prior to urban and agricultural intensification (Figure 9.9) (Maberly *et al*., 2002).

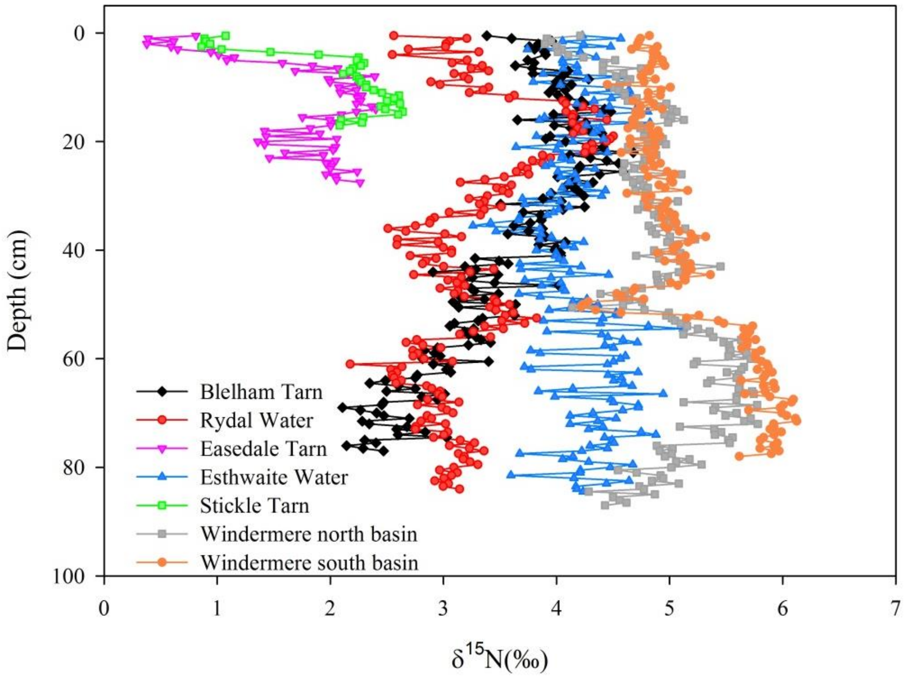


Figure 9.9 $\delta^{15}N_{org}$ values of sediment cores from Windermere catchment lakes for full core depths (cm).

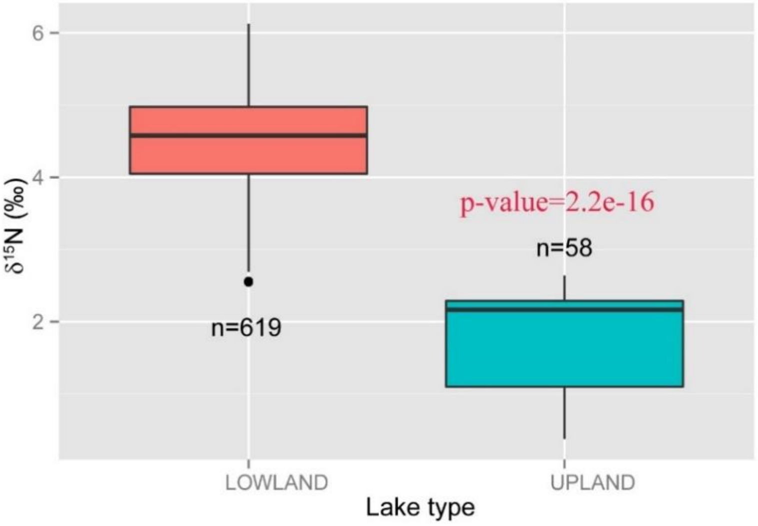


Figure 9.10 Box plot showing $\delta^{15}N_{org}$ values from 1800 between lowland (<100 m.a.s.l.) and upland (>100 m.a.s.l.) lakes. P-value of t-test shows significant difference between the two lake types with $p \leq 0.05$.

Like altitude, WRT is one such variable that led to significant differences ($p \leq 0.05$) between lake sedimentary $\delta^{15}N_{org}$ values from 1800 onwards (Figure 9.12). Lakes with higher WRTs (>100 days) had higher $\delta^{15}N_{org}$ values (mean=4.8‰), whereas more rapidly flushed systems (<100 days) had lower $\delta^{15}N_{org}$ (mean=3.1‰) (Figure 9.12). Previous work investigated N retention (measured by mass balance studies of total N (TN) of inputs minus TN output), and found it was inversely related to water discharge, suggesting that all N, including $\delta^{15}N_{org,}$ was diluted and removed downstream on account of lake flushing rates (Saunders and Kalff, 2001). Sediment $\delta^{15}N_{org}$ in highly flushed lakes in Canada was diluted despite high loads of enriched $\delta^{15}N_{org}$ from salmon fisheries effluent (Holtham *et al.*, 2004). Further, enriched sediment $\delta^{15}N_{org}$ was found in deeper lakes, such as the terminal WNB_{site} and WSB_{site} (mean depths >15m) basins, which both exhibited the highest values and WRTs (Figure 9.11) (Brock *et al.*, 2006). This could indicate that lower flushing, greater depths and higher N loads have increased the scavenging of heavier isotopic N into the sediments of WNB_{site} and WSB_{site} (Brock *et al.*, 2006). However, understanding the finer scale processes which alter N isotopic composition along spatial gradients remains relatively poorly understood due to the complexity of N cycling (Brock *et al.*, 2006).

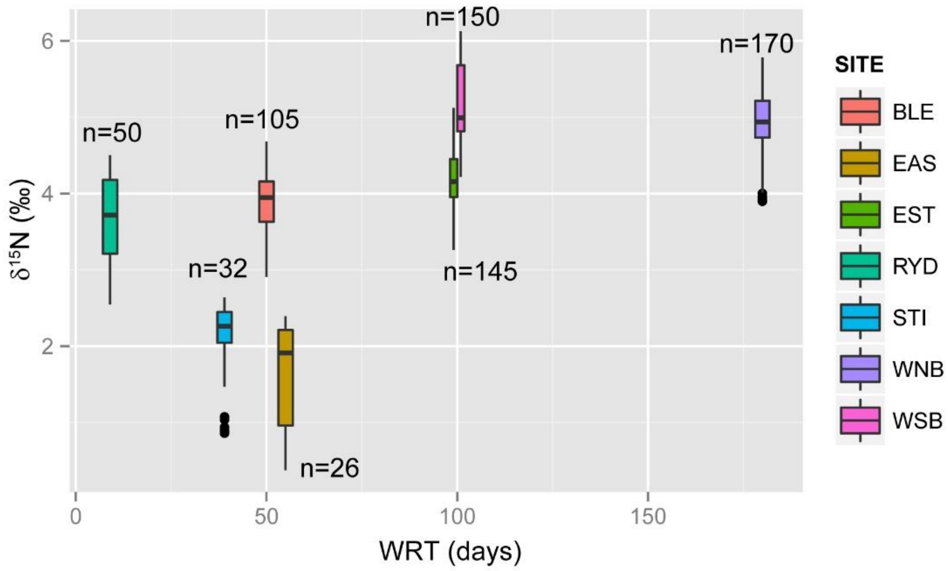


Figure 9.11 Box plot showing $\delta^{15}N_{org}$ values from 1800 onwards against the WRT of each site.

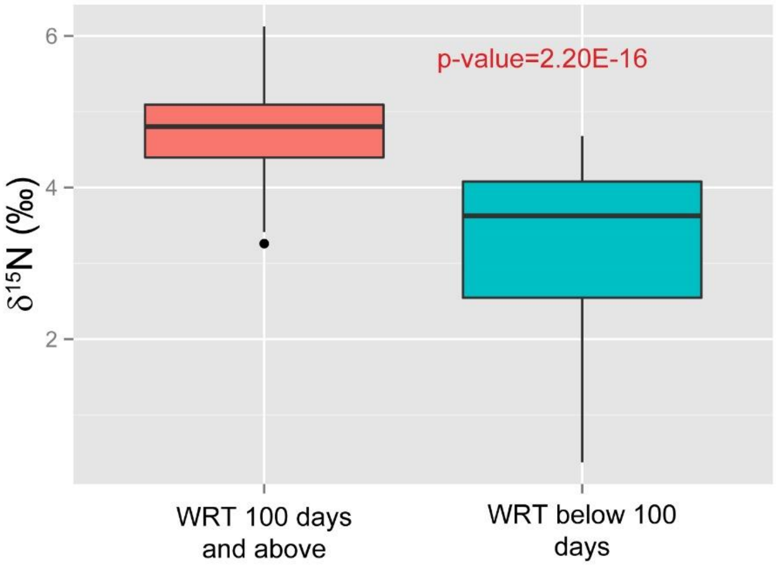


Figure 9.12 Box plot showing $\delta^{15}N_{org}$ values from 1800 between lakes with WRTs ≥100 days and those with WRTs <100 days. P-value of t-test shows significant difference between the two lake types with $p \leq 0.05$.

9.5.3 Atmospheric N deposition in the upland lakes

Variable and notable shifts after 1800 in $\delta^{15}N_{org}$ values suggest that spatial and temporal forcings modified surface water geochemistry in the Windermere catchment (Figure 9.8). For instance, the upland tarns STI_{core} and EAS_{core} had almost identical trends in $\delta^{15}N_{org}$, whereby post-1850 sediment $\delta^{15}N_{org}$ values slowly became isotopically lighter and markedly dropped after 1950 (Figure 9.8). These results match those of other remote Northern Hemisphere lakes whose initial shifts in lower sediment $\delta^{15}N_{org}$ began around the late 19th century and coincided with the onset of rising anthropogenic CO_2 emissions from fossil fuel combustion (Figure 9.13) (Holtgrieve *et al.*, 2011). Accelerated downward shifts in sediment $\delta^{15}N_{org}$ in the latter half of the century chart the "Great acceleration" following World War II, when widespread industrialisation of fossil fuels and artificial N fertilisers led to exponential increases in atmospheric deposition of isotopically lighter $\delta^{15}N_{org}$ (in the range of -15‰ to 15‰ for DIN in wet deposition) (Figure 9.13) (Kendall *et al.*, 2007; Steffen *et al.*, 2007; Holtgrieve *et al.*, 2011). The decline of $\delta^{15}N\text{-}NO_3$ by 12‰ from the summit of the Greenland ice sheet over the last 150 years further supports the hypothesis that sediment $\delta^{15}N_{org}$ ratios have been depleted beyond catchment and pre-industrial levels (Figure 9.13) (Holtgrieve *et al.*, 2011).

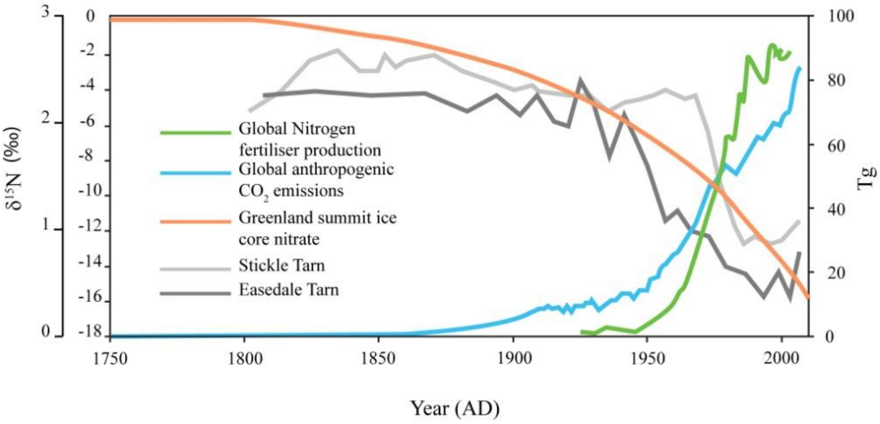


Figure 9.13 $\delta^{15}N_{org}$ values (not standardised) from upland lake sediment cores, EAS_{core} and STI_{core}, superimposed on the results of Holtgrieve *et al*., (2011) including Greenland ice core nitrate, Global nitrogen fertiliser production and CO_2 emissions. European data on fertiliser production and CO_2 emissions are available but follow the global trends (although reductions in fertiliser production in the 1990s was more pronounced in Europe). The global trends were kept to highlight the large scale changes these pollutants have caused

Understanding how atmospheric N deposition has interacted with other stressors such as climate-mediated warming, hydromorphological changes and acidification in the modification of lake primary productivity in upland lakes remains relatively unknown (Holtgrieve *et al.*, 2011). At $\mathrm{STI_{core}}$, initial increases in total algal (Chl. *a*) concentrations began after 1850 and marked increases after 1950 concomitant with opposing shifts in $\delta^{15}\mathrm{N_{org}}$, suggest that N fertilisation from atmospheric deposition increased primary production (Figure 9.14 (a)) (Wolfe *et al*., 2003).

