A geochemical investigation into the drivers of recent algal community change in small English lakes

Blaine Hancock

Doctor of Philosophy

University of York

Environment & Geography

January 2022

Abstract

This thesis presents an investigation into the drivers of algal community change in small English lakes, with a focus on 20th century climate warming.

Sediment cores were extracted from three small lakes across northern England (Lake Gormire, Blea Tarn and Sunbiggin Tarn) and radiometrically dated. Sedimentary photosynthetic pigments were quantified using high-performance liquid chromatography and changes in the source of sedimentary organic matter were established using stable isotopes ($\delta^{13}C$, $\delta^{15}N$). Sedimentary trace elemental data were obtained to elucidate any additional drivers of change. The impacts of 20th century climate warming were investigated through regression analysis, comparing the reconstructed changes in algal biomass and community composition to meteorological data.

The marl lake of Sunbiggin Tarn was shown to have been heavily impacted by a rapid increase in the resident gull population during the 1980s which resulted in an enhanced flux of lutein, zeaxanthin and diatoxanthin pigments. However, an even more dramatic change in the algal community occurred at the start of the 1990s with increases in chlorophyll-*a* and a rapid shift from echinenone to canthaxanthin, both cyanobacterial pigments. This shift occurred due to the large gull populations degrading extensive areas of the surrounding fenland which further enhanced nutrient loading (increased $\delta^{15}N$) to the lake and obscured any direct links to temperature change.

In contrast, temperature had a significant impact on the algal community of the two non-marl lakes (Blea Tarn and Lake Gormire). In Lake Gormire warming stimulated all algal groups from the 1960s where in Blea Tarn only chlorophytes and filamentous cyanobacteria had a relationship to temperature. The greater change in Lake Gormire is predominantly due to its closed hydrological basin and enhanced by its relatively small catchment which makes it particularly sensitive to environmental changes. While closed basin lakes may be particularly at risk of future climate change, the findings of this research also indicate their potential to be used as ‘early warning systems’ for other lakes, both regionally and nationally.

List of contents

List of figures

List of tables

Acknowledgements

Thank you to my PhD supervisors Katherine Selby, Jack Lacey and Glenn Watts for all their advice and support over the course of my PhD. Thank you to my funders NERC, BGS and the Environment Agency who have supported me financially including the following research grants:

- NERC Isotope Geosciences Facilities IP-1869-1118 (£10,000, pilot)
- NERC National Environmental Isotope Facility 2243.0320 (£17,325)
- British Geological Survey University Funding Initiative GA/18S/015 (£1,000)

I would like to thank all the support staff in the Department of Environment and Geography who have all provided countless hours of support and assistance with lab and field work during the course of my PhD. In particular, Matt Pickering for the training and support with my pigment extractions and HPLC analysis, Rebecca Sutton for training and support in elemental analysis through ICP-OES, Mike Beckwith for all the help with the fieldwork, Maria Gehrels and Debs Sharpe for the day to day support in the labs. I would also like to thank Matthew von Tersch from Bioarch for allowing me extensive use of their freeze dryer and microbalance for the many hundreds of sediment samples.

I would like to thank Natural England, The National Trust and Friends of the Lake District for allowing me site access and providing valuable information to support this research. Thank you to Handong Yang at UCL who undertook the dating work and the laboratory staff at the British Geological Survey for processing some of the sediment samples for isotope analysis. Both were performed swiftly and to a high standard.

Personally, I would also like to recognise the support of all the other PhD students in the Environment department. They have provided invaluable advice and company through years, even through the disruption and separation caused by the pandemic. Finally thank you to my partner Kellie for everything she has done over the years, in particular helping me juggle the caring, home schooling and general wellbeing of our two children over a challenging 2020-2021. This has ensured that I could continue to make some progress on my PhD during these highly disrupted last couple of years.

I truly appreciate it. Thank you.

Author’s declaration

I declare that this thesis is a presentation of original work and I am the sole author. This work has not previously been presented for an award at this, or any other, University. All sources are acknowledged as References.

1. Introduction

Climate change is one of the greatest environmental concerns of the 21st century. As the world's population has increased so has the demand to produce more food, provide sufficient clean water and generate more energy (Godfray *et al*., 2010). Growing populations and industrialisation have led to increasing greenhouse gas emissions, and since 1750 atmospheric concentrations of CO_2, CH_4 and N_2O have increased by 40%, 150% and 20%, respectively (IPCC, 2014). These gases are some of the biggest contributors to radiative forcing in the atmosphere and increases in their concentration has led to a net warming effect (Hansen and Sato, 2004). Globally, air temperature has increased around 1°C on average since the industrial revolution and this could rise to 2-3°C by the middle of the 21st century (Fig. 1.1; IPCC, 2021).

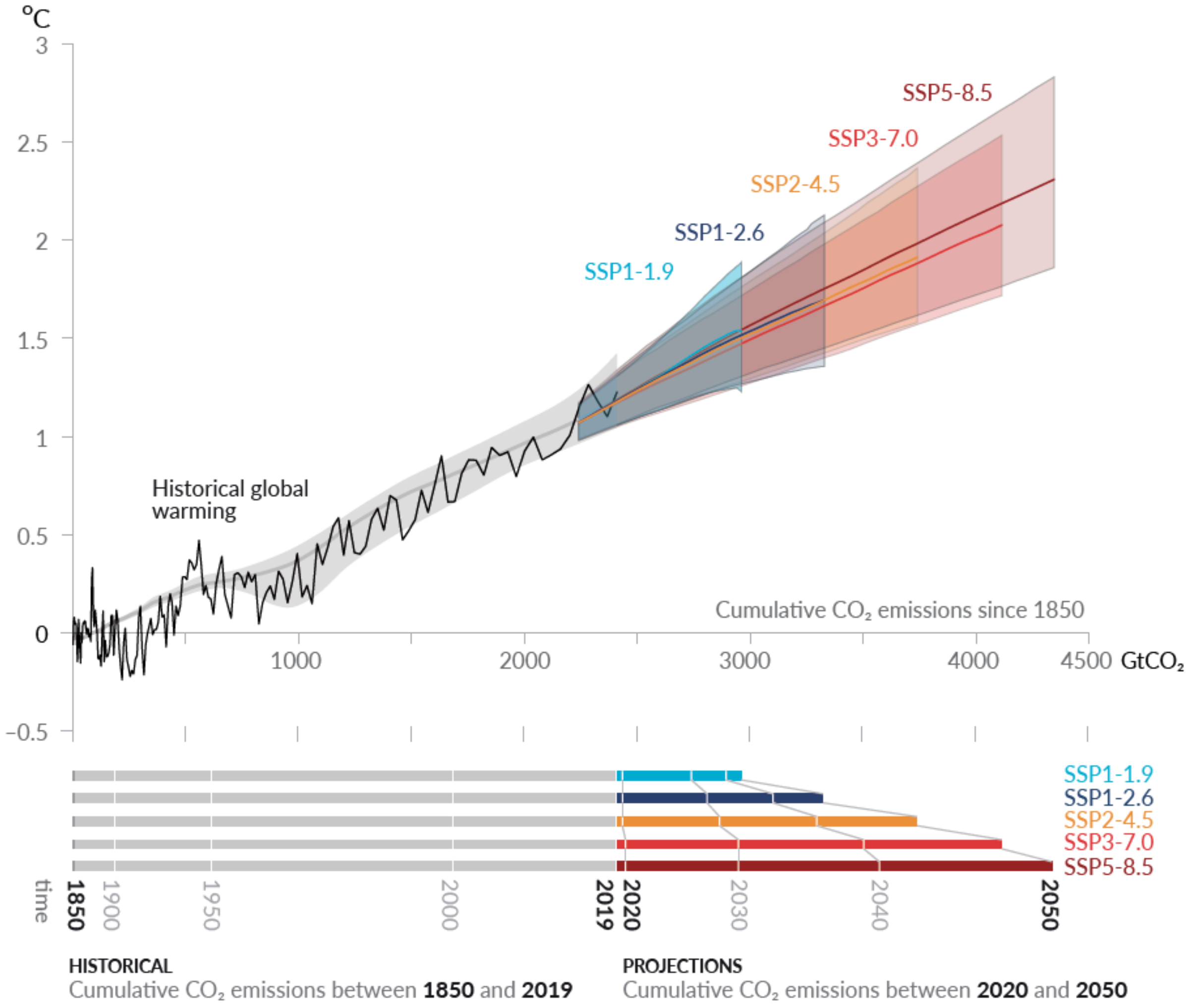

Fig. 1.1 Historic and projected CO_2 emissions and global air temperature change (compared to the 1850 – 1900 average) under a range of future emission scenarios. Adapted from IPCC (2021).

Substantial changes to the global heat budget are likely to lead to wide ranging ecologic, economic and social effects (IPCC, 2014). Along with an increase in temperature, one of the biggest changes predicted is an intensification of the hydrological cycle with evaporation and precipitation increasing globally (Allan, 2011). For the UK, precipitation is expected to shift towards higher proportions in winter months with a reduction in summer (Fig. 1.2). Such seasonal changes will inevitably lead to changes in precipitation driven processes such as flooding and nutrient transport (Crossman *et al*., 2014). As freshwater ecosystems are among some of the most sensitive to environmental change they are expected to respond rapidly to shifts in temperature and precipitation (Adrian *et al*., 2009; IPCC, 2021).

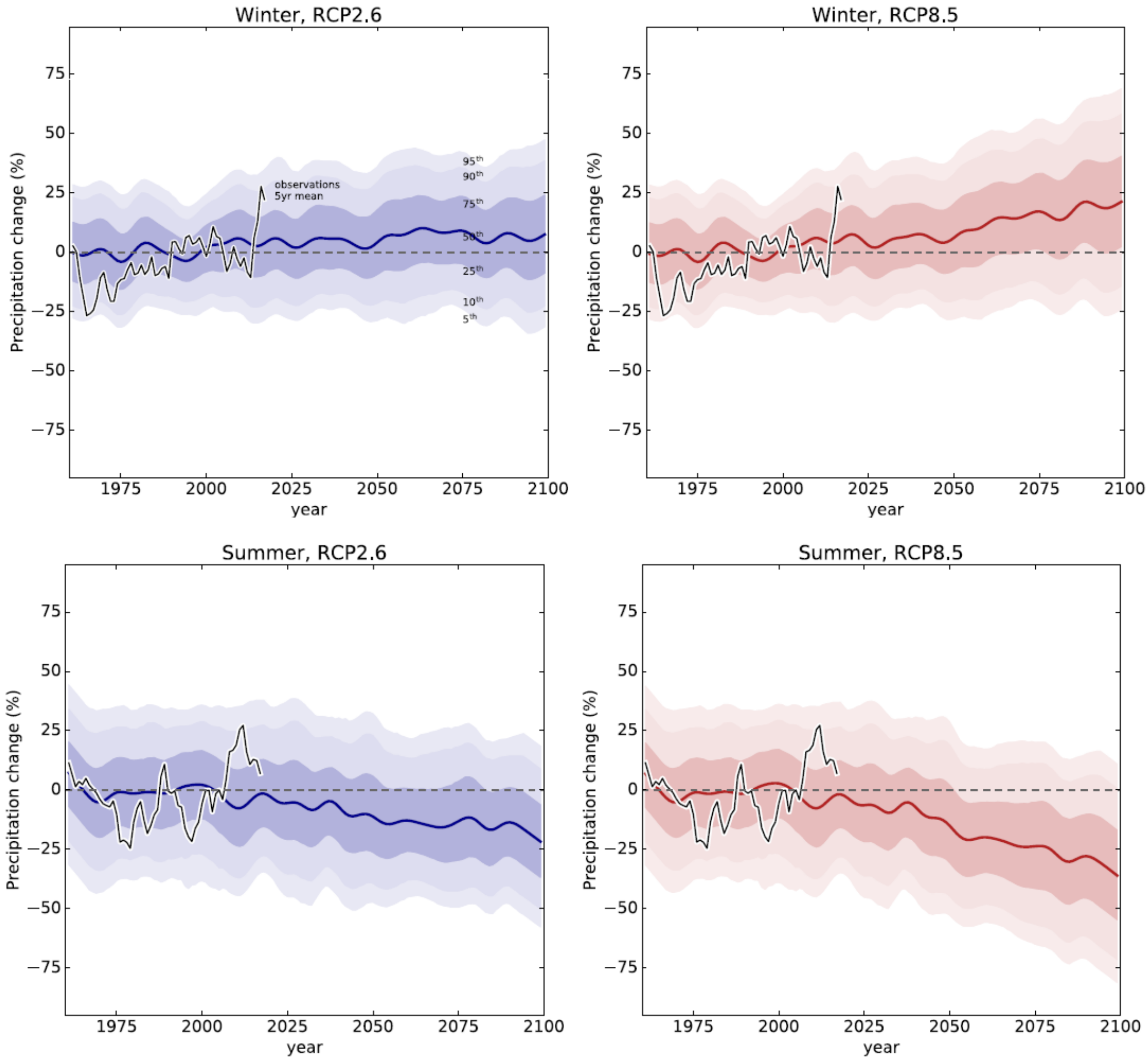

Fig 1.2. Projected seasonal precipitation change for the UK for the lowest (RCP2.6) and highest (RCP8.5) emission scenarios with the solid line representing the median and shaded areas the 5th to 95th percentile range. Adapted from Gohar et al., (2018).

While British rivers and lakes are expected to be impacted by future climate warming, anthropogenic pollution has historically been a major driver of ecological change. The industrial revolution brought about increased nutrient use, land use change and pollution (Battarbee *et al*., 1999). Many lakes were increasingly used as a repository for human sewage reflecting the increase in urban populations during the 19th century (Smol, 2008). The increase in heavy industry and mining activities also resulted in greater point source inputs of heavy metal from industrial sources which resulted in the pollution of the Cumbrian lakes (Miller *et al*. 2014; Schillereff *et al*., 2016). From the middle of the 20th century there have been increasing impacts from diffuse pollution, such as nutrients transported from agricultural land with the wide application of synthetic fertilisers (Dong *et al*., 2011) and atmospheric pollution from fossil fuel combustion (ROTAP, 2012; Tipping and Chaplow, 2011). Today the inputs of these types of point source and diffuse pollution has largely been reduced through a combination of national and international legislation. The Water Framework Directive is one example of legislation that was introduced specifically to improve the ecological and chemical quality of all water bodies, typically through reducing lake water nutrient concentrations (Wiik *et al*., 2014).

Lakes are particularly important sites for nutrients, acting as biogeochemical hotspots where they get readily transformed by processes such as denitrification (Lin *et al*., 2011; Seitzinger *et al*., 2006). These processes often respond directly to environmental factors, such as temperature and catchment changes (Adrian *et al*., 2009; Jeppesen *et al*., 2014). Understanding how these processes will be impacted by climate change is important as many lakes in Britain are relied on for drinking water and their recreational services (O'Reilly *et al.*, 2015; Watts *et al*., 2015). Changes in the quantities and timings of nutrients inputs can affect lake algal productivity and community composition. Extensive eutrophication can potentially result in the formation of harmful algal blooms (HABs), which can have detrimental health impacts to both wildlife and humans (Paerl *et al*., 2001; Paerl and Otten, 2013).

In general lakes provide a wide range of ecosystem services which are essential to human health and wellbeing (Williamson *et al*., 2009). Lakes have the highest relative species richness in comparison with terrestrial and marine ecosystems (Gleick, 1989). Due to their ecological importance, and the wide range of ecosystem services that they provide, many lakes are designated national or international conservation sites such as Sites of Special Scientific Interest (SSSI), National Nature Reserves, Ramsar sites, Special Areas of Conservation, and Special Protection Areas in the UK (Curtis *et al*., 2014). Freshwater ecosystems are among some of the most sensitive to environmental stresses as organisms are highly influenced by the conditions of the lake and the surrounding terrestrial landscape (Schindler and Scheuerell, 2002). Due to their interconnectivity to the surrounding land, rising global populations over the 20th century have resulted in substantial declines in lake water quality and increased extinction rates of freshwater flora and fauna (Ricciardi and Rasmussen, 1999; Krauze and Wagner, 2007). As a result, lakes are considered one of the most threatened ecosystems from human population growth and climate change (Williamson *et al.*, 2009). It is, therefore, essential to understand how lakes have responded to natural change and anthropogenic pressures over the 20th century, both spatially and temporally, in order to predict how lakes could respond in the future (Hannah and Garner, 2015; Mills *et al.*, 2016).

1.1 The importance of small lakes

As most lakes are small (<10ha), and typically shallow (mean depth ~3m), they receive sufficient light and nutrients to sustain highly productive ecological systems supporting a wide range of aquatic life (Cael *et al.*, 2017; Wetzel, 2001). Small lakes tend to be species rich with more species per unit area than larger lakes and promote enhanced regional biodiversity of birds, plants, amphibians and invertebrates (Dodson *et al.*, 2000; Scheffer *et al.*, 2006). Productivity is typically enhanced in small lakes supporting more unique and threatened species than other water bodies in the British lowland areas (Williams *et al.*, 2004). This is partly due to smaller lakes tending to be shallower providing more favourable light conditions in the bottom waters which can often result in them being macrophyte dominated (Scheffer and van Nes, 2007). However, higher trophic status and allochthonous inputs can still limit macrophyte colonisation depths in small lakes through reductions in water clarity (Maberly *et al.*, 2020).

Smaller lakes, or those with relatively high surface area to volume ratios, typically heat up more rapidly than larger lakes due to the increased proportion of water interacting with the atmosphere (Arvola *et al.*, 2010; Jones *et al.*, 2010). Temperature affects the rates of chemical reactions, equilibrium positions of chemical reactions and the solubility of gases (Stumm and Morgan, 2013). As a result, increased temperatures can disproportionately impact small lakes which are important sites for biogeochemical cycling, in particular the processing and storage of nutrients (Botter *et al.*, 2010; Cheng and Basu, 2017; Harrison *et al.*, 2008). Small lakes are also more likely to be sensitive to changes in precipitation and runoff, affecting residence time and nutrient availability when compared to larger deeper lakes (Muir *et al.*, 2012). Therefore, small lakes should be sensitive to climate change and respond more directly to short term variations in weather than larger deeper lakes (Arvola *et al.*, 2010; Gerten and Adrian 2001).

Due to the enhanced sensitivity of small lakes, it is expected that climate change will result in a shift towards increasingly diverse and productive systems (Smol *et al*., 2005). This has already been observed in small mountainous lakes in the USA, where there have been shifts to a more diverse algal community since the 1950s (Oleksy *et al*., 2021). Increases in a chlorophyte derived pigment (lutein) were driven by a combination of increased temperature and atmospheric N deposition since the 1950s (Oleksy *et al*., 2020). Higher temperatures will also enhance internal P loading, which along with greater N availability, will be expected to increase algal productivity (Søndergaard *et al*., 2003). These drivers of change have been widely experienced across industrialised countries, with parts of the UK (e.g. Lake District) having particularly high atmospheric N deposition rates during the 20th century (RoTAP, 2012). Therefore, it is important to assess small British lakes for the impacts of 20th century climate warming as they may be some of the most sensitive water bodies to change.

1.2 Knowledge gaps and rationale

Globally the majority of climate change research has focussed on relatively large lakes, mainly through *in situ* monitoring (Winslow *et al*., 2015) and remote sensing (O'Reilly *et al*., 2015), with smaller lakes (<10 ha) relatively neglected in limnological and ecological research until relatively recently (Downing, 2010). As the vast majority (approximately 99%, accounting for 31% of the total surface area) of the world's lakes are under 10 ha (Downing *et al*., 2006), this has led to a limited understanding of the response of smaller lakes to increasing temperatures and ecological change (Winslow *et al*., 2015).

In general, climate driven changes in UK surface water quality are expected to result in increases in suspended solids, sediment yields, nutrient concentrations and phytoplankton growth (Watts *et al*., 2015). However, as current climate change predictions are based on larger lakes, the greater sensitivity of smaller lakes means these predictions are likely to be unsuitable (Winslow *et al*., 2015). In the UK there is a general lack of long-term water monitoring data (multi-decadal) which makes being able to infer the past environmental conditions difficult for most lakes (Watts *et al*., 2015). There is also a disparity between the research undertaken at the hydroclimatological level (i.e. precipitation, river flows) compared to the hydroecological level in the UK, with a general lack of research into the impacts on lake water quality and ecology (Garner *et al*., 2017). As a result, there is low confidence in making specific predictions as to how individual lakes will respond to climate change (Watts *et al*., 2015).

Due to this lack of knowledge, there is a need for research on the impacts of climate change on small UK lake water quality and ecology (Garner *et al*., 2017). It is especially important to understand the ecological risk in lakes as those with existing poor water quality are likely to be exacerbated by climate change (ASC, 2016). The greater sensitivity of smaller lakes should enable analysis of environmental change at a higher resolution than deeper lakes, at annual or potentially seasonal resolutions (Steinman and Abbott, 2013). Through this, the greater sensitivity of smaller lakes may be able to act as 'early warning systems' and improve the understanding of how the UK lakes may change in the future (Zolitschka *et al*., 2015). Detailed ecological information from a range of small UK lakes can help to establish their usefulness in detecting the impacts of climate change and help identify lakes which may be at particular risk from increasing temperatures. Data from a range of lakes will also help to identify any trends that may be occurring simultaneously at the regional or national level.

Regional and national studies are essential in order to develop country scale assessments of ecological change (Apolinarska *et al*., 2011). Such assessments can help to provide quantitative data to site managers and policy makers to construct mitigation strategies (Mills *et al.*, 2016). Through this it can help to promote adaptation to climate change and ensure the sustainability of the UK's sensitive freshwater resources (Hannah and Garner, 2015).

1.3 Aims and objectives

The overall aim of this research is to investigate the response of small lakes located in England to climate change from the mid-19th century to the present day.

Algal biomass and community level changes will be investigated across a range of lake types to assess the importance of lake and catchment characteristics in responding to climate change. Additional past drivers of change, such as external nutrient loading, will be explored to help establish the relative importance of climate change. The specific objectives are:

1. Develop sediment core chronologies using ^{210}Pb dating in order to derive a chronology of algal community change over the 20th and 21st centuries.
2. Establish changes in algal biomass and community composition in small English lakes since at least ~AD1850 using algal pigments as biomarkers.
3. Identify changes in sedimentary organic matter (OM) sources (e.g. %C) and cycling using stable isotopes of C and N from bulk sediments (δ^{13}C and δ^{15}N).

4. Establish the impact of historic pollution events and changes in catchment inputs using trace element analysis.
5. Compare changes in sedimentary algal communities with meteorological records to identify the role of weather and climatic variations in driving algal community change over the 20th and 21st centuries.
6. Synthesise the impacts of multiple stressors on lake algae communities to help identify the impact of catchment changes, atmospheric and diffuse pollution on algal biomass and community change.
7. Assess differences in response between lake types and how that may impact their future ecological trajectories in response to projected 21st century warming.
8. Synthesise the data to suggest effective remediation measures to address current and future management concerns of small English Lakes.

1.4 Justification site selections

Three lakes from northern England were selected – Lake Gormire, Sunbiggin Tarn and Blea Tarn (Fig. 1.3). These lakes are relatively small (<6 ha) and of shallow depth (2.4 m to 4.7 m), which will likely result in enhanced warming, compared to the larger deeper lakes, due to their reduced volume of water and generally higher surface area to volume ratio (Jones *et al*., 2010; Woolway *et al*., 2015). Due to the rapid response of small lakes to environmental changes, reconstructing past lake conditions can reveal how lake environmental conditions have changed in response to climate (Battarbee *et al*., 2012).

Fig. 1.3 Map of northern England with locations of the study sites: Lake Gormire (1), Sunbiggin Tarn (2) and Blea Tarn (3). Adapted from OpenStreetMap (2020).