However, at $\mathrm{EAS_{core}}$, total algal concentrations increased much earlier in the 20th century, which could be attributed to enhanced primary production from increased water clarity following acidification, corresponding to the increased concentrations of benthic diatom (diatoxanthin), chlorophyte (lutein) and cyanobacterial pigments (Figure 6.14 (3); Figure 9.14 (b)). In addition, the post-1950 increase in Chl. *a* was not replicated in $\mathrm{EAS_{core}}$ and $\mathrm{STI_{core}}$ (Figure 6.6 (3); Figure 6.14 (3)). However, relatively small changes in Chl. *a*/Pheophytin *a* ratios at $\mathrm{STI_{core}}$ and $\mathrm{EAS_{core}}$ indicate minor post-depositional changes and so, support the hypothesis that total algal production as indicated by the labile Chl. *a,* increased at $\mathrm{EAS_{core}}$ and $\mathrm{STI_{core}}$ post-1950.

Declines in C/N ratios indicative of increasing autochthonous inputs further support the hypothesis that total algal production was enhanced in the latter half of the 20th century in the upland sites (Figure 8.7; Figure 9.2) (Wolfe *et al.*, 2003; Brahney *et al.*, 2014). The decreased concentrations of other sedimentary pigments could indicate a shift to planktonic rather than benthic production following reversal of acidification (Figure 6.6 (3); Figure 6.14 (3)) (Wolfe *et al*., 2003).

DOC increased in the latter half of the 20th century across North America and Europe due to changing atmospheric deposition chemistry, whereby decreased sulphur, sea salt and acid deposition to acid-sensitive catchments reversed (Monteith *et al*., 2007). Greater influxes of DOC could have reduced water transparency and shifted algal production at $\mathrm{STI_{site}}$ and $\mathrm{EAS_{site}}$ to the epilimnion. This may then have increased the likelihood of pigment degradation during sedimentation within the water column (Leavitt and Hodgson, 2001). However, this is more likely to have occurred at EAS_{site} than STI_{site}, due to the higher vegetation and bog coverage in its catchment and thus, potentially higher DOC influx (Haworth *et al*., 2003). DOC increases were found elsewhere in the Lake District at Devoke and Levers Waters' following reversal of acidification (Tipping and Chaplow, 2012).

The increased total production (Chl. *a*) in relation to decreased isotopic sedimentary $\delta^{15}N_{org}$ at STI_{core} and EAS_{core}, corresponds to work on oligotrophic upland sites both in the English Lake District and across the Northern Hemisphere. This previous work found increased phytoplankton biomass in response to anthropogenic inorganic N input relative to TP concentrations (Maberly *et al.*, 2002; Bergström and Jansson, 2006). This led to shifts between N, P and co-limitation over the seasonal cycle, altering the nutrient regimes and promoted fertilisation at these previous oligotrophic upland lakes (Maberly *et al.*, 2002; Bergström and Jansson, 2006).

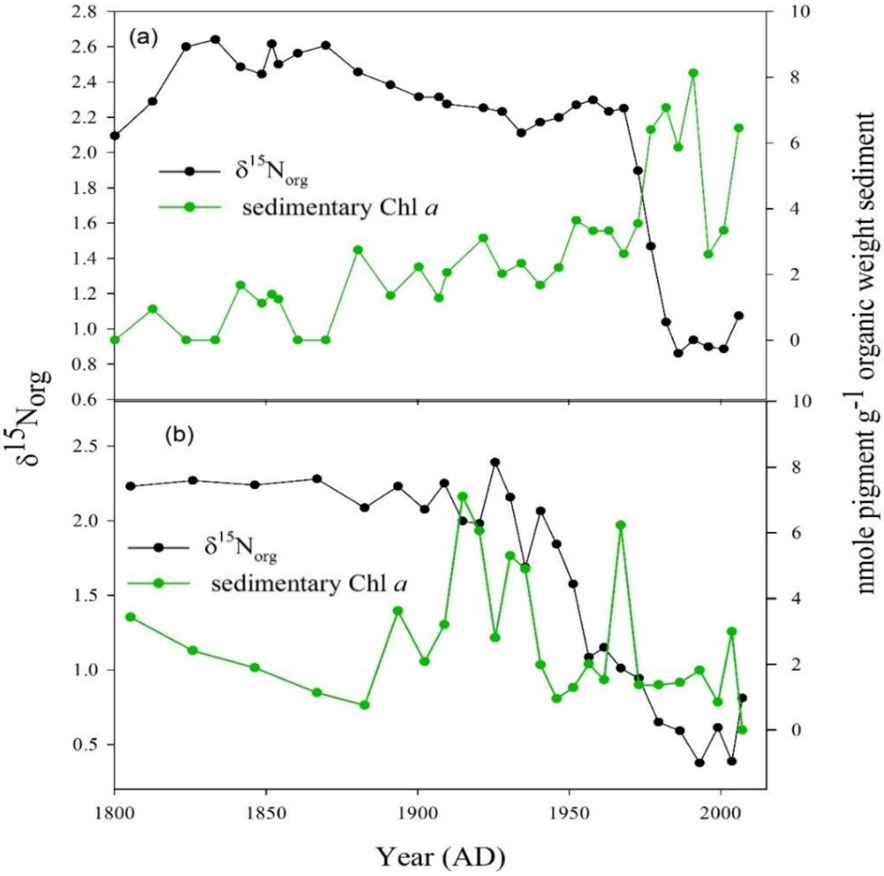


Figure 9.14 Plots showing both sedimentary $\delta^{15}N_{org}$ and Chl. *a* concentrations from STI_{core} (a) and EAS_{core} (b)

9.5.4 Caveats to the atmospheric N deposition hypothesis

Many studies have found other confounding factors altered sediment $\delta^{15}N_{org}$ in upland lakes, thereby complicating the atmospheric N hypothesis. First, in alpine lakes, climate was attributed as the main indirect explanatory variable of sediment $\delta^{15}N_{org}$, via regulating terrestrial DOM and catchment productivity, both of which modified lacustrine sediment $\delta^{15}N_{org}$ values (Bunting *et al.*, 2010). The multiple fates of atmospheric N deposition do include terrestrial uptake, microbial transfer and hydrological transfer to waterbodies. Thus, increasing temperatures and high frequency rainfall events could have altered N delivery and cycling processes thereby altering the relative importance of the atmospheric N source in the upland lakes of the Windermere catchment (Bunting *et al.*, 2010; Holtgrieve *et al.*, 2011).

Second, diagenesis has been shown to explain a greater ‰ negative shift in sediment $\delta^{15}N_{org}$ to that of atmospheric N deposition, as is apparent from increased %N and decreased C/N ratios, in some remote lakes of USA (Brahney *et al.*, 2014). Trends in these proxies can be seen at STI_{core} but not $EAS_{core,}$ which suggests that diagenesis, if an issue for these lakes, was more apparent at STI_{core} (Figure 6.6 (2); Figure 6.14 (2)).

Third, the more enriched $\delta^{15}N_{org}$ sediment values at STI_{core} compared to EAS_{core}, could be due to its lower WRT, max. depth, area and CA:LA, making it more susceptible to hydraulic flushing despite its impoundment, which could have removed DIN and other N pools both from the catchment and the tarn downstream (Maberly *et al.*, 2002; Jones *et al.*, 2004). In addition, surface sedimentary $\delta^{15}N_{org}$ in Cumbrian upland lakes was correlated to the $\delta^{15}N$ of TDN in their waters, which can be mediated not only by N deposition, but catchment plant and soil microbial fractionation which alters the $\delta^{15}N$ of TDN of catchment runoff (Jones *et al.*, 2004). Thus, catchment-mediated changes to $\delta^{15}N$ and hydraulic flushing could be more important than N deposition.

$\delta^{15}N$ of NH_4 and NO_3 in UK rainfall (-7‰ and 0‰ respectively) is much lower than the $\delta^{15}N_{org}$ values at STI_{core} and EAS_{core} which further points to catchment mediated fractionation of N (Heaton *et al.*, 1997; Jones *et al.*, 2004). However, addition of autotrophic, heterotrophic and detrital OM to lake sediments would enrich the $\delta^{15}N_{org}$ beyond the UK rainfall values either way (Meyers and Teranes, 2001). Cumbrian upland lakes have comparatively high N deposition rates compared to other regions in the UK, which would reduce N-limitation as supply exceeds demand (Jones *et al*., 2004). However, bioassay experiments showed Cumbrian upland lakes to be N-limited on account of low P, low pH and high flushing, and the extent of nutrient limitation could be explained by land-cover and plant type (Maberly *et al.*, 2002; Maberly *et al.*, 2003). In essence, low sediment $\delta^{15}N_{org}$ is not just a function of atmospheric N loading but nutrient limitation and catchment transformations (Maberly *et al.*, 2002; Jones *et al.*, 2004). The consistent pattern of sediment $\delta^{15}N_{org}$ trends across a wide geographic distribution of sites and coherent temporal shifts indicate that climatic variability and diagenesis from region to region could not adequately explain these broader patterns (Holtgrieve *et al*., 2011). Thus, the most logical conclusion is that atmospheric N deposition from anthropogenic N activity has delivered isotopically lighter $\delta^{15}N_{org}$ which has then been assimilated in sediment OM of the upland tarns in the Windermere catchment and elsewhere in the Northern Hemisphere (Wolfe *et al*., 2003). Nonetheless, further investigation into the relative importance of diagenesis, upland catchment N loads and cycling and atmospheric N deposition would be recommended (Brahney *et al*., 2014).

It is also likely that climate change and atmospheric N deposition may have synergistically promoted planktonic and littoral algal growth at STI_{site} and EAS_{site}. Climate warming has increased stratification duration and so, increased the length of the growing season in many remote lakes (Wolfe *et al*., 2006). Shifts to planktonic diatoms were found corresponding to the timing of the Medieval Climate Anomaly at EST_{site} (Dong *et al*., 2011). This is supported by the results of the RTs which chose CET as the main explanatory variable at STI_{core} and EAS_{core} (Figure 8.3 (a/c)). Longer growing seasons and increased nutrient loading from atmospheric deposition may have led to the increased total primary production (Chl. *a*) at $\mathrm{STI_{core}}$ and $\mathrm{EAS_{core}}$ in the latter half of the 20th century (Figure 9.14).

Both climate and atmospheric N deposition may have also worked indirectly. This could have resulted in enhanced terrestrial catchment productivity from longer growing seasons and assimilation of isotopically lighter $\delta^{15}\mathrm{N_{org}}$ in catchment soil, after which climatic hydrological shifts would have regulated the transfer of OM between terrestrial and aquatic systems (Bunting *et al.*, 2010). However, the marked decline in sedimentary $\delta^{15}\mathrm{N_{org}}$ at both $\mathrm{STI_{core}}$ and $\mathrm{EAS_{core}}$ after 1950 to values previously unseen at these sites points to the overriding effects of atmospheric N deposition to that of climate on the geochemical sediment record (Figure 9.9). Further investigation is needed to understand the relative importance of the processes involved in sedimentary $\delta^{15}\mathrm{N_{org}}$ pools so that the response of sedimentary algal communities at these upland sites can be more clearly understood (Holtgrieve *et al.*, 2011).