1.4.1 Lake Gormire

Lake Gormire (SE50318 320; Fig. 1.3(1)) lies in a glacial overflow channel on the boundary between limestone (Ravenscar Group) and Jurassic sandstone bedrocks formed 168 to 170 million years ago (Oldfield *et al.*, 2003). The Gormire basin is of relatively low altitude (155m a.s.l) and situated on the edge of the North Yorkshire Moors 5 miles east of Thirsk and was formed by glacial erosion (Fig. 1.4). The lake is hydrologically closed, with no surface inflow or outflow, a simple bathymetry with maximum water depth ~6 m and a surface area of 6ha (Oldfield *et al.*, 2003). The lake is surrounded by a relatively small catchment (30 ha) with steep sided slopes of a maximum relief of 150 m (Fisher *et al.*, 2003). As a closed-basin lake with a small steep catchment, this should result in Lake Gormire being particularly sensitive to changes in weather and climate (Bates *et al.*, 2008; Maberly *et al.*, 2003). Precipitation in the catchment would readily deliver organic materials and nutrients to the lake with minimal flushing (Oldfield et al., 2003).

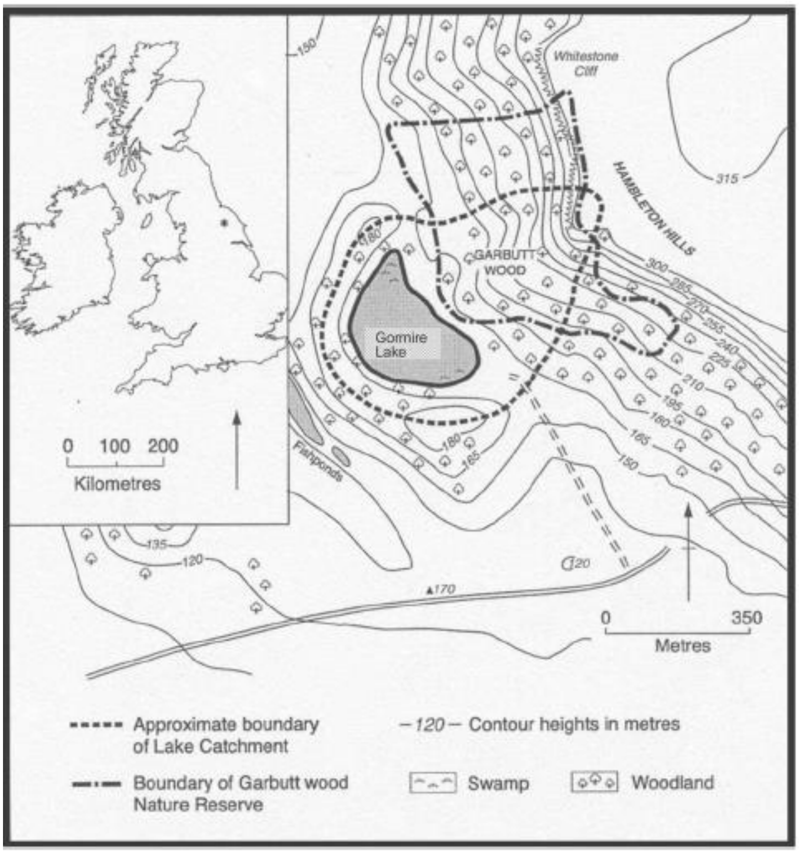

Fig. 1.4 Location and land cover of the Lake Gormire catchment (from Fisher *et al*., 2003).

It is evident from previous assessments that there are currently concerns over the ecological condition of Lake Gormire due to the poor distribution of aquatic macrophytes (Smith, 2010). Natural England recommended a more complete assessment was required to better understand the past conditions of the lake, ideally through palaeoecological methods, due to the absence of long-term monitoring data (Natural England, 2010). A study of this nature may indicate if the lake has always been species poor or whether conditions have deteriorated over time.

There have been two palaeoecological studies previously undertaken on Lake Gormire with Oldfield *et al*. (2003) and Fisher *et al*. (2003) reconstructing the land use history and catchment flora rather than assessing in-lake changes. Additionally, the radiometric analysis undertaken indicated that the cores were missing the top 8-10 cm, roughly equivalent to the period since 1970 (Oldfield *et al*., 2003) representing a period of modern climatic change This previous study also highlights the potential for Lake Gormire as a repository of recent environmental change, as the data generated indicated minimal sediment focussing and stable marginal sediments with the area of permanent sedimentation, i.e. that which is not resuspended, to be below 2m water depth. This means that the deep sediments of Lake Gormire should have remained relatively undisturbed allowing for high resolution sampling.

1.4.2 Blea Tarn

Blea Tarn (NY293 044; Fig. 1.3(3)) is a small upland basin (192 m asl) in a hanging valley in the Langdale mountains (Fig. 1.3(3)). The tarn was formed by glacial ice moving over a mountain col which was cut off as the glacier waned leaving moraines behind. Blea Tarn has a surface area of ~3.5 ha, a maximum depth of 8 m and a relatively large catchment of 115 ha (Haworth *et al*., 2003; Pennington, 1991). Blea Tarn is hydrologically open with several streams draining into the tarn and the largest flow in the north through an area of *Sphagnum* bog (Fig. 1.5). The lake drains south into the River Brathay (Haworth, 1969). The Blea Tarn catchment lies within the greater Windermere catchment (23,500 ha) in the Lake District National Park which comprises 11 lakes and tarns that feed into Windermere (Moorhouse, 2016).

Fig. 1.5 Map of Blea Tarn and the surrounding catchment. Adapted from OpenStreetMap (2020).

Previously studies on cores spanning the Holocene have indicated that Blea Tarn may be resilient to change with the diatom community found to have changed relatively little over thousands of years (Haworth, 1969). This apparent stability suggests that the tarn has not experienced any substantial atmospheric acidification or pollution up until at least the 1960s. When reassessed in 2012 in a palaeoecological study, increased pigments in recent sediments indicated a shift towards higher algal productivity potentially driven by an additional nutrient source (Moorhouse, 2016). However, the cores were not dated and no geochemical analysis was undertaken which would have helped to uncover changes in catchment input and nutrient dynamics. As a result there is little evidence that the increase in algal productivity is due to external nutrient loading which is less likely due to the upland location of the tarn and the low intensity land use history of the catchment. Due to the lack of chronology and geochemical evidence further investigation as to whether climate is a primary driver of these changes is warranted. As there are no signs in the sedimentary record of any substantial bioturbation this site allows for high resolution sampling which will be important to establish links to modern climate warming (Moorhouse *et al*., 2016).

1.4.3 Sunbiggin Tarn

Sunbiggin Tarn (NY676076; Fig. 1.3(2)) is a small (3.7 ha) upland (255m asl) marl lake within a Carboniferous limestone catchment (Bennion *et al*., 2017; Fig. 1.6). The tarn is probably the remnant of a much larger lake formed on a dense clay laid down during glacial retreat (Holdgate, 2016). Sunbiggin Tarn has a surface area of 3.7 ha, a maximum depth of 11m and a relatively large catchment of 124 ha (Bennion *et al*., 2017). The maximum depth of 11m represents a relatively small hollow west of the centre although substantial areas of the lake exceed depths of 5m (Holdgate, 2016). Sunbiggin Tarn has no major streams flowing into the lake but it is fed by calcareous springs to the north with outflows to the south (Natural England, 2008).

Fig. 1.6 Map of Sunbiggin Tarn and the surrounding catchment. Adapted from OpenStreetMap (2020).

As a marl lake, the highly calcareous waters impact almost every aspect of the system from water chemistry to ecology (Wiik *et al*., 2015a). Marl lakes are generally seen as being resilient to nutrient enrichment due to the coprecipitation of phosphorus with calcite (House, 1990; Robertson *et al*., 2007). As a result, Sunbiggin Tarn provides a uniquely different type of environment to the other two lakes and it is, therefore, important to incorporate the lake to provide a more complete assessment of climate impacts on small freshwater lakes in England. The ability of marl lakes to mitigate the impacts of external nutrient loading will support a robust investigation into the impact of changes in temperature and precipitation. Climate change impact assessment in marl lakes is supported by the presence of sedimentary carbonates, which are precipitated in the water column and their isotope composition can be linked to the temperature of the water at the time of precipitation (Leng and Marshall, 2004). In general marl lakes provide an important tool for assessing climate change although the impacts on the lake itself can often be complex (Wiik *et al*., 2015b)

A palaeoecological study used macrofossil remains to indicate macrophyte change over the 20th century (Bennion *et al*., 2009). This assessment was undertaken relatively close to the shoreline in shallower waters and used a broad sampling resolution which along with the inconsistent nature of the macrofossil record, made interpreting changes difficult. It is clear from previous assessments that the tarn catchment has been impacted by the changes in black-headed gull population and there have been some changes in the charophtye community over time (Natural England, 2015). However there has been little evidence of nutrient enrichment impacts to the aquatic environment, although a diatom inferred habitat shift suggests there may have been some other changes in the lake conditions during the 1990s (Goldsmith *et al*., 2003). To date few assessments of the lake itself have been undertaken and site observations by Natural England in 2008 suggest that the tarn itself is in good ecological condition (Natural England, 2008). However, it had long been acknowledged that the in-lake conditions are not fully understood and warrant further investigation, in particular the water chemistry, nutrient status and marl deposition (Natural England, 2015; Holdgate, 2016).

1.5 Thesis outline

The structure of this thesis is designed to address the aims and objectives outlined in section 1.3. Chapter 2 will provide a literature review encompassing the past, current and future pressures on English lake systems, along with the techniques used to assess environmental changes over time. Chapter 3 will describe the fieldwork and laboratory methods used and Chapter 4, 5 and 6 will present the results of the multiproxy core analysis and their interpretations for the individual study sites. Chapter 7 will present a synthesis of the findings from the three sites to aid in answering the main research questions. Chapter 8 will present a conclusion and make recommendations for site managers and suggest areas for future research.

2. Literature review

This chapter provides an overview of the past, current and future stressors on UK lake ecosystems. It introduces the use of algae as biological indicators and a range of analytical techniques that can be used in palaeolimnological studies to reconstruct past changes in lake systems.

2.1 Past and current stressors on UK lake ecosystems

Globally, lake catchments have experienced a wide range of anthropogenic impacts, especially over the last 150 years due to increased nutrient use, land use change and pollution (Zolitschka *et al*., 2015). In the 21st century climate change is widely being acknowledged as a driver of ecological degradation and loss of ecosystem services. In general, higher water temperatures are expected to increase the rates of chemical and biological processes, increase productivity, lower dissolved oxygen concentrations and lead to the extinction of more sensitive species (Wilby *et al*., 2010). Precipitation is also a major control on water chemistry as changes in rainfall are the main drivers of the quantity of catchment inputs that are delivered via runoff (Apolinarska *et al*., 2011). Changes to precipitation will impact sediment loads, metal transport and nutrient leaching from soils (Wilby *et al*., 2010). Therefore, climate change is expected to result in chemical and biological change in lakes.

In the UK, there are around 44,000 lakes and ponds larger than 0.1 ha (Hughes *et al*., 2004). Lakes have a long history of environmental degradation in the UK, particularly through eutrophication (Bennion *et al*., 2014). Eutrophication becomes a persistent problem for many lakes and can typically take 10-20 years to recover after the cessation of external nutrient loading due to prolonged recycling of historically deposited nutrients (Jeppesen *et al*., 2005). It is therefore important to ensure that pressures to the freshwater resources of the UK are managed to prevent any irreversible, detrimental changes in the future. These pressures to UK lake ecosystems are discussed in more detail in the following sub-sections.

2.1.1 Eutrophication

The industrial revolution of the 19th century brought about agricultural change in much of the UK with the intensification of farming through mechanisation and increased abundance of livestock (McGowan *et al*., 2012). A growing population also resulted in an increased amount of raw sewage discharged into lakes, such as those in the Lake District which have experienced eutrophication since the 1850s (Barker *et al*., 2005; Moorhouse *et al*., 2014). Many lakes across the UK have experienced large increases in lakewater P and N concentrations during the second half of the 20th century, largely due to enhanced external loadings. The increase in nutrient flux has been driven by the increased use of land for agriculture, synthetic fertilisers (Dong *et al*., 2011) and sewage discharge (Dong *et al*., 2011; Reynolds *et al*., 2012). As a result, enhanced eutrophication has been experienced in lakes across the UK since the 1960s including the Lake District (Dong *et al*., 2012; Moorhouse *et al*., 2018), Yorkshire (May *et al*., 2010), Norfolk (Bennion *et al*., 2001), Staffordshire (Bennion *et al*., 2008), Northumberland and Cornwall (Bennion *et al*., 2006). In the 1990s, the implementation of P stripping treatments in sewage treatment works led to reduced phosphate loading to surface waters (Parker and Maberly, 2001). However, nitrate concentrations remained high mainly due to leakage from grasslands that were either directly fertilised or had accumulated atmospherically deposited N (Tipping *et al*., 2008). The recovery from eutrophication has also been hampered by the re-release of P from sediments which have historically been loaded with nutrients over the 20th century (Lacey *et al*., 2018). This is the case for many of the Shropshire-Cheshire meres (e.g. Rostherne Mere) which still have a persistently high nutrient status that may take several decades to resolve despite a substantial reduction in external inputs (Bennion *et al*., 2006; Lacey *et al*., 2018; Moss *et al*., 2005).

A consequence of eutrophication is enhanced phytoplankton productivity which can result in extensive blooms especially during the summer months (McGown *et al*., 2012). Eutrophication can favour cyanobacteria by reducing N:P ratios which promote heterocystous species to dominate (Schindler *et al*., 2008). The proliferation of cyanobacteria can lead to the formation of HABs which can present more severe impacts to lakes (Paerl and Otten, 2013). HABs can result in water quality degradation, whilst producing toxins that are harmful (and even lethal) to wildlife and humans (Paerl *et al*., 2001). When these blooms die their material becomes oxidised by micro-organisms which can result in O_2 depletion in lake waters and often anoxia in stratified waters (Friedrich *et al*., 2014). Anoxic waters can lead to a range of other ecologically and water quality problems, for example a deterioration in O_2 concentrations leading to concerns over the fish population in Lake Windermere (Jones *et al*., 2008).

Lakes do become naturally more eutrophic over time, as P containing algal material that fills the lake basin gets re-released in summer months to stimulate further algal growth (Whiteside, 1983). However, anthropogenic eutrophication has accelerated the process of nutrient accumulation in lakes altering biogeochemical cycles through accelerated storage and transformation of C, N and P with impacts on lake ecology (Howarth *et al*., 2011). Overall, eutrophication has resulted in substantial costs to the UK, in terms of the loss of recreational space for heavily polluted lakes and economic costs in remedial treatments (Pretty *et al*., 2003).

2.1.2 Acidification

Atmospheric sulphur dioxide (SO_2) reacts with water to form sulphate (SO_4^{2-}), which can then enter lakes through precipitation causing acidification (Battarbee *et al*., 2010). Since the mid to late 19th century, increasing SO_2 emissions from fossil fuel combustion resulted in a lowering of lake water pH by 0.7 to 1.5 (Juggins *et al*., 1996; Tipping and Chaplow, 2011). The differences in pH decline have been largely dependent on regional acid deposition rates, along with the acid neutralising capacity (ANC) of the catchment (Davies *et al*., 2005). The lakes with a higher ANC, such as those in limestone catchments, experienced smaller reductions in pH (0.3 to 0.5) with many not exhibiting declines in until the 20th century (Juggins *et al*., 1996). Emissions of SO_2 in the UK peaked in the 1980s and declined sharply through the early 1990s with a decrease of 94% between 1970 and 2010 (Review of Transboundary Air Pollution, 2012). The reduction in emissions resulted in a 50% reduction in SO_4^{2-} deposition from 1986 to 2005 (Fowler *et al*., 2005). The reduced SO_2 emissions were driven largely from the switch between coal and natural gas combustion in power plants (Review of Transboundary Air Pollution, 2012). By the beginning of the 21st century N emissions became an important contributor to acidity although SO_4^{2-} was still the dominant contributor (Tipping and Chaplow, 2011). One of the main sources of N emissions is from agricultural activity with nitrogen oxides decreasing by 58% from 1970-2010 (Review of Transboundary Air Pollution, 2012).

Reductions in SO_4^{2-} deposition have led to a rise in the ANC of lakes which in turn has led to increases in pH (Evans and Monteith, 2001). The recovery of ANC and pH has been observed to be a gradual trend across many UK lakes between 1988 and 2008 and this is expected to continue over the coming decades (Battarbee *et al*., 2014). However, many UK lakes have not seen a return to their pre-acidification state (Kernan *et al*., 2010). The slow recovery is likely exacerbated through leaching of S and N previously deposited in the catchment (Curtis *et al*., 2005; Monteith and Evans, 2005). Atmospherically deposited N coupled with climate change is likely to slow the rate of recovery from acidification and in some lakes over the coming decades and potentially place ecological recovery on new trajectories (Review of Transboundary Air Pollution, 2012).

The effects of acidification include diatom community change to more acid tolerant species (Battarbee, 1984; Birks *et al*., 1990) and toxicity induced reproductive failure in salmon which has caused severe population reductions over the 20th century (Kernan *et al*., 2010; Gray *et al*., 2016). Environmental change has also resulted from the link between acidification and dissolved organic carbon (DOC) as the lowering of pH induces the precipitation of DOC from the water column which decreases water transparency (Vinebrooke *et al*., 2002). In most UK lakes there has been an increase in DOC concentrations in response to increasing pH (Monteith *et al*., 2005) with the most rapid improvements in pH at sites with lower DOC concentrations (Monteith *et al*., 2014). Changes in DOC, through the progression and recovery from acidification, has likely had a large impact on water clarity (Evans *et al*., 2005; Evans *et al*., 2006).

2.1.3 Heavy metal pollution

UK freshwater environments are increasingly identified as being contaminated by anthropogenic pollutants (Tipping *et al*., 2005). Some heavy metal contamination has occurred for centuries with sedimentary records from the Lake District showing that lead (Pb) concentrations first started to rise around 1700 reflecting the first documented activity of Pb extraction (Schillereff *et al*., 2016). The rapid development of industry powered by fossil fuels from the 1850s coincided with increased heavy metal contamination in many UK lakes and their catchments (Yang and Rose, 2003). This accelerated over the 20th century due to industrialisation, urbanisation and the greater use of motor vehicles (Grayson and Plater, 2008; Miller *et al*., 2014). The increased consumption of leaded petrol resulted in a dramatic increase in atmospheric Pb emissions in the UK during the 1960s and 1970s (Komárek *et al*., 2008). After the 1970s, atmospheric emissions of trace metals such as cadmium (Cd), nickel (Ni), copper (Cu) and zinc (Zn), declined dramatically in the UK due to the introduction of emission controls (Rose *et al*., 2012).

Regions such as the Lake District have a long history of mining activity resulting in a range of freshwater contamination since the 19th century from Zn (Schillereff *et al*., 2016), Cu (Miller *et al*., 2014) and Pb (Miller *et al*., 2015). Although declines in metal concentrations (e.g. Pb) in some lakes have occurred, in response to reductions in atmospheric emissions, many lakes have not recorded any detectable change (National Atmospheric Emissions Inventory, 2014). Heavy metal concentrations in these lakes are not reducing largely due to the historic atmospheric deposits stored in catchment soils (Rose *et al*., 2012). Pollutants that are deposited atmospherically in catchments can adsorb to soil organic matter due to their high binding affinity (Graham *et al*., 2006). In catchments of historical mining activity contamination of soils is likely to be high (Foulds *et al*., 2014). When these soils are disturbed, such as through erosion and precipitation driven runoff, this can increase remobilisation and transport heavy metals to lakes (Kernan *et al*., 2010; Yang, 2010). As a result, catchment inputs of heavy metals can still be high today with soils providing a constant supply despite reductions in atmospheric emissions (Yang *et al*., 2002).

Recovery from acidification has also elevated metal transport to UK lakes, through increasing organic matter solubility, with Fe concentrations having doubled from the early 1980s to the early 2000s (Neal *et al*., 2008). The pH of soils also affects Zn sorption and as catchments recover from acidification, mobilisation from soils is reduced (Tipping *et al*., 2005). Climate change has also increased the transport of metals to lakes with increased precipitation driven erosion of catchment soil, elevating the input of soil associated heavy metals (Helliwell *et al*., 2007). In some lakes (e.g. Red Tarn, Cumbria) there have been increased sedimentary heavy metal concentrations since the start of the 21st century, most likely caused by an increase in extreme winter precipitation events increasing catchment inputs (Yang and Smyntek, 2014). The increase in the supply of organic matter to lakes has resulted in increased trace metal concentration in sediments (e.g. As, Cd, Br, Ni) over the 20th century across the UK (Oldfield *et al*., 2003; Yang and Rose, 2005a).

2.1.4 Land activities and sedimentation rates

Forestry and agriculture activity in a lake catchment have a strong influence on organic matter (OM) inputs and DOC concentrations (Finstad *et al*., 2016; Kritzberg, 2017). Forest clearance, increases soil instability with enhanced soil erosion (Barlow *et al*., 2009) and increases sediment delivery to streams and lakes (Foster *et al*., 2003). As a result, sediment accumulation rates (SARs) in agricultural catchments have experienced increases during the 20th century as recorded in Semerwater, North Yorkshire (Chiverrell *et al*., 2008), Esthwaite Water, Cumbria (Dong *et al*., 2011) and Bassenthwaite Lake (Orr *et al*., 2004). Since the 1990s there is evidence for a slowdown in SARs in response to the reduction in particulate emissions of fossil fuel power stations, the decline of heavy industry (Rose, 2001) and afforestation (Orr *et al*., 2004). However, in some lakes, SARs have increased again since the 1990s potentially due to greater seasonality and more frequent intense winter rainfall events in the latter part of the 20th century (Hatfield *et al*., 2008).

There are a range of ecological impacts from an increase in terrestrial inputs to lakes through influencing acidity, trace metal transport, photochemistry, nutrient supply and water transparency (Evans *et al*., 2005; Evans *et al*., 2006). DOC has a strong influence over water transparency as lakes with higher DOC concentrations generally have reduced light penetration (Snucins and John, 2000). The impacts of land activity are often compounded by meteorological conditions, elevated temperatures increase the decomposition of organic material in a catchment, which is exported to lakes following rainfall events (Freeman *et al*., 2001). Laboratory and field experiments have shown the influence of rainfall and runoff distribution affecting DOC transport to water (Evans *et al*., 2005). In the autumn of 2006 and 2007 exceptionally large DOC concentrations were recorded in several lakes in the west of the UK following the particularly warm and dry summer of 2006 which would have stimulated decomposition rates. This period was followed by heavy rain in September transporting terrestrial organic material to lakes (Monteith *et al*., 2014). Therefore in lake catchments with reduced soil stability elevated temperatures followed by intense precipitation can lead to substantial increases in allochthonous OM inputs (Werritty, 2002). In lakes which experience a substantial reduction in light penetration submerged macrophyte productivity and colonisation depths can be severely restricted (Moss, 2014).

2.1.5 Climate change

I. Temperature

Air temperature has been largely stable in the UK over much of the 20th century but increased by around 1°C from the period 1961-1990 to 2005-2014 (ASC, 2016). The rapid warming over recent decades means that the 21st century has so far been warmer than the previous three centuries with the eight warmest years on record all having occurred since 2002 (Kendon *et al*., 2017).