9.5.5 Multiple controls on N cycling in the lowlands

The lowlands had higher sediment $\delta^{15}\mathrm{N_{org}}$ values and less coherent temporal trends since 1800 because of urban and agricultural enrichment and the degree of sequestration (Figure 9.8) (Leavitt *et al.*, 2006). Smoother trends of sediment properties are often attributed to multiple factors acting on lakes (Edwards and Whittington, 2001). But the variable and incoherent sediment $\delta^{15}\mathrm{N_{org}}$ values of the lowlands could suggest fluctuations between different and often confounding sources. Delivery and assimilation mechanisms of sediment $\delta^{15}\mathrm{N_{org}}$ occurred at these sites in a much more complex and localised manner. Such processes could have included human and agricultural inputs, atmospheric N deposition and internal microbial cycling which can be modified by lake morphometry and primary production (Figure 9.15) (Botrel *et al.*, 2014). However, the sediment $\delta^{15}\mathrm{N_{org}}$ values of all the lowland lakes remained relatively low ($\delta^{15}\mathrm{N_{org}}$=<7‰), despite agricultural and human N loads and enhanced primary productivity, which would have delivered increased $\delta^{15}\mathrm{N_{org}}$ values to the sediments. This could reflect the dilution by terrestrial plants and humic acids which are depleted in $\delta^{15}\mathrm{N_{org}}$ (~0‰) via delivery of allocthonous OM as shown by the C/N ratios >11 (Bragazza *et al.*, 2005; Woodward *et al.*, 2012).

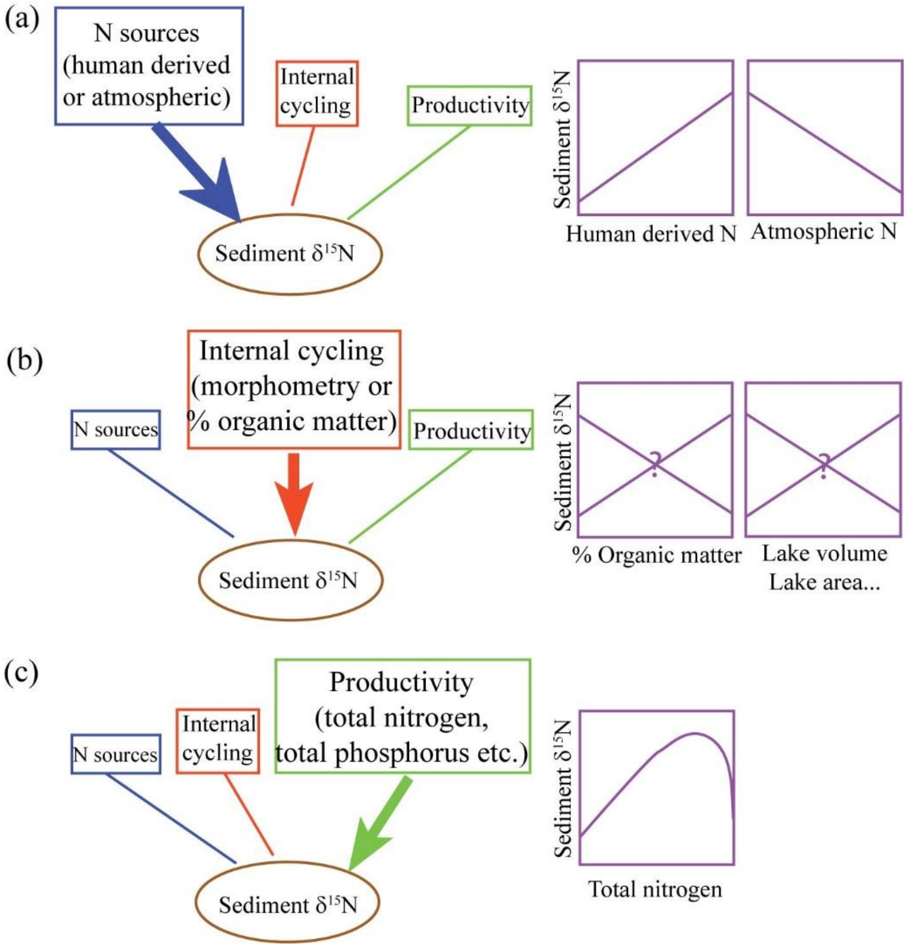


Figure 9.15 Conceptual diagram showing different processes and hypothetical effects on sediment $\delta^{15}N_{org}$. Suggested relationships based on published observations. (a) Human derived sources and atmospheric deposition, (b) internal microbial cycling (expressed as % organic matter or morphometry indices) and (c) productivity (TN used as example). Modified from Botrel *et al.*, (2014).

9.5.6 Sewage effluent enriched $\delta^{15}N_{org}$

Shifts to more enriched $\delta^{15}N_{org}$ corresponded to the establishment of treated sewage effluent discharges in 1962 at Outgate at BLE_{core}, 1973 at Hawkshead WwTW at EST_{core} and 1914 at Ambleside WwTW at WNB_{core} (Figure 9.8). Primary treated and untreated effluent may have enriched sediment $\delta^{15}N_{org}$ prior to this at WNB_{core} and elsewhere in the lowlands from ~1870 to 1950 from the growing resident and tourist populations at Ambleside, Bowness, Windermere, Hawkshead and upstream at Grasmere (Sabater and Haworth, 1995; Bennion *et al.*, 2000; Barker *et al.*, 2005; McGowan *et al.*, 2012). Sequestration of urban N in lake sediments has been identified by heavy sediment $\delta^{15}N_{org}$ values (~14‰) (Leavitt *et al.*, 2006). Much like agricultural waste, human waste has a high $\delta^{15}N_{org}$ signal from increased fractionation attributed to ammonia volatilisation (Kendall *et al.*, 2007; Botrel *et al.*, 2014). The stimulation of primary production by both agricultural and human waste at EST_{core}, BLE_{core} and WNB_{core} indicated by increased pigment concentrations and decreased C/N ratios, may have further promoted heavier sediment $\delta^{15}N_{org}$ (Figure 7.1 – Figure 7.7; Figure 9.3; Figure 9.8). Increased primary production in eutrophic lakes can lead to heavier ^{15}N assimilated by algae as depletion of lighter ^{14}N from preferential uptake continues (Meyers and Teranes, 2001).

In contrast, development of Tower Wood WwTW in 1924 at $WSB_{core,}$ which explained the greatest amount of variation in algal community change (52.9%), corresponded to depleted sediment $\delta^{15}N_{org}$ (Figure 8.3 (k); Figure 9.8). Indeed, declines in $\delta^{15}N_{org}$ between 1800 to 2009 from 5.8‰ to 4.8‰ respectively, and a distinct decline at 1875-1895 (mean=4.6‰) occurred when inadequately treated effluent input into the basin was at its greatest at WSB_{core} (Figure 8.3 (k); Figure 9.8) (McGowan *et al.*, 2012). Similarly at RYD_{site}, the establishment of the River Rothay WwTW in 1971 upstream at $GRA_{site,}$ correlated to a shift in more negative $\delta^{15}N_{org}$ (Figure 9.8). This implied that alternative N sources dominated at GRA_{core} and RYD_{core}. At WSB_{site}, in the late 19th century, one lighter isotopic source of $\delta^{15}N$ may have been the gas works at Windermere, which discharged ‘ammoniacal liquor’ into the lake and was likely transported downstream to the south basin (McGowan *et al.*, 2012).

9.5.7 Agricultural effluent enriched $\delta^{15}N_{org}$ values

At BLE_{core} increased $\delta^{15}N_{org}$ values from 3.4‰ to 4.7‰ were concomitant with increased livestock densities between 1850 to ~1970 (Figure 6.44 (2); Figure 9.8). Previous research showed increased algal pigments were positively correlated with local cattle and sheep stocking densities, important sources of fertiliser (Moorhouse *et al.*, 2014). Similar enrichment of $\delta^{15}N_{org}$ at EST_{core} to a mean of 4.3‰ between 1866 to ~1900, corresponded to increased sheep and cattle densities at this time (Figure 6.27 (2); Figure 9.8).

However, at both EST_{site} and BLE_{site}, agricultural intensification was most pronounced on account of land used for production (% permanent grass) and fertiliser use rather than livestock densities which were lower than other lake catchments in the region (Figure 6.27 (1-2); Figure 6.44 (1-2)) (Heathwaite and Johnes, 1996). Inorganic N fertilisers and livestock manure was applied to soils to support increased livestock densities, leading to increased volatilisation of ammonia and denitrification processes in soils from high inputs, all of which result in soil NO_3 that has isotopically higher $\delta^{15}N_{org}$ (+15‰ to +30‰) (Kendall, 1998; Woodward *et al.*, 2012). In addition, poaching and compaction from livestock would have increased topsoil erosion and so, transport of enriched N to sediments (van der Post *et al.*, 1997). Elsewhere in the UK, decades of N manure application to soils was directly proportional to enriched N in runoff (Bunting *et al.*, 2007). At both EST_{core} and BLE_{core}, timings of enriched sediment $\delta^{15}N_{org}$ in the late 19th to mid-20th centuries corresponded to increasing OM, decreasing C/N ratios, and increasing fossil pigment concentrations, all of which strongly suggest livestock management degraded water quality at these sites (Figure 6.26 - Figure 6-43) (Moorhouse *et al.*, 2014).

9.5.8 Artificial N fertilisers lowered $\delta^{15}N_{org}$ values

Marked increased livestock densities in the catchments of RYD_{site}, WNB_{site} and WSB_{site} after 1950 and at BLE_{site} in the 1970s, corresponded to depleted rather than enriched sedimentery $\delta^{15}N_{org}$ (Figure 6.23 (2); Figure 6.44 (2); Figure 9.8) (McGowan *et al.*, 2012). This could be attributed to synthetic N fertilisers that increased in the latter half of the 20th century. Artificial N fertilisers have low $\delta^{15}N_{org}$ values as they are produced via industrial atmospheric N_2-fixation (-4‰ to +4‰), and inputs have been shown elsewhere to lead to marked lower sediment $\delta^{15}N_{org}$ (Wu *et al.*, 2008; Botrel *et al.*, 2014). Artificial N fertilisers have been shown to correlate strongly to water column NO_3 at BLE_{site}, EST_{site}, WNB_{site} and $WSB_{site,}$ particularly in the 1960s, suggesting they were a dominant source of N to these lakes, although marked negative shifts were only seen at RYD_{site} and EST_{site} at this time (Figure 9.8) (George *et al.*, 2000).

Conversely, the amount of NO_3 entering lowland lakes in the Windermere catchment decreased in milder winters from greater terrestrial vegetation uptake, would have increased the $\delta^{15}N_{org}$ value (George *et al*, 2004). Further, bacterial denitrification and NH_4 volatilisation also increase in milder temperatures, and the wet poorly drained soils found in the catchment would have further promoted denitrification (Davidson and Swank, 1986; Groffman and Tiedje, 1991; George *et al.*, 2004). Thus, climate-mediated terrestrial assimilation of artificial fertilisers may have actually enriched the $\delta^{15}N_{org}$ value (Woodward *et al.*, 2012). No information on denitrification in the catchment currently exists, so it is difficult to determine the extent to which this may have altered the delivery of isotopically lighter $\delta^{15}N_{org}$ from artificial fertilisers within the catchment (George *et al.*, 2004). In addition, variability in timing and intensity of rainfall may have altered terrestrial assimilation of N as with P, which would have further complicated the $\delta^{15}N_{org}$ trends (George *et al.*, 2004).