Lake water temperature is highly correlated to changes in air temperature, with increased water temperature recorded in several lakes in the UK during the 20th century (Watts *et al*., 2015). However the trends are very site specific as lake water temperature is influenced by weather conditions (winds in particular), lake area, volume and stratification (George *et al*., 2007a). In addition, catchment characteristics such as topography, land use and vegetation density also influence the lake water temperature (Hannah and Garner, 2015). Forest cover shading and greater groundwater inputs can both moderate the response to rising air temperatures with surface fed water bodies generally increasing in temperature more rapidly than those which are spring fed (Mackey and Berrie, 1991). There is indication that lakes in northern Europe are warming faster than the global average (0.34°C decade^{-1}) with surface water temperatures increasing by 0.75°C decade^{-1} in Loch Leven, Scotland (O'Reilly *et al*., 2015). In England, the surface water temperature of Lake Windermere (Cumbria) has increased by 1.1°C between the periods of 1961-1990 and 1991-2005 (Jeppesen *et al*., 2012; Winfield *et al*., 2008). This trend of increasing lake water temperature has been experienced across the Lake District, with shallower lakes warming more than the deeper lakes most probably as a consequence of a greater proportion of their water volume interacting with the atmosphere (Woolway *et al*., 2015).

Increased surface water temperature has caused an increase in the duration and strength of stratification (Feuchtmayr *et al*., 2012). These changes coupled with the temperature-driven decrease in O_2 saturation means that increased water temperature can result in reductions in dissolved O_2 concentrations (Daufresne *et al*., 2004). At Grasmere (Lake District) summer water temperatures have increased between 1 and 2°C from 1971 to 2010 which has strengthened thermal stratification and enhanced O_2 depletion (Reynolds *et al*., 2012). Lake Windermere has undergone advanced thermal stratification since the 1980s potentially caused by milder winters (Thackeray *et al*., 2008). At Blelham Tarn thermal stratification occurred 38 days earlier in 2008 compared to 1968 and extending the duration of anoxia in the hypolimnion (Foley *et al*., 2012; Winfield *et al*., 2008).

Increased stratification and O_2 depletion can stimulate algal blooms once the stratification period ends. As P release is favoured under reduced conditions enhanced O_2 depletion can increase the release of nutrients from sediments simulating algal blooms (Jensen *et al*., 1992). Temperature also impacts N availability with higher temperatures increasing bacterial de-nitrification. This was recorded at Hornsea Mere (East Riding of Yorkshire) where nitrate concentrations decreased between 2000 and 2010 with increasing temperatures (May *et al*., 2010). In general warming can exacerbate eutrophication and inhibit a lake's recovery from historical nutrient loading (Friedrich *et al*., 2014).

II. Precipitation

Instrumental records have shown that precipitation over England has not significantly changed since records began in 1766 (Jenkins *et al*., 2009; de Leeuw *et al*., 2015). However, regions such as the Lake District have experienced a substantial increase in average rainfall over recent decades from 5.7 mm day^{-1} in 1970 to 7.1 mm day^{-1} in 2000 (George *et al*., 2007b). This has led to increased runoff, especially in upland areas of the north-west from 1961-2010 (Hannaford, 2015). Since the 1960s UK rainfall patterns trend towards increasing winter rainfall (de Leeuw *et al*., 2015; Kendon *et al*., 2019) which is concentrated in the uplands (Burt and Ferranti, 2012). Precipitation has also occurred as intense precipitation events with six out of seven of the years with the greatest number of days of heavy rain (>10mm) having occurred since 2000 (Kendon *et al*., 2017). The trend of increasingly intense rainfall events has been experienced across much of England but particularly in the north and west (Prosdocimi *et al*., 2014). Compared to the relatively dry 1880s, seasonal precipitation in the Lake District had clearly change by the 1990s, with increases in winter (37%), spring (24%) and autumn (11%) precipitation, offset by marked declines in summer (-9%) (Barker *et al.*, 2004). Decreasing summer precipitation has been observed across all regions of England during the 20th century (Jenkins *et al*., 2009). However there is evidence to suggest that reduced summer precipitation has reversed since 2007 with anomalously wet summers from 2007-2012 (de Leeuw *et al*., 2015; Kendon *et al*., 2019).

There has been an increase in severe storms over the UK during the second half of the 20th century (Alexander *et al*., 2005). This is probably due to a warmer atmosphere, that can hold more water enhancing the frequency of intense events (Arnell *et al*., 2015). A consequence of increases in the number of extreme precipitation events is the resulting increase in runoff (IPCC, 2014). Heavy rains remobilise P which dissolves into the overlying water or transports phosphate adsorbed to soil minerals via surface runoff (Gburek *et al*., 2002). Therefore, wetter conditions often increase the concentration of dissolved reactive P in lakes (George *et al*., 2004). As a result, wetter winters in Esthwaite Water and Blelham Tarn (Cumbria) have led to an increased concentration of dissolved reactive P during winter months (George *et al*., 2007a).

III. UK Climate Projections 2018 (UKCP18) projections

UKCP18 (Gohar *et al*., 2018) presents the most recent climate projections for the UK using the Meteorological Office's HadGEM3-GC3.05 global model run for 1901-2100 under the RCP4.5 scenario (emissions peak around 2040). The projections indicate that with a global mean warming of 2°C above pre-industrial levels the UK mean air temperature would increase between 1 to 2°C by the end of the 21st century (relative to the present day). Summers warm more than other seasons with the south of England increasing by 3 to 4°C under the central (median) projection (Fig. 2.1).

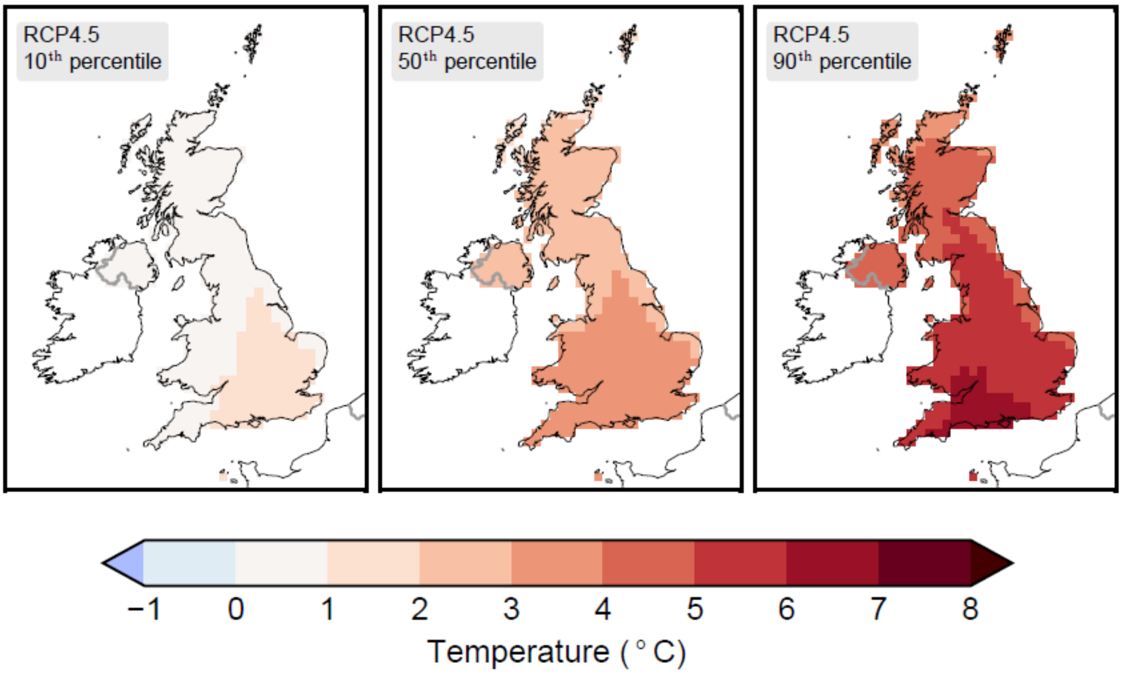

Fig. 2.1 Changes in 20-year mean summer temperature for the period 2080 to 2099 relative to a 1981-2000 baseline under the RCP4.5 emission scenario.

In winter months the coldest days warm slightly more than warmer days which would likely lead to less snowfall and more rainfall. Annual precipitation shows little change with slight increases in the winter precipitation across the country with the west experiencing the largest increase. In contrast summer precipitation would decrease across much of England. If the climate model is run using 4°C of global warming all of the changes become more pronounced with winter temperatures increasing by 2.5 to 3°C across the country, winters 20% wetter and summer days becoming up to 40% drier. Overall, the projections are consistent with previous UK climate modelling studies, with the UK predicted to warm more rapidly than the global average causing greater, more intense winter precipitation and reduced summer precipitation (e.g. Chan *et al*., 2014; Kendon *et al*., 2014).

IV. Ecological implications from future climate warming

In general, the rate of biological and chemical processes, in particular nutrient cycling, increase with temperature (Charlton *et al*., 2018). The warming of soils will lead to an increase in the rate of N mineralisation and availability especially in extended dry summer periods which are projected to increase over the 21st century (Whitehead *et al*., 2006). However as denitrification increases with temperature there could also be N loss, especially in lakes with long residence times (Arnell *et al*., 2015). Along with catchment delivery, P inputs are derived through their re-release from sediments which increases with temperature (Jeppesen *et al*., 2005; Liu *et al*., 2018) and can be further exacerbated through enhanced O_2 depletion (Fig. 2.2; Arnell *et al*., 2015). The release of P from sediments will stimulate primary productivity increasing biological O_2 demand (Cox and Whitehead, 2009). Therefore, a positive feedback loop can be produced where further P release from sediments can lead to severe deoxygenation in bottom waters that may result in a permanent anoxic state (Friedrich *et al*., 2014). Considering these drivers of nutrient dynamics, it seems likely that there will be greater availability of P relative to N in the future.

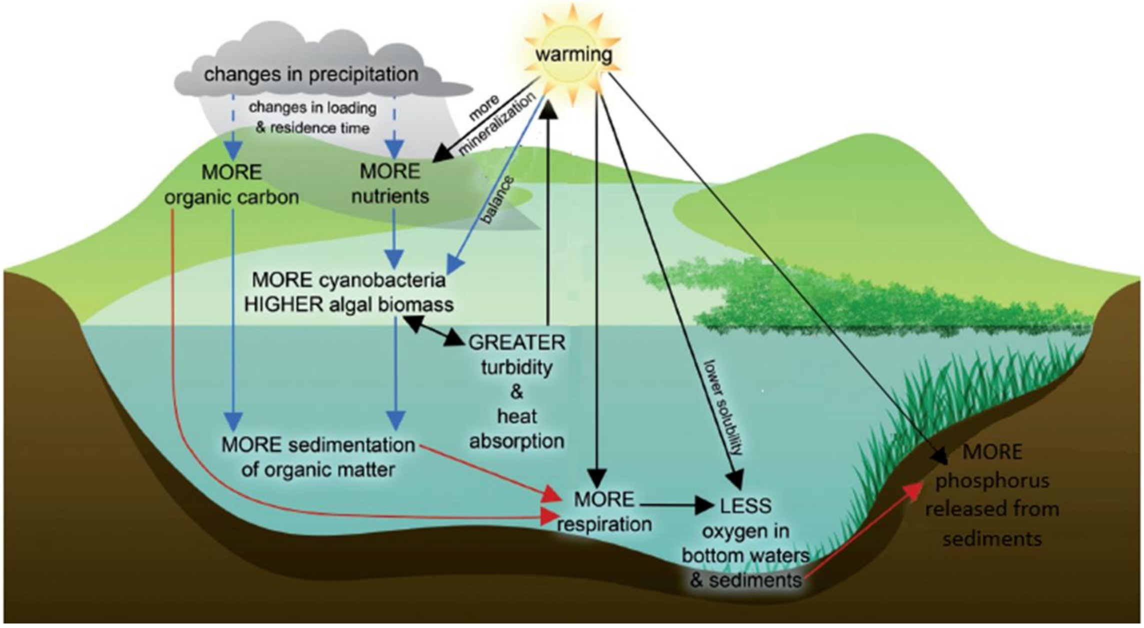

Fig. 2.2 Conceptual diagram of the response of a lake system to changes in temperature and precipitation. Adapted from Moss *et al*. (2011).

The transportation of nutrients is expected to be enhanced through the increasing frequency and magnitude of winter rainfall events (Jin *et al*., 2012; Muir *et al*., 2012). In contrast during summer months there is likely to be increased residence times and reduced dilution through a reduction in precipitation and flow rates (Johnson *et al*., 2009). The combination of increased internal and external nutrient inputs means that the amount of extent of eutrophication events will likely be greater in the future (Jeppesen *et al*., 2014). Therefore, the expected recovery from a reduction in agricultural nutrient loading is likely to be offset in some historically impacted lakes (Battarbee *et al*., 2012). Wetter and warmer winters are expected to enhance the flux of DOC from catchments to lakes in the future (Arnell *et al*., 2015; Monteith *et al*., 2014). Increases in organic matter will change the optical and chemical properties of lake water (Larsen *et al*., 2011) and increase heavy metal transport to lakes that have accumulated in catchment soils over the industrial period (Rose *et al*., 2012; Yang *et al*., 2016). This could present a situation of prolonged high heavy metal input for some historically impacted sites which may take decades to reduce to background levels (Schillereff *et al*., 2016; Yang, 2010).

As temperature increases photosynthetic rate, climate change is expected to drive enhanced productivity in most lakes (Elliott *et al*., 2005; Padilla-Gamino and Carpenter, 2007). This will reduce water transparency which will be further exacerbated by increased nutrient loading (Mooij *et al*.,

2007) and DOC concentrations (Seekell *et al*., 2015). As a result, climate change will increase the likelihood of lake ecosystems switching from clear to turbid states (Jeppesen *et al*., 2014). Transparency is important, especially in shallow lakes, as high light penetration is essential to sustain submerged photosynthetic activity (Johnson *et al*., 2009). A shift from a clear to turbid state has the potential to reduce macrophyte populations, completely change food webs and ultimately lead to a less complex state dominated by micro-organisms (Rawcliffe *et al*., 2010; Friedrich *et al*., 2014). In general, a shift from a clear to turbid state is expected to have adverse effects impacting water quality, biogeochemical cycling and productivity (Winder and Sommer, 2012).

Increased temperatures will extend the length of the growing season for algae which is expected to produce more favourable conditions potentially allowing growth all year round (Mooij *et al*., 2007). Spring blooms are likely to be enhanced with earlier summer peaks as a result of nutrient depletion occurring earlier in the season (Elliott *et al*., 2005). Increasing temperatures also enhance internal P loading which can favour cyanobacterial growth as they are able to fix their own N (Elliott, 2012; Elliott, 2016). Although rises in temperature are expected to bring changes towards more tolerant species, changes in flow and flushing rate may have a greater impact on algal community composition in some lakes (Carvalho *et al*., 2011). Changes in community composition have the potential to affect the rest of the lake ecosystem (Rawcliffe *et al*., 2010) impacting the diversity and abundance of higher organisms (Moss, 2010).

2.1.6 Algae as indicators of environmental stressors and ecological change

Algae is the commonly used name to describe a diverse group of aquatic photosynthetic protists and prokaryotes (e.g. cyanobacteria) (Douglass *et al*., 2004). Algae are an important component of nearly all aquatic systems representing species with a range of forms and traits that increase productivity (Gökçe, 2016; Omar, 2010). Due to their short life spans and fast reproduction rates algae respond rapidly to environmental changes (Gökçe, 2016; Leavitt and Findlay, 1994). Algae are small and mostly sessile meaning that they are typically sensitive to pollution, and other perturbations, making them useful indicators of anthropogenic impacts (Law, 2016; Omar, 2010). Algae can provide information which cannot be obtained through chemical and physical measurements alone, providing the ability to make an assessment on an ecological level (Gökçe, 2016; Law, 2011). As a result, algae are commonly used in freshwater ecological assessments to indicate water quality (Williamson *et al*., 2009) as they can act as an early warning system for potential impacts to higher organisms (McCormick and Cairns, 1994).

In general algal primary productivity is controlled by temperature, light and nutrient availability (Geider *et al*., 1997; Salmaso *et al*., 2012). Algae typically have very specific requirements for growth and reproduction making the presence of particular taxa indicative of the conditions in the parts of the lake they habit (Devlin *et al*., 2011; Taranu *et al*., 2015). Although individual taxa have well defined optima, the algal community have a wide range of environmental tolerances which can adapt to multiple stressors (Paerl *et al*., 2001). As a result, changes in population and community structure may provide a more reliable indicator of environmental change than productivity alone (McCormick and Cairns, 1994). Changes in algal productivity are important as greater algal growth can change the water colour, reduce water transparency and impact the recreational uses of lakes. Community changes resulting in greater proportions of cyanobacteria may also produce more toxins when their cells decay impacting wildlife and even human health (Omar, 2010). The effects of algal expansion on fish stocks may be of particular importance, as they are a key ecological component of many lake ecosystems.

Typically, nutrients are the dominant driver of algal community change although temperature often amplifies the impacts in eutrophic lakes (Dong *et al*., 2012). Many UK lakes have experienced unprecedented levels of algal change during the second half of the 20th century (Dong *et al*., 2011). In Lake Windermere eutrophication has caused a shift in diatoms to more eutrophic species during the mid-20th century (Sabater and Haworth, 1995). More recently warmer temperatures have advanced the spring diatom bloom which in turn stimulates earlier *Daphnia* proliferation (Thackeray *et al*., 2013). Diatoms are typically limited by the availability of silica (Si), which is a major nutrient and Si limitation often terminates a diatom bloom in spring months (Billen *et al*., 2001; Kong *et al*., 2021). Earlier diatoms blooms can result in longer growing seasons for other summer growing taxa (e.g. cyanobacteria) with an enhanced pool of P, and to a lesser extent N, resulting in larger algal blooms (Elliott *et al*., 2006; Johnk *et al*., 2008). As algal communities go through these seasonal changes, algae can be used as a tool to infer ecological impacts in a lake on an annual and intra-annual timescale (McCormick and Cairns, 1994).

2.2 Palaeolimnology to assess past and current ecological change

Palaeolimnology is commonly used to assess lake changes over time in the absence of historical water data (McLauchlan, 2013). As lake sediments accumulate vertically over time preserving a record of chemical and biological material at the time they were deposited (Smol, 2008). Preserved algal remains and chemical residues can be used to provide a record of past ecological communities, indicate human perturbations and climatic events (Schindler, 2009). These materials can be measured directly to infer a range of past environmental conditions in a lake and the surrounding catchment (Smol, 2008).

Diatoms are the most extensively used group of algae due to their ubiquity and hard frustule shells, formed out of biogenic silica, that can protect against degradation upon death (Leng and Barker, 2006). Typically, diatom frustules have been used as a proxy to quantify past environmental conditions through the development of diatom-based transfer functions (Battarbee *et al*., 2012). However, dissolution can be a problem in lakes with a higher pH (e.g. carbonate lakes) and only a relatively small proportion of diatom frustules may be preserved (Mackay *et al*., 2000; Ryves *et al*., 2006). As the preservation of diatom frustules is dependent upon the environmental conditions of a lake (e.g. water chemistry, sediment composition, grazing and water depth of a lake) they may not be found in sufficient quantities to enable palaeoenvironmental reconstructions (Flower, 1993).

More recently fossil pigments have started to be widely used in palaeolimnology, providing a measure of past algal biomass (Bunting *et al*., 2007; Leavitt and Hodgson 2001). As pigments are derived from a range of algal groups they can enable a more comprehensive assessment of past lake algae and how communities have changed over time (e.g. McGowan *et al*., 2012; Moorhouse *et al*., 2018; Wiik *et al*., 2015a). Algal pigments are often used in multiproxy studies to reconstruct an ecological response to a known environmental change, such as increased temperature, and help separate this response from other human impacts (e.g. nutrient loading, land use change) (Birks *et al*., 2010; Mills *et al*., 2016; Ouyang *et al*., 2015).

Through a multiproxy approach, biological records can be used solely as the evidence of ecosystem response to environmental changes (Battarbee, 2000) whilst increasing confidence in the data and enabling a more accurate reconstruction (Bard, 2001; Fortin and Gajewski, 2009). Additionally, the use of multiple proxies has the potential to help untangle the various processes that are operating in lakes (Meyers, 2003) and help to overcome some of the problems encountered when using a single proxy (Bennion *et al*., 2001). These problems include particular proxies being absent from sections of the core or the impacts of confounding influences, which may be identified when using a multiproxy approach (Castañeda and Schouten, 2011). Utilising a combination of organic, inorganic and biological proxies can help to make a more robust assessment of environmental changes in a lake over time (Castañeda and Schouten, 2011; Pędziszewska *et al*., 2015). Some of these proxies are described in the following subsections.

2.2.1 Organic matter, C/N and stable isotopes

Organic matter plays an important biogeochemical role in lake ecosystems as it influences physical (aggregation/deposition), chemical (adsorption) and biological (productivity) processes (Hassett and Anderson, 1982; von Wachenfeldt, 2008; Seekell *et al*., 2015). Organic matter comprises of a mix of materials produced in the lake and its catchment. Algal detritus can provide the dominant source of organic matter to lake sediments (Cohen, 2003) although the influence of both aquatic and terrestrial plants is often important (Meyers, 1997). Only a relatively small percentage (1-35%) of the organic carbon synthesised by algae reaches the surface sediments, while the distance travelled by the organic matter source to the sediments impacts on the degree of transformation and degradation that occurs (Meyers and Iswhatari, 1993). During deposition, organic matter is subject to microbial alteration and diagenetic processes which tend to be more intense in bioturbated oxygenated surface sediments (Meyers, 1997; Meyers and Lallier-Vergès, 1999). Lake depth and morphometry greatly influence carbon burial with shallower lakes providing less opportunity for carbon mineralisation before it gets deposited in the sediment (Sobek *et al*., 2009). Within the first five years after deposition around 20% of the carbon is mineralised and preservation becomes more stable (Gälman *et al*., 2008). Analysis of the organic component of sediments over time can provide an important insight into how lake environmental conditions have changed over time (Liu *et al*., 2013).

I. Use of C/N

The C/N ratio of lake sediments can be used to indicate changes in the source of OM and trace eutrophication sources (Lacey *et al*., 2018; Meyers, 1994). As algae contain none, or very little, cellulose compared to vascular plants, they are relatively protein rich and as a result have lower C/N (<10) compared to protein poor C3 plants (C/N >20) (Curtis *et al*., 2010; Meyers, 2003). In comparison to C3 plants, C4 plants have a generally higher C/N but a narrower range (C/N >35; Fig. 2.3). This difference in C/N reflects the greater nitrogen use efficiency of C4 plants which results in enhanced CO_2 assimilation compared to C4 plants increasing C/N (Ghannoum *et al*., 2011). As algae have a much lower C/N ratio than plants, sedimentary C/N can be used as a proxy of past algal vs plant production (Smol, 2008). The difference in C/N can be used to distinguish whether the source of sedimentary organic matter is autochthonous or allochthonous but as most lakes have a mixture of algal and plant material they typically have C/N ratios between 10-20 (Meyers and Teranes, 2001). The source of OM is important to identify as higher allochthonous content can indicate catchment modifications resulting in higher organic content rather than an increase in productivity (Smol, 2008). For example deforestation can increase C/N through the increase in terrestrial OM transported to the lake (Kaushal and Binford, 1999). Conversely, the lowering of C/N ratios have been observed in soils due to the absorption of ammonia derived from decomposition of terrestrial organic matter with the remineralisation of carbon (Meyers, 1997; Sollins *et al*., 1984).