9.5.9 Atmospheric N deposition in the lowlands

It is possible that atmospheric N deposition, in particular from the atmospheric volatilisation of inorganic and organic fertilisers, and fossil fuel combustion from tourism and industrial development from the late 19th century in the north west of England, led to the diluted $\delta^{15}N_{org}$ values at BLE_{core}, RYD_{core}, WNB_{core} and WSB_{core} within this period (Figure 9.8) (Vitousek *et al.*, 1997). Volatilisation of N from agricultural land has been found to be a significant source to the atmospheric N pool, and may well have been deposited from dry and wet deposition into the lowlands, following global intensification of agriculture in the late 19th century (Howarth *et al.*, 1996; Vitousek *et al.*, 1997). However, NH_4 and nitric acids measured in precipitation in the lowlands of the catchment were determined to have originated from industrial activity at Manchester and Leeds beginning in the Industrial Revolution (Crowther and Ruston, 1911; Sutcliffe, 1983). In the Windermere basins, atmospherically-derived N and S have contributed to the high ionic content of these waters (Talling and Heaney, 1988). Although this supports regional N deposition from the mid-19th century, it suggests the origins of the source were from beyond the catchment itself.

Determining the relative importance of atmospheric N in the lowlands is difficult due to a number of factors. First, although high N deposition has been recorded across the catchment, its importance is harder to extricate in the lowlands due to other anthropogenic confounding factors (Allott *et al.*, 1995). Second, there are significant difficulties in quantifying the amount and range of N volatised then deposited within the region from fossil fuel and fertiliser use, although there is documentation of a larger fraction of UK NOx emissions being deposited in the UK rather than exported (Howarth *et al.*, 1996; RoTAP, 2012). Much is known about N losses from manure and synthetic fertilisers in runoff, and the influence of application timing, quantity, rainfall and vegetation cover, but little is known about losses from the atmospheric volatilisation of fertilisers (Carpenter *et al.*, 1998). Although it has been determined that reduced N deposition such as ammonia from agricultural activity will continue to be an important form of deposited N in the UK (RoTAP, 2012). Notwithstanding these difficulties, N deposition has contributed to N accumulation throughout the catchment with measurements of 3500 kg N km^{-2} $year^{-1}$ between 1986-1988, averaged for the whole Lake District (Talling and Heaney, 1988; Tipping *et al.*, 2008). Furthermore, the concentration of wet deposition of NO_3 and NH_4 in the Windermere catchment was one of the highest in the UK in 2005, at >7.1 and >8.5 kg N ha^{-1} yr^{-1} respectively (UKEAP, 2010; RoTAP, 2012). This may have led to the depletions of $\delta^{15}N_{org}$ in the lowland lacustrine sediments since the early 20th century, despite the lack of evidence about the fate of deposited N in terrestrial and freshwater environments (RoTAP, 2015).

9.5.10 The role of N_2-fixing cyanobacteria

The incoherent temporal relationship between sediment $\delta^{15}N_{org}$ and enhanced primary production shown by decreased C/N ratios at all the lowland lakes beginning in 1800 is common when C/N ratios are <20 (Woodward *et al.*, 2012). It could point to the dominance of N_2-fixing cyanobacteria in the primary producer populations, as cyanobacterial atmospheric N_2-fixation results in lower $\delta^{15}N_{org}$ values (-1‰ to -2‰) (Gu *et al.*, 2006). Increasing positive trends of the filamentous cyanobacterial pigment aphanizophyll within these lowlands, may have related to N_2-fixing genera, although aphanizophyll is also found in non-diazotrophic taxa (Bunting *et al.*, 2007).

However, in Windermere in 1965-66, N_2-fixation accounted for <1% of the total N sources, and increases in regional N supply in recent decades would select against cyanobacterial N_2-fixers (Horne and Fogg, 1970; Maberly *et al.*, 2002). Preliminary investigations into sedimentary heterocysts (specialised cells involved in N_2-fixation) in the sediments of BLE_{core} found <2 occurrences of such cells from *Anabaena* spp. which further imply cyanobacterial communities in the catchment were dominated by non-N_2 fixing genera (*pers. comm.* Van Geel, B., 2012). Thus, like other eutrophied lakes N_2-fixation may have only played a minor role in altering the longer centennial trends in the lowlands of the catchment (Lewis and Wurtsbaugh, 2008; Botrel *et al.*, 2014).

9.5.11 Site-specific controls on sediment $\delta^{15}N_{org}$

The asynchrony of lowland lake sediment $\delta^{15}N_{org}$ suggests that site-specific controls of assimilation play a greater role when multiple confounding N sources are apparent (Figure 9.8). Site-specific controls could have included internal microbial cycling and lake-catchment morphometry modifications of internal microbial processing and the dominant N source (Botrel *et al.*, 2014). At BLE_{core} and RYD_{core}, decreasing $\delta^{15}N_{org}$ values from ~1995 and ~1958 respectively, corresponded to increased %N and OM values, suggesting lower microbial processing of N in OM, lower fractionation and so, depleted $\delta^{15}N_{org}$ at this time (Figure 6.40 (1b/2a/2d); Figure 6-43 (1b/2a/2d)) (Freudenthal *et al.*, 2001). At BLE_{site}, the progressively more anoxic hypolimnion over the last 40^+

years would have slowed OM degradation, which is often higher in oxygenated waters (Foley *et al.*, 2012).

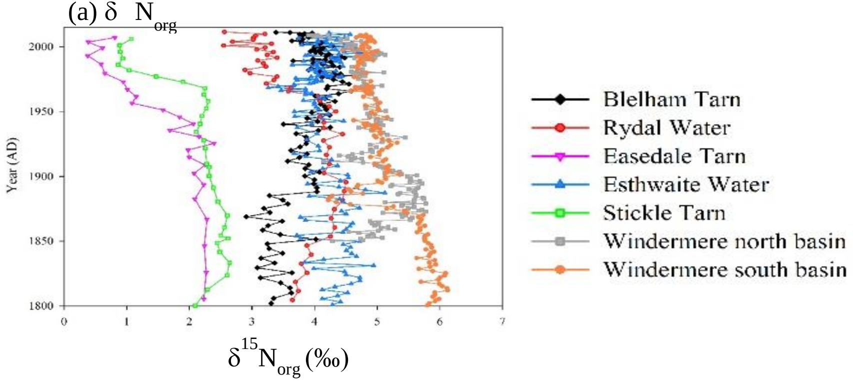
Smaller, shallower lakes with shorter residence times in the catchment such as RYD_{site} (WRT=9 days) and BLE_{site} (WRT=50 days), could have limited the processing of OM and N, as previously shown by the significantly lower sediment $\delta^{15}\text{N}_{\text{org}}$ of lakes with WRTs below 100 days ($p \leq 0.05$) (Figure 9.12) (Kalff, 2002; Botrel *et al.*, 2014). In contrast, the terminal deep basins of WNB_{core} and WSB_{core} had the highest overall $\delta^{15}\text{N}_{\text{org}}$ values, but the most long-term depletions beginning c.1900 (Figure 9.8). It could be that the larger volume (WNB_{site}=201.8 10^6 m^3, WSB_{site}=112.7 10^6 m^3) and greater CA:LA (WNB_{site}=21.6, WSB_{site}=37.3) of these basins diluted heavily labelled $\delta^{15}\text{N}_{\text{org}}$ from human and agricultural catchment activity and terrestrial fractionation. But their larger lake surface area (WNB_{site}=8.1 km^2, WSB_{site}=6.7 km^2) magnified the inputs of isotopically lighter atmospheric N over the 20th century (Kendall *et al.*, 2007; Botrel *et al.*, 2014). At EST_{core}, increasing values after 1900 may be attributed to its CA:LA ratio (17) which is smaller than the other lowland lakes (>20). This could have magnified $\delta^{15}\text{N}_{\text{org}}$ enrichment via agricultural and terrestrial denitrification and NH_4 volatilisation in its smaller, more productive catchment (Botrel *et al.*, 2014). Ultimately however, these hypotheses must be treated with caution due to lack of process-based testing (Jones *et al.*, 2004).

9.5.12 Relationship between sediment $\delta^{15}\text{N}_{\text{org}}$ and algal pigment changes

Increased positive trends in total algal production (β-carotene), cryptophyte (alloxanthin), chlorophyte (lutein), cyanobacterial (canthaxanthin, zeaxanthin) and siliceous algae (diatoxanthin) over the last 200 years in the lowlands of the Windermere catchment are concomitant with changing $\delta^{15}\text{N}_{\text{org}}$ trends (Figure 7.1 – Figure 7.7; Figure 9.8; Figure 9.16). Much like the $\delta^{15}\text{N}_{\text{org}}$ records, pigment concentrations were often the lowest in the upland lakes (STI_{core} and EAS_{core}) compared to the lowlands, and the terminal basin WSB_{core} had the highest concentrations for most pigments (Figure 9.16). However, for most sites pigments increased since 1800, whereas the $\delta^{15}\text{N}_{\text{org}}$ records were much more variable, thus making a causal link between nutrient source and biological response difficult. At BLE$_{core}$ and EST$_{core}$ enriched $\delta^{15}N_{org}$ and increased concentrations of all algal pigments from the 20th and mid-20th century respectively, suggest heavily labelled agricultural and sewage effluent fertilised the lakes of these productive lowlands (Figure 6.26 (2d/3); Figure 6-43 (2d/3)). In contrast, at WNB$_{core}$, WSB$_{core}$ and RYD$_{core}$ depleted $\delta^{15}N_{org}$ occurred as algal pigment concentrations increased from the 19th century onwards (Figure 6.2; Figure 6.3; Figure 6.40 (2d/3); Figure 9.8). In arctic lakes, depleted $\delta^{15}N_{org}$ and increased diatom and chrysophyte concentrations are consistent with enhanced atmospheric N deposition from 1850 and attendant fertilisation (Holmgren *et al.*, 2010). In the Windermere catchment lowlands, atmospheric N deposition could have been an important source involved in eutrophication.

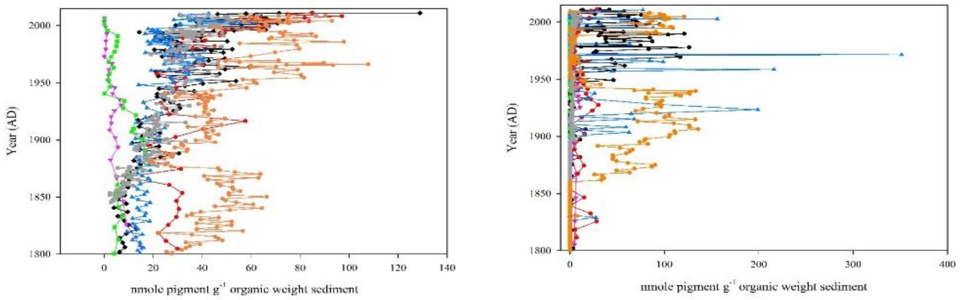
Overall, sediment $\delta^{15}N_{org}$ values showed considerable long-term disruption to N cycling in the lowland lakes at a time when P loading increased, resulting in fertilisation and enhanced primary production (McGowan *et al.*, 2012; Moorhouse *et al.*, 2014). Although P has been identified as the primary nutrient causing eutrophication, continued N fertilisation has now being recognised as important in promoting cyanobacterial blooms and algal biomass, particularly in P-rich waters (Donald *et al*., 2013). However, responses of primary producers to N vary dependent on the chemical forms of N added (Donald *et al*., 2013). The competitive advantage of diazotrophic cyanobacteria can be suppressed following N fertilisation which can inhibit heterocyst production (Flores and Herrero, 2005; Finlay *et al.*, 2010). NH_4 and urea ($[NH_2]_2CO$) fertilisation can lead to non-N_2 fixing cyanobacteria and chlorophytes outcompeting diazotrophic taxa, due to efficient light and NH_4 uptake kinetics (Blomqvist *et al.*, 1994; Jensen *et al.*, 1994; Finlay *et al.*, 2010; Donald *et al.*, 2011).