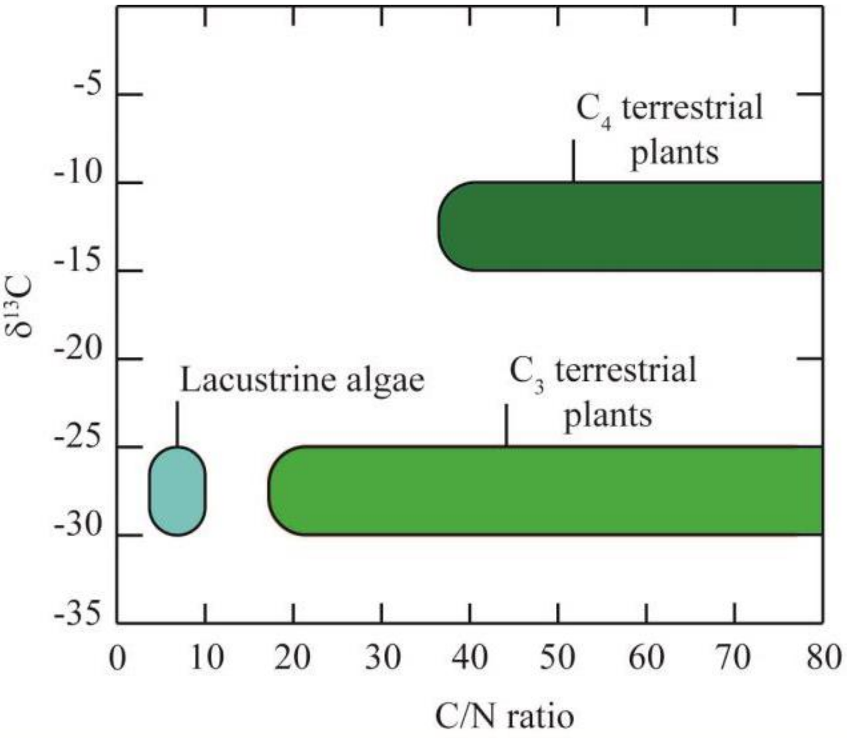

Fig. 2.3 The $\delta^{13}C$ and atomic C/N ratios of organic matter derived from lacustrine algae, C3 terrestrial plants and C4 terrestrial plants (Meyers and Teranes, 2001).

An increase in the C content of sediment does not necessarily mean an increase in lake productivity as lake conditions (e.g. dissolved O_2, temperature) affect both productivity and decomposition (Smol, 2008). Additionally, post depositional changes can affect the interpretation of C/N. Once deposited, more labile N rich compound can be preferentially broken down during early diagenesis compared to the more resistant C fractions (Meyers, 1997). This can raise the C/N ratios of sediments over time, especially in oxic sediment whereas in anoxic sediments the C/N often remains largely unchanged due to reduced microbial activity (Lehmann *et al*., 2002). However, the rate of C/N change from diagenesis is highest within 5 years after deposition after which change is much slower (Gälman *et al*., 2008). These longer-term post depositional changes are not usually of sufficient magnitude to affect larger scale change in source over time (Meyers and Ishiwatari, 1993).

Therefore, shifts in sedimentary C/N ratios typically reflect a change in OM source over decadal and centennial time scales.

II. Carbon isotope ratios in organic matter

The carbon isotope composition of organic matter ($\delta^{13}C_{org}$) in aquatic sediments can provide information about changes in lacustrine biogeochemical cycles (Lehmann *et al.*, 2004). $\delta^{13}C_{org}$ is also a widely used proxy for aquatic productivity in lakes with algal biomass often found to be the most important factor influencing the $\delta^{13}C_{org}$ of sediments (Gu *et al.*, 1996; Meyers, 2003). Algae preferentially utilise ^{12}C over ^{13}C due to the lower energy requirements to break the bonds in photosynthesis (Lizumi, 2007). The selectivity of ^{12}C produces an isotopic fractionation of ~−20‰ to the inorganic carbon source, such as atmospheric CO_2, which is reflected by the lower $\delta^{13}C$ of algal cells (Fogel and Cifuentes, 1993; Meyers, 1994).

The carbon isotopic ratio, expressed in delta (δ) notation, can be calculated using the following equation:

$$\delta_{Sample} = \left(\frac{R_{Sample}}{R_{Standard}} - 1\right) \times 1000$$

Equation 1

where R_{sample} is the raw ratio of ^{13}C to ^{12}C in a sample and $R_{standard}$ is the ratio of ^{13}C to ^{12}C of a standard, which for carbon is related to the Vienna Pee Dee Belemnite (VPDB) international reference scale. Stable isotope results are normally expressed in δ notation and permil (‰), due to the relatively small difference between the $\delta^{13}C$ of the sample and standard (Lizumi, 2007).

Higher productivity can result in lower sedimentary $\delta^{13}C_{org}$, when there is a large proportion of algal-derived OM and recharge of ^{12}C is constant such as through oxidation of detritus or via dissolution in the catchment (Meyers, 1997). In eutrophic conditions where recharge of ^{12}C is not constant, high primary productivity would deplete ^{12}C in the dissolved inorganic carbon (DIC) pool via algal uptake, death and burial leaving relatively more ^{13}C available for photosynthesis. This can result in sedimentary organic matter with higher $\delta^{13}C_{org}$ in some highly productive lakes (Brenner *et al*., 1999; Lizumi, 2007).

Algae typically have a $\delta^{13}C$ of −30 to −25‰ with differences between benthic (−26‰ ± 3) and planktonic (−32‰ ± 3) algae (France, 1995; Kohn, 2010). These differences are influenced by a number of factors such as growth rates and algal groups using different fractions of C (Fry and Wainright, 1991; Lehmann *et al*., 2004).As dissolved CO_2 is usually in isotopic equilibrium with atmospheric CO_2 (recent $\delta^{13}C$=~−8.5‰, Graven *et al*., 2017), the $\delta^{13}C$ of algae is similar to that of C3 plants (−37 to −20‰) although with a wider range (Lizumi, 2007; Kohn, 2010). As many algae and plants share the same value range in $\delta^{13}C_{org}$ it can be difficult to interpret alone (Meyers and Teranes, 2001). Overall, the effect of carbon isotope fractionation during photosynthesis dominates the $\delta^{13}C_{org}$ signal in sediment (Lehmann *et al*., 2004).

Changes in $\delta^{13}C_{org}$ can also help to indicate changes in the sources of organic matter (Meyers and Teranes, 2001). In small and oligotrophic lakes terrestrial inputs may be the dominant driver of $\delta^{13}C_{org}$ change due to greater catchment inputs and lower primary productivity (Gu *et al*., 1996; Lehmann *et al*., 2004). The $\delta^{13}C$ of the DIC in lake water is also controlled by various processes including rates of atmospheric CO_2 exchange, carbonate weathering, OM decomposition rate, photosynthesis and respiration rate (Brenner *et al*., 1999). Vegetation and catchment inputs also play a large role in $\delta^{13}C_{org}$ values as increased catchment productivity can result in DIC with lower $\delta^{13}C$ being transported to lakes upon decomposition and subsequently used by algae during photosynthesis (Moorhouse *et al*., 2014). Conversely, increasing $\delta^{13}C$ values can result from deforestation leading to a reduction in catchment soil respiration (Wang *et al*., 2013). As a result, lakes which receive substantial quantities of terrestrial inputs may record $\delta^{13}C_{org}$ values reflective of vegetation changes in the catchment with higher productivity leading to a source of DIC with lower $\delta^{13}C$ (Castañeda and Schouten, 2011; Maberly *et al*., 2013).

The $\delta^{13}C$ of atmospheric CO_2 has been declining over the last 200 years, by up to 1.6‰, as a result of fossil fuel combustion, with most of this change having occurred since the 1960s (Verburg, 2007). This is known as the Suess effect (Fig. 2.4), which needs to be accounted for when interpreting $\delta^{13}C$ changes in lakes that are in equilibrium with atmospheric CO_2 although this is not necessary in lakes that respire more C than they produce (O’Reilly *et al*., 2005).

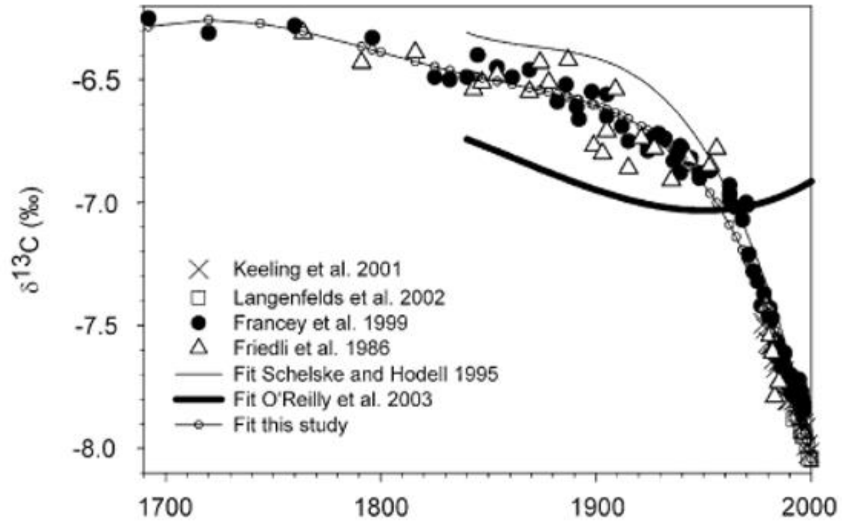

Fig. 2.4 The change in $\delta^{13}C$ in the atmosphere caused by anthropogenic activity, also known as the Suess effect (O'Reilly *et al.*, 2005).

III. Nitrogen isotope ratios in organic matter

Nitrogen entering catchments can get taken up by macrophytes, be microbially transformed and then transported to lakes where the N can stimulate algal growth before being deposited in the sediment (Holtgrieve *et al.*, 2011). To help understand the drivers of changes in productivity, the N isotope composition ($\delta^{15}N$) of sediments can be used to establish changes in the source of organic N ($\delta^{15}N$), productivity and N cycling (Meyers, 2003). $\delta^{15}N$ for algae are typically −3 to +18‰ with terrestrial plants having similar but slightly lower range and terrestrial OM around +3‰ (Fogel and Cifuentes, 1993; Rau *et al.*, 1989; Schoeninger and DeNiro, 1984). Algae preferentially incorporate ^{14}N over ^{15}N which produces lower $\delta^{15}N$ values in algal cells than the inorganic source, when this inorganic source is in excess (Fogel and Cifuentes, 1993; Meyers and Teranes, 2001). Therefore, increased algal productivity can lead to lower $\delta^{15}N$, when the dissolved inorganic nitrogen (DIN) source is abundant and until P availability becomes limiting (Anderson *et al.*, 2018; Gu *et al.*, 1996; Teranes and Bernasconi, 2000).

The isotope ratio of N, expressed in δ notation, can also be calculated using equation 1 (section 2.4.2.I). Where R_{sample} is the raw ratio of ^{15}N to ^{14}N in a sample and $R_{standard}$ is the ratio of ^{15}N to ^{14}N in a standard material with a known $\delta^{15}N$, relative to the international standard (atmospheric N; Lizumi, 2007).

There are numerous sources of N in the environment including fossil fuel emission, fertilisers and soil emissions (Holtgrieve *et al.*, 2011). The $\delta^{15}N$ value is often used to determine sources of pollution as NH_3 emissions from livestock waste (20–30‰) can contribute to higher $\delta^{15}N$ values where synthetic fertilisers have a $\delta^{15}N$ of around 0‰ (Choi *et al.*, 2003; Costanzo *et al.*, 2001). Raw manure becomes enriched with ^{15}N as the exposure to the atmosphere results in rapid loss of $^{14}NH_3$ through NH_3 volatilisation with composted manure having higher $\delta^{15}N$ than raw manure (Table 2.1; Kim *et al.*, 2008). As a result, the $\delta^{15}N$ of agricultural soils (+1 to 12‰) is generally higher than natural soils largely due to manure application. The wide range of $\delta^{15}N$ reflects the differences in application of N sources and the magnitude of N loss processes such as NH_3 volatilisation, denitrification and leaching (Choi *et al.*, 2017). Elevated $\delta^{15}N$ in sediments has been shown to be correlated to DIN concentrations indicating $\delta^{15}N$ to be a useful indicator of eutrophication (Lake *et al.*, 2001).

Table 2.1 The $\delta^{15}N$ of different types of fertilisers, adapted from (Choi *et al.*, 2017).