(a) $\delta^{15}N_{org}$



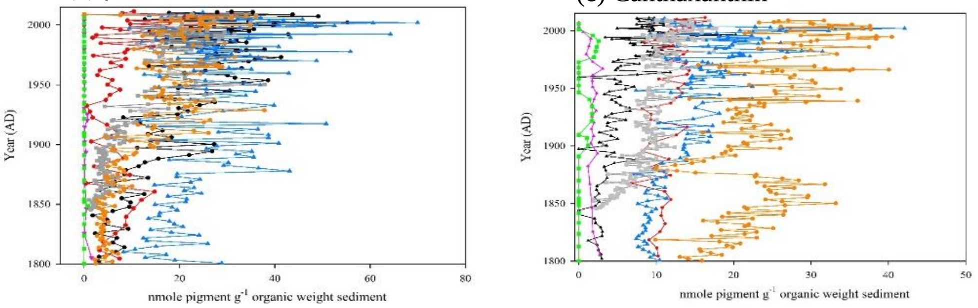
(b) Alloxanthin

(c) Aphanizophyll



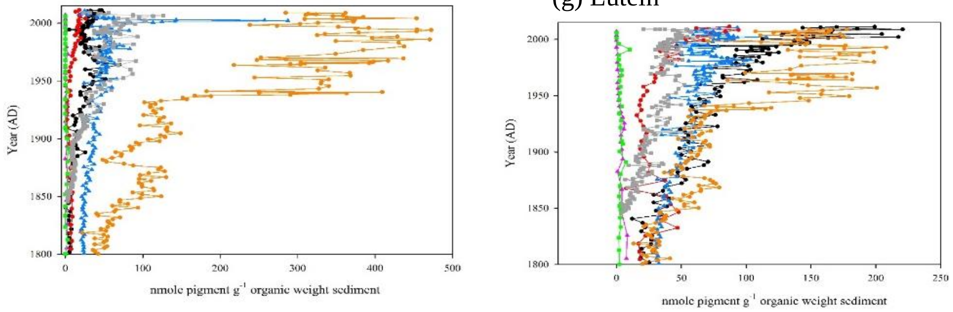
(d) β-carotene

(e) Canthaxanthin



(f) Diatoxanthin

(g) Lutein



(h) Zeaxanthin

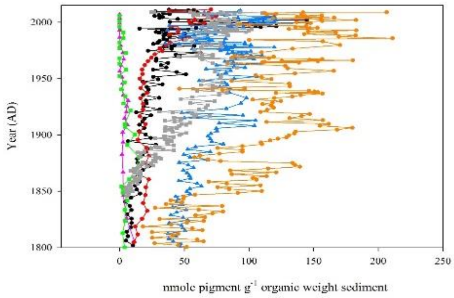


Figure 9.16 $\delta^{15}N_{org}$ values (a) and algal pigments (b-h) of dated sediment cores from the Windermere catchment since 1800AD.

This could have occurred in all the lowland lakes where higher positive Mann-Kendall coefficients of non-diazotrophic cyanobacterial (canthaxanthin, zeaxanthin) and chlorophyte (lutein) pigments to that of the potentially N_2-fixing filamentous cyanobacterial pigment aphanizophyll was recorded over the last ~200 years (excluding ELT-MID$_{core}$ and ELTOUT$_{core}$) (Figure 7.2; Figure 7.4; Figure 7.6 – Figure 7.7). The higher positive Mann-Kendall coefficients of diatoxanthin to that of aphanizophyll in the lowlands (excluding LOU$_{core}$, ELTMID$_{core}$ and ELTOUT$_{core}$) could indicate NO_3 addition which favours diatoms in P-rich waters when Si is available (Figure 7.2; Figure 7.6) (Tilman *et al*., 1982). It should therefore be recommended that remediation should not be limited to point P sources, particularly as N influx into the biosphere from fertiliser usage is set to double by 2050 to meet global food demands (Vitousek *et al.*, 1997; MEA, 2005). N loading is likely to be focussed on agricultural landscapes such as the Windermere catchment, where applications of N fertilisers will exceed 275 Tg N year^{-1} on already saturated P soils from centuries of farming (Foy *et al.*, 1995; Carpenter, 2005). However *Catchment Sensitive Farming* initiatives that reduce diffuse pollution already adopted in the region, could buffer these future changes (WCRP, 2010).

9.6 Summary

Evidence from individual pigment stratigraphies and stable isotopes indicate that change in lake ecosystem functioning began much earlier in the late 19th century caused by agricultural intensification and urban expansion in the lowlands and acidification in the upland lakes from the fossil fuel combustion in industrial northern cities. In the lowland lakes, evidence from sedimentary $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ isotopes revealed increased catchment primary productivity from inputs of isotopically light $\delta^{15}N$ synthetic fertilisers and heavy $\delta^{15}N$ animal manure since the late 19th century. Thus, agricultural land use changes could have played a more important underlying role than identified by the RTs in chapter 8. Globally, anthropogenic nutrient inputs have altered aquatic ecosystems since the 19th century and our demand for food has led to saturation of N and P in terrestrial and aquatic environments (Smith *et al*., 1999). This post-1850 activity has further altered biogeochemical cycles as enhanced GHG emissions have led to inundation of atmospheric CO_2 concentrations and reactive N (Nr) (Wolfe *et al.*, 2013). The changes after 1950 in $\delta^{15}N_{org}$ and algal assemblages in the Windermere catchment correspond to wider stratigraphic evidence from lake and marine sediments and ice cores elsewhere that have helped define the Anthropocene (Lewis and Maslin, 2015).

The sedimentary $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$ records across the Windermere catchment show regional heterogeneity spatially and temporally. Regional studies looking at drivers of sediment $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$ often show variability in sources and processes, but extrication of the dominant mechanism required greater depth of study beyond the scope of this thesis (Botrel *et al.*, 2014). Interestingly, the significant difference of $\delta^{15}N_{org}$ values between lowland and upland lakes, and those with shorter (<100 days) and longer (≥100 days) WRTs, highlights how important landscape position and morphometry have been in modifying N pools in the Windermere catchment. These results were then used to help derive the conclusions and management recommendations presented in the subsequent chapter.

CHAPTER 10. SUMMARY, POTENTIAL MANAGEMENT MEASURES AND FUTURE WORK

10.1 Overall summary

This section presents a summary of the main findings and the contribution of this thesis to current palaeolimnological research.

10.1.1 Key findings

In reference to the thesis aims outlined in section 1.6, the key findings of this thesis are as follows:

Total algal production in most of the Windermere catchment lakes increased from 1800 onwards. In the lowland lakes, all algal groups (cryptophytes, cyanobacteria, diatoms, and chlorophytes) increased according to pigment concentration increases. Whereas in the upland lakes, the response of the algal pigments was more varied, but decreases in pigment abundance dominated particularly at EAS_{core}.

Overall, synchronous change in algal pigments was greatest from 1900 rather than 1800 onwards, and higher synchrony values of summer-blooming taxa such as cyanobacterial and chlorophyte pigments compared to spring-blooming taxa (e.g. diatoms) was found. This indicates that regional-scale nutrient additions and climate warming could have worked synergistically in promoting these taxa. However, it was the lowland lakes not the upland lakes which had higher synchrony values, particularly in the 20th century. At this time, agricultural and sewage development in the lowlands, likely led to the fertilisation and increase in algal production at these lakes. By the latter half of the 20th century, synchrony values were lower in the lowlands, likely caused by the influence of multiple stressors and difference in timings of point source development. Whereas in the upland lakes, climate change and atmospheric deposition, coupled with landscape filtering could have caused the asynchronous changes in algal communities throughout the 19th and 20th centuries.

In most lakes, algal community change was gradual and began in the late 19th to early 20th century. However, the timings of breakpoints of algal community change occurred in the latter half of the 20th century in most lakes. This was concomitant with mass tourism and agricultural intensification in the region. Interestingly, the upland lakes followed similar trends to the lowlands in the timings of change. This could have been due to regional-scale drivers of change such as climate change.

Regression trees (RTs) indicated that point sewage development explained the most algal community change in the lowland lakes, whereas changes to atmospheric pollutants and temperature explained most community variability in the upland lakes since 1800. However, caution must be applied to the results of the upland lakes due to the lack of adequate historical records.

Water retention time (WRT) had the highest correlation to algal community change than any other landscape characteristics. This was likely caused by the high annual precipitation of the region which would have increased the strength of its role in nutrient and algal inoculum removal and renewal.

Algal community change was greatest in lakes with long WRTs which overlay productive Silurian flags and slates (SIL) geology. Although there was a correlation between algal community change and catchment area to lake area ratio (CA:LA), whereby lakes with low CA:LA’s had higher community changes due to its closer connectivity between lake and catchment, the presence of human activity in the lake catchment outweighed this effect. Similarly in lakes with short WRTs overlaying less productive Borrowdale volcanic group (BVG) geology, nutrient fertilisation and flushing worked synergistically in increasing community change.

Stable isotopes supported the pigment results. $\delta^{13}C_{org}$ and C/N ratios indicated increased inputs of autochthonous organic matter from 1800 onwards, suggesting lake primary production increased across the catchment. Heavy values of $\delta^{15}N_{org}$ in the lowlands point to the inputs of heavily labelled sewage and agricultural runoff since 1800, whereas declines in $\delta^{15}N_{org}$ in some lowland lakes and in the upland lakes from the 20th century onwards, could be evidence of atmospheric N deposition. In the upland lakes, no clear algal response matched the decline in $\delta^{15}N_{org}$, although some increases in pigments were seen at STI_{core}. At EAScore, pigment and $\delta^{15}N_{org}$ values declined which may indicate a shift from benthic to planktonic production. These hypotheses are tentative due to the lack of supporting evidence.

10.1.2 Knowledge gaps addressed by thesis

In terms of the knowledge gaps outlined in section 1.6, this study addressed the following:

The knowledge gaps on heterogeneous landscapes have been addressed by identifying and quantifying the difference in algal community changes in upland and lowland lakes, lakes of long and short WRTs, and lakes of different geological types. This study has shown that for some characteristics lakes can be split into distinct types (e.g. upland and lowland, SIL and BVG geology) and have distinct differences in algal communities, but when coupled with other characteristics changes are much more complex. Specifically, the role of geology and WRTs on shaping algal community changes has likely been amplified and disrupted by local nutrient enrichment. Although these characteristics may not be as important in other lake catchments, it highlights the need to understand the extent the position and characteristics of a lake shape its response to environmental change.

This study has addressed the role of multiple stressors and similar to the findings of Taranu *et al.*, (2015) showed that nutrient enrichment caused the greatest amount of algal community change compared to other stressors in the Windermere catchment. It suggests that lake enrichment studies elsewhere may be accurate in their focus, although the future importance of other stressors such as climate change and diffuse pollutants should be noted.

The broader spatial scale of the study has furthered our knowledge that past environmental change was not restricted to lowland lakes. It highlights that pinpointing the drivers and understanding the complex response of algae in the upland lakes was difficult due to the diffuse nature of the stressors and lack of studies on upland lakes. The broader temporal scale of the study highlighted difficulties in determining baselines of change and alternative stable states from single to catchment-scale and will be discussed in section 10.1.4.

The community scale study of this thesis supports and expands on the single species studies (namely diatoms) of past palaeolimnological work in the catchment (e.g. Sabater and Haworth, 1995; Dong *et al*., 2012). It has furthered knowledge by showing that summer-blooming taxa have behaved more synchronously than spring-blooming taxa since 1800, overlooked by studies focussed on spring taxa (diatoms). But these results support past work by pointing to the importance of point sources and stable water columns (from long WRTs and warmer temperatures) in promoting lake fertilisation in the lowland lakes (Dong *et al*., 2012).

10.1.3 Thesis novelty

The novelty of this study exists predominantly in its catchment approach. Primarily, it is the first palaeolimnological catchment-wide study conducted in the Windermere catchment, and has both added to and synthesised past work in the region. It differs to catchment palaeolimnological studies conducted elsewhere because it compares algal community response between upland and lowland lakes to drivers of change, with very few palaeolimnological studies focussed on headwaters to terminal basins. Further, it has used statistical techniques other than transfer functions to quantify environmental change, and has sought to quantify the role played by different landscape characteristics which is often overlooked in palaeolimnology. Its strengths are found again in the systematic and consistent approach of the methods used. Sediment cores were retrieved from all lakes in the catchment, and every lake had a core which underwent sedimentary pigment analysis by HPLC. Studies that focus on biological communities like this one are rare in palaeolimnology, particularly those that use taxonomic assessment of proxies due to time constraints of working on multiple cores. But the rapid method of pigment identification and quantification using HPLC overcame this issue. Nearly all lakes underwent ^{210}Pb dating and stable isotope analyses, which in addition to pigment identification made the comparisons between the nature, causes and timings of lake authocthonous production and community changes more approachable.

10.1.4 Reflections on methods

Past research in the Windermere catchment supported the main finding that nutrient enrichment drove algal production but, inherent issues with trying to combine sediment and monitoring records means that a degree of caution must be applied when interpreting this and other palaeo-contemporary studies. For instance, robust chronologies are required for sediment cores, so at sites such as ELTIN$_{\text{core}}$, GRA$_{\text{core}}$, LOU$_{\text{core}}$ and CT$_{\text{core}}$, where ^{210}Pb counts were either sparse or low, reduced confidence in the chronology and so, results of the timings and causes of algal community changes must be noted. However, validation with ^{137}Cs and ^{241}Am and past work increased the confidence in the chronologies of these cores. The usefulness of sediment cores in providing long-term patterns of change was felt to outweigh these caveats, and helped to determine the 20th and late-20th century as important timings of algal community change (Battarbee *et al.*,2012).

In terms of the historical environmental data, although the best available data was collected, it may not be truly representative of the real environmental changes in the catchments of the lakes, or be mismatched with the spatial and temporal scales of this study. For instance, the agricultural and human population records used in this study were on a parish level rather than lake catchment scale, temperature records were measured in Central England, rainfall data was collected in the lowlands of the catchment, which likely does not reflect the climate of the uplands and finally, NO_x and SO_2 emissions data was used rather than deposition data. However, the lowland historical environmental datasets were adapted to fit the lake-catchment scale and matched the higher sedimentation rates in these lakes. In the uplands however, the lack of atmospheric deposition and climate data from these high altitude sites meant that less confidence must be given to the conclusions made here. However, results from work in upland lakes elsewhere was useful in addressing the extent acidification, atmospheric N deposition and climate change may have played in the Windermere catchment.

Interpretation of the sedimentary pigment stratigraphies was aided by the large body of literature on pigment degradation (McGowan, 2013). However, it is hard to quantify the relative importance of each factor (e.g. grazing, lake depth etc.) that acts on each individual lake and the extent it alters the pigment record unless investigations into these processes are undertaken. Contemporary sediment trap data may have been useful in verifying the sediment pigment record, as well as helping to quantify the relative importance of planktonic to benthic production, particularly in the upland lakes. However, interpreting the extent diagenesis may have played was aided by pigment degradation products such as pheophytin *a*, and the millennial timescale of degradation processes once pigments are incorporated into sediments, validated the sediment pigment record (McGowan, 2013). Similarly, stable N and C isotopes are part of complex geochemical cycles and multiple processes (not limited to autochthonous production and human activity) which could have altered these values. However, the $\delta^{15}N_{org}$, $\delta^{13}C_{org}$ and C/N ratios were useful to support the trends of the algal pigment records and historical environmental data.

10.1.5 Contribution to current debates on freshwaters

This study is one of a handful of palaeolimnological studies that have investigated ecological response of lakes in terms of their spatial location and interactions with landscape characteristics, and is unique in the heterogeneous setting of the headwaters to the terminal basins. It provides evidence that these spatial interactions and the location of a lake in its catchment are important in defining the temporal response of lakes to environmental change (Anderson, 2014). These results are more useful to managers because of their ability to pinpoint were ecological change has been greatest in the catchment.

The next steps of landscape-scale palaeolimnological studies should be conducting similar studies elsewhere to continue to improve our understanding about the relative importance of spatial interactions between a lake's landscape and drivers of change, particularly as management in the EU is focussed on addressing multiple stressors on the catchment scale. In addition, further studies are required to address how to overcome methodological issues related to dating or the ability of a single core to represent whole lake and catchment environmental change (Anderson, 2014).

Current debates on threshold changes, regime shifts and alternative states in lakes have determined that most studies lack convincing evidence that sudden shifts to alternative states have occurred in many lakes (Capon *et al*., 2015). The predominantly wide 95%CI's of the breakpoints, indicated gradual, more linear algal community composition and abundance changes over time in the Windermere catchment and so, supported this argument (see section 8.2). Furthermore, different detection methods have been shown to alter threshold values and so, more research into the use of breakpoints and other statistical approaches would be required to determine whether or not threshold changes in algal communities in the Windermere catchment lakes occurred (Dodds *et al*., 2010).

This study did not address the relative dominance of one species to another over time and thus, could not contribute to whether an alternative state had been reached in the Windermere catchment lakes. Specifically, although cyanobacterial pigments increased, so too did pigments from other algal groups in the lowland lakes, and in the uplands, most algal pigments decreased. Thus, changes to the algal communities did not provide evidence for sudden shifts to alternative algal community states or dominance of a particular species over long periods of time. However, the ability of cyanobacteria to outcompete other algal groups over different nutrient concentration and temperature ranges and their increasing trends in the Windermere catchment indicate cyanobacterial blooms could become more prevalent in the future (O'Neil *et al*., 2012).

The results of the RTs showed point nutrient sources induced nonlinear effects on algal communities in the lowland lakes, which is supported by increases in the raw pigment data following WwTW development (see Chapter 6 and section 8.3). However, as previously mentioned this did not induce a state change, and timings of breakpoints did not correspond to the timings of WwTW development, which again supports the view that lake response to multiple stressors can be nonlinear, lagged and often more complex than a sudden shift (Dodds *et al*., 2010). However, some could argue that the increased abundance and changes to community composition in the Windermere catchment could indicate loss of resilience to other stressors and so, an early warning signal for a shift change (see Carpenter *et al*., 2011). But knowledge gaps on understanding the mechanisms of the stability-resilience relationship in freshwater ecosystems and the role primary producers play in this, limit the ability of this study to add to this particular argument (Capon *et al*., 2015; Dai *et al*., 2015).

Current debates on the practicality of reference conditions as restoration targets under the WFD revolve around whether conditions should be type-based or site-specific, how to differentiate between pristine (no human influence) to reference conditions (no or minimal human influence), and whether or not current and future stressors such as climate change would prevent the reference condition ever being met (Hering *et al*., 2010; Bennion *et al*., 2011a). Although this study showed that lakes can be split into different types of landscape characteristics such as upland and lowland, BVG and SIL geology etc. in terms of shaping and determining the response of algae to drivers of change, other characteristics such as human catchment activity overrode these effects and thus, perhaps site-specific reference conditions would be more appropriate.

Further, this study was conducted on sediments from 1800 onwards, and like many lakes elsewhere in Europe, the lowlands in particular had experienced centuries of human activity prior to the often recommended 1850AD reference date before the Industrial Revolution (Bjerring *et al*., 2008; Dong *et al*., 2012). Because of the time period of this study it relied on past palaeolimnological work in the catchment to characterise lake conditions prior to 1800, but the time period chosen for this study showed that the extent of algal community change in the Windermere catchment was greatest in the latter half of the 20th century, particularly in terms of increased primary production beyond that seen at any other point in time. This is further supported by the dominant increasing pigment concentration trends from the lowland lakes. Thus, a reference date of 1945 may be a more realistic target for the Windermere catchment lakes, particularly considering the social, political and economic factors, which continue to drive management decisions (Moss, 2008).

Ecological changes to both upland and lowland lakes in the absence of point nutrient sources have occurred (e.g. $\mathrm{STI}_{\mathrm{core}}$ and $\mathrm{LOU}_{\mathrm{core}}$), and this supports the notion that regional-scale environmental drivers such as agricultural runoff and climate change, which are more difficult to manage and quantify, could reduce the ability to restore lakes to reference conditions (Bennion *et al*., 2011a). Stressors such as climate change and agricultural diffuse pollutants will continue to incur environmental modifications due to our continued reliance on fossil fuels and for food security (Steffen *et al*., 2007). However, despite difficulty in quantifying the relative importance of diffuse and future stressors, reference conditions are still a useful tool to managers because of their ability to pinpoint which lakes in a catchment have experienced the biggest changes.

10.1.6 Management implications

The establishment and development of WwTWs accounted for the biggest algal community changes in the Windermere catchment. Management should therefore focus on mitigating the negative impacts of point sources in lakes with longer WRTs such as $\mathrm{ELTIN}_{\mathrm{site}}$, $\mathrm{EST}_{\mathrm{site}}$, $\mathrm{WNB}_{\mathrm{site}}$ and $\mathrm{WSB}_{\mathrm{site}}$, to reduce the impacts of algal blooms and increasing trends in cyanobacteria.

Similarly, lakes with low WRTs and point sources such as $\mathrm{BLE}_{\mathrm{site}}$ and $\mathrm{GRA}_{\mathrm{site}}$, should also be a priority considering the climate projections for drier summers and wetter winters (Murphy *et al*., 2009). Observations by past work that wetter winters caused reductions in the inoculum for spring diatom growth and in years of smaller diatom blooms, cyanobacteria populations were greater

(McGowan *et al*., 2012), coupled with the results from this study that algal community change has been high at sites with low WRTs such as BLE_{core}, suggests that these lakes could be susceptible to frequent algal blooms and disrupted algal seasonal succession in the future. Such high algal turnover is caused by the interplay between enrichment and flushing (Reynolds *et al*., 2012).

The role diffuse agricultural and human pollutants could have contributed to the nutrient enrichment of the lowland lakes requires further investigation. The lack of data on septic tank numbers, tourist populations and catchment fertiliser application reduces the confidence in the proportional role these sources may have shaped past algal communities. However, the timings of increasing pigment concentrations at lowland lakes prior to point source development and the similar responses of algal community in lowland lakes without point sources, coupled with RT results of catchment human population/livestock changes and UK trends in fertiliser application support the hypothesis that diffuse pollutants played an important part in the enrichment of the lowland lakes. LOU_{site} would be an ideal focus site for such an investigation because of the absence of point sources and presence of human and agricultural diffuse sources. Modelling and monitoring nutrient pathways and constructing P budgets would be recommended. Further, its eutrophic status necessitates the need to investigate the factors which have caused the decline in its water quality.

The cause of algal community change in the upland lakes requires further investigation. Recommendations would be to monitor the physical and chemical limnological variables and characterise the benthic and planktonic phytoplankton communities. Sites involved in the UK upland waters monitoring network were selected on the basis that acid deposition caused extensive ecological and chemical change and have consequently overlooked environmental change in other UK upland lakes. Recommendations would be to extend the network to include the upland lakes of the Windermere catchment to help extricate the effects of climate change and atmospheric N deposition (AWMN, 2015).

10.2 Potential management measures

Attempts at remediating point nutrient sources have already been made in the Windermere catchment including installation of tertiary treatments, discharging waste in periods of wet weather and retaining a greater proportion of drain and wastewater on site (e.g. at the River Rothay WwTW). This study and others (e.g. Reynolds *et al*., 2012) have not shown the reversal of algal production trends or trophic community changes that are necessary to improve the ecological status of lakes within the Windermere catchment. True efficiency of P stripping is rarely achieved as heavy rainfall characteristic of the area decreases P adsorption and therefore P precipitation from the treated effluent (Pickering, 2001).

Hydromorphological adaptations that re-connect basins to inflows to increase flushing such as proposed at $\mathrm{ELTIN_{site}}$ are likely to modify and reduce algal standing crops but the water quality of the inflow will determine the success of this strategy (Cross *et al*., 2014). Thus, more effective long-term nutrient management requires sustainable approaches and some suggestions are made below.

10.2.1 Sustainable remediation of eutrophication

Priority of point source management should focus on lakes with long WRTs, overlaying productive geology such as $\mathrm{EST_{site}}$, $\mathrm{WNB_{site}}$ and $\mathrm{WSB_{site}}$, as these sites are more likely to harbour potentially toxin-producing cyanobacterial populations. These lakes also have the largest urban areas in their catchments and are the most popular tourist destinations meaning that they are subjected to high anthropogenic pressures. Top-down, bottom-up management could be one viable approach, in which manipulation of algal resources such as nutrients (bottom-up) and predators (top-down) attempts to reduce the abundance of algal biomass (Power, 1992). The top-down, bottom-up approach is currently being deployed at $\mathrm{EST_{site}}$ and its effectiveness is being monitored (CEH, 2015). The bottom-up aspect involves removing external nutrient inputs by improving the WwTW.

10.2.2 Bottom-up remediation

Options for sustainable improvements to WwTWs in the catchment could include phyto- and phycoremediation, which use plants and algae respectively to remediate wastewater particularly in the tertiary stages and produces potentially C neutral biofuel (Pittman *et al*., 2011). The use of vegetation filters such as fast-growing trees (e.g. willows), that rapidly take up N and heavy metals and promote denitrification in the root zone are an example of phytoremediation (Aronsson and Perttu, 2001). Where land is inadequate for plant crops, CO_2 enhanced high rate algal ponds can remove NH_4 and orthophosphate by up to 99%, and attendant algal lipids can be refined for biofuel production or can be used as low-cost fertilisers or animal feed (Woertz *et al.*, 2009; Pittman *et al.*, 2011). This is an example of phycoremediation.

The applicability of phyto- and phycoremediation in the Windermere catchment is difficult to determine as studies into its use have mainly involved laboratory microcosm and mesocosm scales, and the high rates of hydrological renewal in the catchment could complicate the efficiency of “open” systems (Williams, 2002). Further challenges for phycoremediation include start-up costs, providing the correct conditions and inoculum for algal growth, inefficient algal harvesting techniques, the need to demonstrate high yields of biofuel from algae on an industrial scale and whether or not wastewater could provide the CO_2 from aerobic bacterial respiration needed for algal ponds (Pittman *et al*., 2011). Notwithstanding these caveats, this technology could be a potential future sustainable WwTW measure after further investigation and, coupled with investment in Cumbria’s drains and pipes, could reduce the efficiency with which high nutrient inputs enter these lakes (UU, 2015).

10.2.3 Top-down remediation

The top-down aspect consists of bio-manipulation which involves removing zooplanktivorous and benthivorous fish such as the invasive *R. rutilus* found in Windermere or reduced stocking of game fish such as the rainbow trout at EST_{site}, to permit a clear water state of sufficient length to allow submerged macrophytes to develop (Søndergaard *et al*., 2007). Long-term fisheries records such as those from Windermere could help guide suitable numbers of fish removal (Winfield *et al*., 2008). Macrophyte planting could further enhance the clear water state.

Although top-down measures are relatively straightforward to apply, there exist several limitations to their long-term success. Top-down measures are restricted to shallow basins and the long-term success is poor on account of migration of zooplanktivorous fish back into basins, insufficient numbers of fish removed, benthic chemistry and ecology preventing macrophyte germination, sediment re-suspension and internal P-loading (Perrow *et al.*, 1997; Søndergaard *et al.*, 2007). Ultimately shifts in trophic assemblages would create new regimes rather than return to baseline communities especially if continued manipulation occurred and high nutrient loading continued (Perrow *et al*., 1997). It would be recommended to monitor the success of the scheme at $\mathrm{EST}_{\mathrm{site}}$ before extending it to the wider catchment.

10.2.4 End-of-pipe measures

"End-of-pipe" measures refer to those undertaken at the end of a process or once the causes and effects have occurred. They may be necessary considering the increasing risk of HABs within lakes with long WRTs in the catchment in the face of a warming climate. Techniques include chlorine treatments (which have been found to reduce the cyanotoxin microystin-LR (Xagoraraki *et al*., 2006), the use of electrolytes to increase the flocculation of algae to clay particles for removal (Avnimelech *et al*., 1982), and the use of micro-sieves for effective filtration of the algae (Piontek and Czyzewska, 2012). However, such techniques are costly and would only be recommended if HABs were apparent annually which currently they are not.

10.2.5 Diffuse nutrient remediation

Although point sources have been shown by this study to explain the greatest modifications of algal communities, investigating the role of diffuse sources needs to be more thoroughly addressed. $\mathrm{LOU}_{\mathrm{core}}$ is a particularly good case study as it receives no point inputs but has undergone enrichment since ~1850. Human population in its catchment followed similar trends to agricultural development and it is therefore likely that both of these factors worked synergistically. Nonetheless, disentangling the role each could have played would better inform remediation efforts. CEH reviewed the age, number and maintenance of septic tanks in the Loch Leven catchment in Scotland and found significant evidence to suggest that septic tanks were underestimated point sources of pollution to surface waters and groundwater (Dudley and May, 2007). It would be recommended that a similar investigation within the Windermere catchment be undertaken. The UK should also consider licensing and inspection programmes of septic tanks similar to those recently introduced in France and Ireland in 2009, which may prove unpopular with local communities due to the high penalties and replacement costs, but would benefit the local environment.

Diffuse agricultural pollutants could have played an underlying role in enhancing the nutrient enrichment of lowland lakes and their importance may become more apparent once remediation of point sources has been achieved. DEFRA-funded programmes such as the England Catchment Sensitive Farming Delivery Initiative and other Environmental Stewardship schemes have provided grants to fund environmentally sound farming practices in the region, such as the restoration of woodland areas and the construction of wetlands (Hodge and Reader, 2010). The use of the model PSYCHIC (**P**hosphorus and **S**ediment **Y**ield **CH**aracterisation in **C**atchments) to determine exports of P from the catchment has played an important role in determining pollution “hotspots”, and highlighted Windermere as such (Collins *et al.*, 2007; Broadmeadow and Nisbet, 2010). Such strategies that are suggested by the initiative do need careful consideration before application. For instance, there is little opportunity for the development of woodland within the Windermere catchment due to existing towns, woodland and SSSIs (Broadmeadow and Nisbet, 2010). Constructed wetlands are also another option but may be a source of GHGs, and their retention capacity of nutrients is variable (Vymazal, 2007). Lack of compliance to such initiatives also remains a major obstacle (Collins and Anthony, 2008). Nonetheless, further research into soil and nutrient management, such as that undertaken by the River Eden Demonstration Test Catchment in the north of Cumbria, will be invaluable in developing techniques that are able to decrease diffuse pollution while maintaining agricultural productivity (EdenDTC, 2015).

10.2.6 Tackling effects of tourism

Managing tourism in the region is necessary to alleviate environmental pressures not limited to wastewater remediation. The main aim of the Lake District National Park Authority (LDNPA) is to promote “sustainable” tourism, but little focus falls upon the most “unsustainable” aspects of tourism. For instance, there is no option for promoting other areas within the Lake District that would alleviate pressure in the catchment. The Waterfront Programme promotes the idea of a Waterbus aimed to reduce personal boat use, which would require the development of several new jetties within the lake, including the west of WSB_{site}, an area not currently accessible to tourism (LDNP, 2011). This would damage the hydrosere community within this area, and the development of on-board and shoreline facilities such as toilets would increase the risk of further nutrient input.

Other management strategies should involve the continued pursuit of engaging tourists, residents and local businesses in individual stewardship. For example, the Windermere Reflections organisation uses media campaigns and organises projects with local and visitor groups to encourage greener living such as buying P-free detergents (WR, 2015). Another initiative working in the region is the South Cumbria Rivers Trust project: Cumbria Freshwater Invasive Non-Native Species Initiative, which aims to coordinate action on reducing invasive species and increasing awareness of freshwater biosecurity (SCRT, 2010).

Unfortunately such schemes are costly and unlike international parks which are wilderness areas and cut off from road infrastructure, managing entrance fees or road pricing for National Park conservation is much more complex in the context of the open-access “living landscapes” of the UK (Kendal *et al.*, 2010). Recently the LDNPA has begun selling land such as that surrounding STI_{site} in a bid to raise money for reinvestment and improvements. They argue that 96% of the land is already under alternative ownership and environmental protection would be unaffected (LDNP, 2015). However, fears that future economic development would be prioritized over conservation remain, and conflicts will continue if governments promote reliance on the region's natural resources (Defries *et al*., 2007). Investigating other management paradigms of UK protected areas needs to be undertaken, such as reviewing resources that lie on the boundaries of, or outside, national parks (Defries *et al*., 2007).

10.2.7 Tackling internal sediment-P loading

In the lakes of the Windermere catchment, like many lakes worldwide, internal P loads continue to delay remediation despite controls on external nutrient inputs and can hinder bio-manipulation success (Bennion *et al.*, 2000; Søndergaard *et al.*, 2007). In such instances, approaches to speed-up the recovery by reducing sediment-P loads could be viable. Techniques include sediment removal (Hupfer and Hilt, 2008), hypolimnetic oxygenation (Gächter and Müller, 2003), and P-capping agents (Gibbs *et al*., 2011) such as Phoslock® a Lanthanum (La)-bound bentonite clay matrix (US Patent 6350383) that binds to dissolved P to form a stable mineral that is subsequently retained in bed sediments (Douglas, 2002; Meis *et al.*, 2013).

However, caution to these approaches must be noted for a number of reasons. First, disruption to not only the benthic ecology but also the wider lake ecology could occur. Peer-reviewed ecotoxicological assessments of La leaching from Phoslock® are limited so the wider ecological impacts remain relatively unknown (Spears *et al*., 2013). Second, dredging has been found to have immediate success but low long-term sustainability as poor P-sorption of new sediments leads to increased algal biomass and accumulation of nutrients (Søndergaard *et al*., 2007). Third, P-capping technologies can have limited success under different physicochemical conditions and inadequate dosing quantities whereby anaerobic conditions, such as those seen at BLE_{site} in summer months, reduce the retentive capabilities of the agent and require successive applications (Meis *et al*., 2013). Fourth, mechanical hypolimnetic oxygenation in deep lakes could actually enhance sediment-P retention by lowering sulphide production and requires long-term treatment otherwise anoxia will reappear (Gächter and Müller, 2003; Søndergaard *et al.*, 2007). Finally, internal P loading does abate when external sources are effectively controlled using the approaches mentioned in section 10.2.1 and this would be the most sustainable and effective, albeit difficult and relatively slow, restoration approach (Søndergaard *et al*., 2007).

10.2.8 Managing global drivers of change

The upland tarns of the Windermere catchment have shown evidence of global environmental change driven by climate warming and atmospheric N deposition and these could become increasingly important drivers in the lowlands in future. There may be other impacts not investigated in this study from toxic trace metals such as lead (Pb) and mercury (Hg) and persistent organic pollutants which are released by fossil fuel combustion and are transported over long-ranges (Curtis *et al*., 2014). Although banned, some of these substances can be remobilised by upland soil erosion (Rose *et al*., 2012). This highlights two main management issues. First, pollutants are often only banned once alternatives are found (Toman and Withagen, 2000). Alternative economic markets and incentives, which increase the market value and development of cleaner technologies are needed. Second, persistence of pollutants can occur long after release has stopped. Thus, management must remain adaptable to these “legacy” pollutants (Curtis *et al*., 2014). Either way, the importance of upland sites such as $\mathrm{STI}_{\mathrm{site}}$ for the regulation of freshwater quality and quantity and the provision of potable water (68% of UK drinking water is from upland areas), C sequestration and flood regulation, demands the need for more integrated monitoring and management of these systems (Van der Wal *et al.*, 2011; Curtis *et al.*, 2014).

In comparison with other habitats across the globe, freshwaters such as the lakes of the Windermere catchment are predicted to experience relatively less environmental degradation, which may reduce political and economic investment into sustainable water management. For instance, northern temperate freshwaters are predicted to experience lower biodiversity change than other ecosystems such as Mediterranean grasslands (Sala *et al*., 2000). Furthermore, social and economic instability continue to ensure that freshwater management remains a lower priority on global and national political agendas (Hazell and Wood, 2008). Thus, management of global drivers of change involves considerable resources into the discovery of technological advances and policies that will improve water quality while increasing food security and reducing fossil fuel reliance against a background of an expanding human population (Tilman *et al*., 2001). Local, regional and global incentives to educate, incentivise and restrict behaviour are required (Pahl-Wostl *et al*., 2008).

Removing the focus from global to local stewardship could be an option. Schemes in the Lake District that fund hydropower, land uses that sequester C and the cultural and conservation projects undertaken by the Windermere Reflections organisation are examples of local environmental stewardship. However, changing individual attitudes to global environmental issues and poor government investment hinder their success (Hares *et al*., 2010). An example is the negative attitudes to public transport in the Lake District from both residents and tourists which have led to continued individual car use despite schemes such as golakes (golakes, 2015) which try to promote green awareness and use of public transport (Cullinane and Cullinane, 1999). Continued promotion and development of individual and business stewardship that is cost-effective is therefore recommended.

10.3 Future work

Below are suggestions of future work that could improve the accuracy of the results and conclusions made by this study and develop topic knowledge.

Thorough understanding of the sources, delivery and deposition of C and N isotopes remains a gap in palaeolimnogical studies. Often these proxies are used to derive algal production changes but this relies on assumptions not often tested. Further anthropogenic alteration of geochemical cycling makes interpreting these sedimentary isotopes more complex. Therefore, the use of compound-specific isotope analyses to measure stable N and C isotopes incorporated into the chemical structure of algal pigments (Chls and carotenoids) would help determine whether atmospherically-derived N which is labelled “isotopically light” is taken up by algae and so, could demonstrate a direct fertilization effect of atmospheric N deposition (Enders *et al*., 2008). C stable isotopes from carotenoids can directly assess responses in algal productivity among different algal classes for a more complete understanding of how lake primary production and, hence, C cycling is influenced.

The role of trophic interactions should be investigated to extricate the effects of these on primary production and community changes. Drivers of ecosystem change can alter food-web dynamics such as climate-driven asynchrony between zooplankton and algal blooms (Thackeray *et al*., 2012). Additionally, understanding changes in food-web assemblages and interactions remains poorly understood in palaeolimnology (Rawcliffe *et al*., 2010). This study provides a useful starting point from which to expand such an investigation. Possible approaches could involve using the sediment cores from this project to collect sedimentary cladoceran remains and or collating past historical data on zooplankton and fish composition and abundance. These data could then be used in conjunction with the sedimentary pigment data to investigate the relationship not only between primary producers and their wider food-webs but the drivers of such interactions and the role invasive species such as *R. rutilus* may have played in altering trophic dynamics.

Managing sedimentation rates in the Windermere catchment is a key objective of the WCRP, as catchment-derived sediments transport heavy metals and nutrients such as P to lakes, which can then disturb lake ecological communities. This is particularly the case in catchments such as Windermere with a long history of mining and agriculture and high precipitation (Miller *et al*., 2014). Although this study provides insight into changing sedimentation rates, it has not investigated the minerogenic, heavy metal, and nutrient content of the sediment in detail. Work undertaken by Smith (2014) used lake sediment cores from CT_{site}, EAS_{site} and GRA_{site} to identify rainfall events and agricultural land use change as the main drivers for increased and variable sediment erosion in the 20th century. Some attempts have been made in this study to use these erosion proxies to interpr*et al*gal community response but scope exists for a more in-depth investigation. Work on sediment processes and heavy metal composition has been, and is continuing to be carried out in the catchment by a NERC-funded project led by the University of Southampton and the British Geological Survey. Their study has yet to relate this work to changes in past primary producer assemblages. Thus, there is scope to investigate the role of catchment and in-lake sedimentation processes, as well as heavy metal pollution, to assess if and how these may have affected past algal communities in the Windermere catchment.

Due to policy drivers such as the WFD, research into the impacts of human activity on aquatic ecology has expanded substantially over recent decades. It is hoped that the holistic and sustainable approach to management promoted by the WFD will enable surface waters to reach “good” status by 2027 at the latest (EU, 2000). A palaeolimnological investigation into cyanobacterial biomass in the Northern Hemisphere noted a decline in lakes that had undergone restoration in which nutrient inputs were reduced, but increases in lakes at the larger spatio-temporal scale (Taranu *et al*., 2015). This highlights the importance of recognising where management has or has not been hindered by wider patterns of global change. Thus, it would be suggested that this study be re-visited after 2027 to identify management impacts on the algal communities and to assess whether climate change and other drivers do indeed prevent re-establishment of community compositions that existed prior to fertilisation (Bennion *et al*., 2011a).

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APPENDIX A. Contemporary limnology

Contemporary limnology was not a focus of this thesis, however its usefulness in interpreting past lake environmental conditions is widely recognised (e.g. Sayer *et al*., 2010). Time constraints of this project prevented limnological monitoring and published work by CEH on contemporary lake chemistry, physical and biological variables meant that this was not paramount. However, monitoring is focussed on the lowland lakes, so out of interest epilimnion (BT, LLT and LOU in July 2013, EAS and STI in November 2011) and littoral (CT, EAS and STI in July 2013, BT, LLT and LOU in November 2012) water samples were collected from the upland tarns to get a very simplistic overview of relationships between the chemical variability between summer and winter TP and SRP, and summer algae (Chl. *a*) concentrations at these sites (igure A.1). The selected lowland lakes (LOU_{site} (both P and Chl. *a* data), GRA_{site} 1 and 2 sampled were done so out of interest whilst retrieving sediment cores and allow for comparison to the productivity of the upland systems, between basins ($ELTIN_{site}$/MID_{site}/OUT_{site}), and sites in the lake (GRA_{site} 1-2).

TP and SRP measurements were conducted on water samples which were kept in an airtight, dark, cool (~4°C) environment before standard colourimetric analysis following Mackereth *et al*., (1989). TP is a measure of all forms of P, dissolved and particulate so required unfiltered water samples. Whereas SRP is the measure of orthophosphate, that which is biologically available and required filtered water samples using 0.7µm Whatmann GF/F filter papers. Chl. *a* concentrations were determined using HPLC on extracted pigments from 0.7µm Whatmann GF/F filter papers following Chen *et al*., (2001).

TP and SRP concentrations (Figure A.1 (1-2)) were lower at all sites in summer compared to winter, perhaps due to the utilisation of P by spring and summer-blooming algae. This temporal variability was more pronounced at BT_{site}, EAS_{site} and STI_{site} compared to the eutrophic LOU_{site} which had the highest TP concentrations in summer and winter (18.4 and 23.6 µg l^{-1} respectively), suggesting continuous annual P delivery at LOU_{site}.

The productive lowland sites had higher total algal production than the oligotrophic upland sites (Figure A.1 (3-4)). GRA_{site} 2 had the highest epilimnion total algal production of all sites (3.2 nmole pigment l^{-1}) which could be due to its proximity near the River Rothay which delivered 13% of GRA_{site}'s TP from 1994-1995 (Reynolds *et al.*, 2012). Interestingly the most eutrophic basins LOU_{site} and $ELTIN_{site}$, had lower Chl. *a* concentrations which may be attributed to zooplankton grazing or dominance of cyanobacteria at these sites which bloom deeper and later in the summer than at the time of sampling. BT_{site} had the highest algal production of the upland lakes (0.01 nmole pigment l^{-1}) alongside the highest winter SRP (7.5 µg l^{-1}) suggesting that this lake is more productive due to a nutrient source not found at the other upland lakes. In the BT_{site} and LLT_{site} catchment, % cover of rough grazing increased from the 1970s, which may be delivering diffuse P to these lakes (Figure A.1 (1-2)). LLT_{site} is less likely to experience an enrichment effect due to its very short retention time (3.3 days).

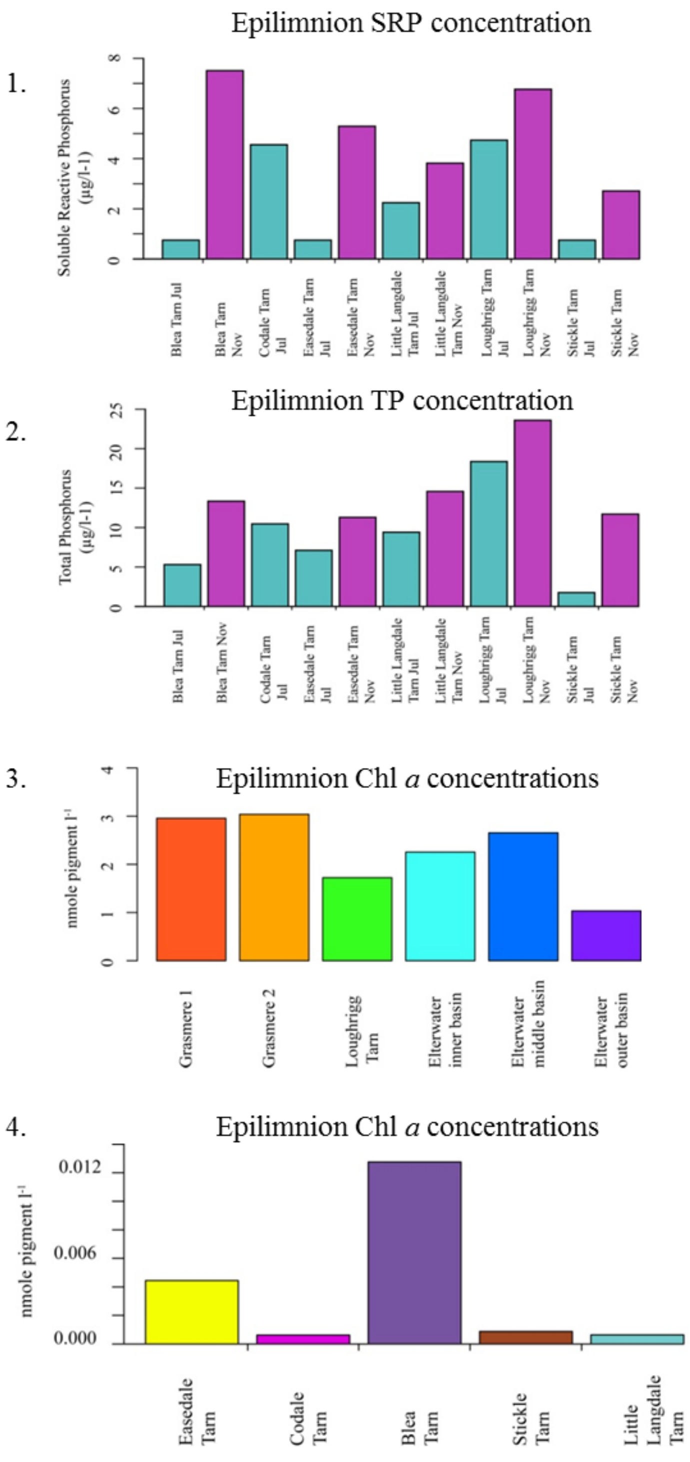

Figure A.1 Epilimnion water chemistry (SRP and TP) collected in November 2012 and July 2013 (1-2). Chl. *a* concentrations from filtered epilimnion water samples collected in July 2013 (3-4). Grasmere 1 refers to location where core retrieved in eastern basin (NY34030, 06398), Grasmere 2 refers to western basin (NY33629, 06697).