N source	$\delta^{15}N$
Synthetic fertiliser	
Urea	-1.2
Ammonium sulphate	-0.5
Ammonium nitrate	+0.1
Raw manure	
Cattle manure	+8.4
Pig manure	+6.7
Poultry manure	+7.1
Composted manure	
Cattle manure composted	+6.8
Pig manure composted	+16.5
Poultry manure composted	+11.8

Synthetic fertiliser use has accelerated since the industrial revolution through the invention of the Haber Bosch process (Holtgrieve *et al.*, 2011). Inputs of N produced through fertiliser use can be detected in sediments as they will have lower $\delta^{15}N$ compared to catchment sources (Hastings *et al.*, 2009; Heaton *et al.*, 2004). N from atmospheric sources (N fixation, N deposition) will also result in lower $\delta^{15}N$ values as they are derived from atmospheric N_2 (Teranes and Bernasconi, 2000). Lower $\delta^{15}N$ values in sedimentary records has been observed even in remote lakes especially since the start of the 20th century and in particular the last 40-50 years (Anderson *et al.*, 2018; Elser, 2011;

Holtgrieve *et al.*, 2011; Fig. 2.5) although there is indication of this trend slowing since the 1990s (Gąsiorowski and Sienkiewicz, 2013).

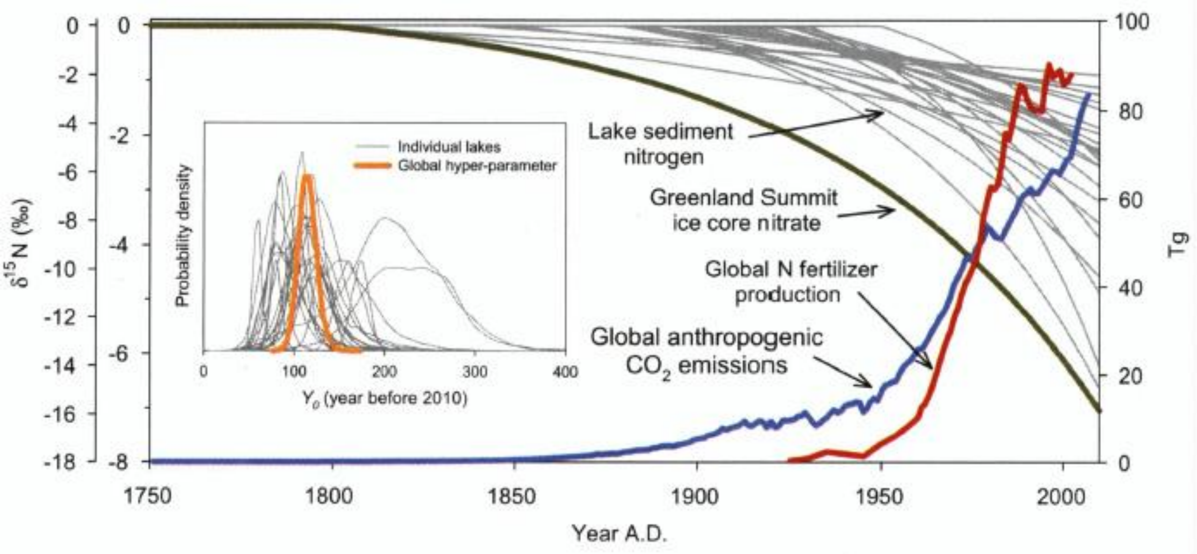

Fig. 2.5 Relative change in sedimentary $\delta^{15}N$ from 25 Northern Hemisphere lakes over the past 260 years with global CO_2 emissions and N fertiliser production (Holtgrieve *et al.*, 2011).

While diagenesis typically has a negligible impact on $\delta^{13}C$ (Meyers, 1994) there is a small impact on the $\delta^{15}N$ and C/N ratio of the sediments soon after deposition (Galman *et al.*, 2009). The breakdown of labile fractions of N compounds can affect their isotope composition in sediments with an increase in $\delta^{15}N$ as ^{14}N is preferentially utilised by bacteria due to the lower energy requirements to break the bonds (Brahney *et al.*, 2014). The longer the time spent in the water column before deposition the greater the change from the initial $\delta^{15}N$ value (Teranes and Bernasconi, 2000). $\delta^{15}N$ increases of up to 1-2‰ can be observed in oxygenated lake sediments within the first 50 years of deposition as a result of diagenesis (Brahney *et al.*, 2014; Sobek *et al.*, 2014). This also leads to an increase in the C/N ratio as N rich compounds are preferentially degraded over C compounds (Lehmann *et al.*, 2002). Under anoxic conditions $\delta^{15}N$ alterations through OM degradation are minimal and so the magnitude of $\delta^{15}N$ increase through diagenesis is proportional to bottom water O_2 concentrations (Sachs and Repeta, 1999). Although these diagenetic effects tend to be minor their influence means that changes in $\delta^{15}N$ cannot always be used as a quantitative indicator to the source of N but can help to understand the qualitative impact of different N sources (Enders *et al.*, 2008; Robinson, 2001).

N cycling in lakes is complex with $\delta^{15}N$ influenced by the source of organic matter, atmospheric inputs, fractionation during ammonia and nitrate assimilation, N fixation and internal recycling of organic compounds through ammonification, nitrification, and denitrification (Teranes and Bernasconi 2000; Talbot 2001). Nitrification, denitrification and ammonia volatilisation are known to have large fractionation effects with ammonification, microbial immobilisation and plant uptake having a lower effect on N fractionation (Choi *et al.*, 2017). Sediments can also become enriched in ^{15}N through nitrification which results in the microbial immobilisation of ^{15}N enriched NH_4^+ while ^{15}N depleted NO_3 is lost through denitrification and leaching (Choi and Ro, 2003). In general, nitrification by bacteria may increase $\delta^{15}N$ values (Fogel and Cifuentes, 1993) while denitrification results in the enrichment of ^{15}N organic matter increasing sedimentary $\delta^{15}N$ values (Lehmann *et al.*, 2004; Talbot, 2001; Teranes and Bernasconi 2000). As several N transformation processes occur simultaneously the process with the greater $\delta^{15}N$ fractionation will be reflected most prominently in the sediment (Lim *et al.*, 2015). Overall, the N cycle is much more complex than for C and as such interpretation of sedimentary $\delta^{15}N$ values should be carried out with caution (Lehmann *et al.*, 2004). However, in conjunction with other biogeochemical proxies $\delta^{15}N$ values can be a valuable tool to understand changes in lake nutrient cycling and productivity.

2.2.2 Sedimentary photosynthetic pigments

Photosynthetic pigments are water insoluble lipophilic molecules that are present in all autotrophic organisms (Jeffrey *et al.*, 1997; Millie *et al.*, 1993). Pigments are readily preserved in sediments providing a record of algal biomass and community composition at the time of deposition (Airs *et al.*, 2001; Leavitt and Hodgson, 2001). Sedimentary pigments are often the only remains of non-siliceous algae and have been shown to correlate with overall algal abundance and abundance of specific algal groups in the water column (Leavitt and Findlay 1994; Leavitt *et al.*, 1999). Pigments, along with their transformation products, provide a well-established tool to reconstruct past algal communities and environmental conditions (Paerl *et al.*, 2003; Squier *et al.*, 2004).

Like all forms of OM, photosynthetic pigments are subject to transformation with rates of degradation highly dependent on environmental conditions (Leavitt and Hodgson, 2001). In the water column pigment degradation is typically very rapid with around 95% of all pigments degrading before they reach the sediment due to exposure to heat, light and O_2, along with being biologically transformed through herbivore grazing and microbial activity (Fig. 2.6, Reuss, 2005; Louda *et al.*, 1998). Concentrations of O_2 have been shown to be one of the most important factors which affect pigment concentrations in lake sediments, with anoxia at the sediment-water interface reducing ingestion of pigments and bioturbation from the benthic community (Bianchi *et al*., 2000; Ingalls *et al*., 2000; Szymczak-Żyła *et al*., 2017). Therefore, in productive lakes, algal pigments tend to be well preserved due to the rapid burial of OM into anoxic sediments (Leavitt, 1993). In general, benthic taxa often contributes a larger proportion of pigments to the sediment through lower degradation than pigments derived from the water column (Buchaca and Catalan, 2007).

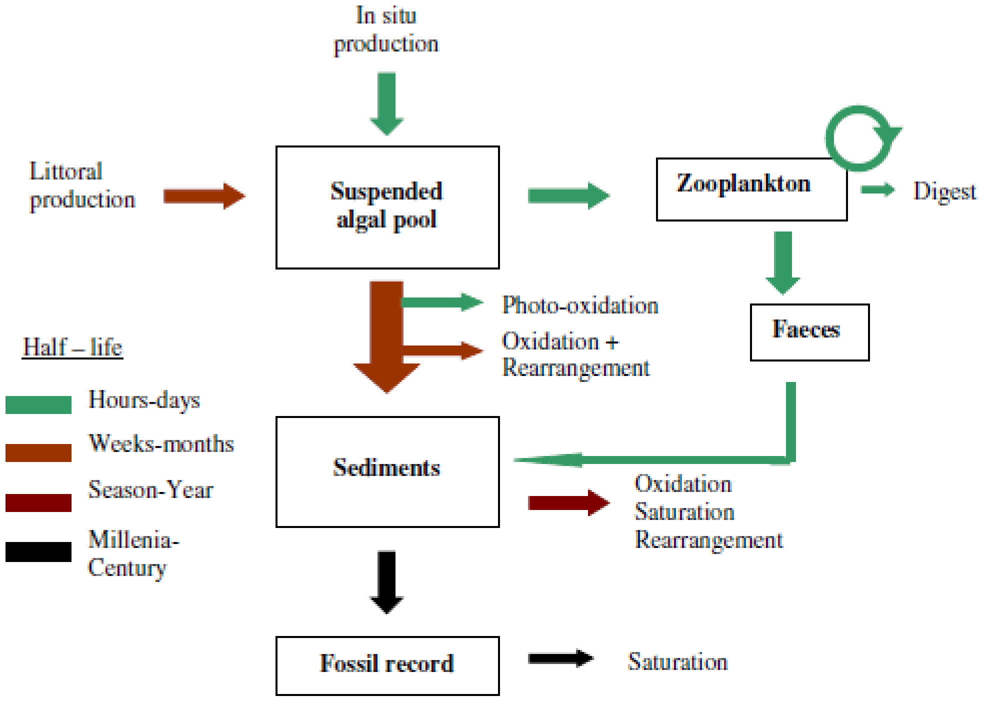

Fig. 2.6 Major fluxes of autochthonous pigments in freshwater lakes. Arrows indicate degradation processes and their approximate transformation rates (Reuss, 2005).

Some pigments are derived from all algal groups (e.g. chlorophyll-*a*, pheophytin-*a*) and provide a useful indicator of total algal abundance. Some carotenoids (e.g. alloxanthin, echinenone) are taxonomically specific indicating groups such as cryptophytes and cyanobacteria (Table 2.2, Leavitt and Hodgson, 2001). These specific markers enable the reconstruction of past environmental conditions of lakes as some groups will have preferences for particular environmental conditions (McGowan, 2013). However, differences in molecular stability between pigments results in some being well preserved in the sediment where other more labile pigments can be completely absent (Leavitt and Hodgson, 2001).

Table 2.2 Summary of sedimentary pigments, their taxonomic affinities/environmental interpretation. The relative degree of stability is ranked from most (1) to least stable (4). Adapted from Leavitt and Hodson (2001), Squier *et al*. (2005) and Krajewska *et al*. (2019).

Pigment	**Affinity (major group)/interpretation**	**Stability**
Chlorophylls		
Chlorophyll-*a*	All photosynthetic algae	3
Chlorophyll-*b*	Chlorophytes	2
Chlorophyll-*c*	Dinoflagellates, diatoms	4
Carotenoids		
β-carotene	Most algae	1
α-carotene	Cryptophytes	2
Alloxanthin	Cryptophytes	1
Fucoxanthin	Diatoms, some dinoflagellates	2
Diadinoxanthin	Diatoms, some dinoflagellates	3
Diatoxanthin	Diatoms, some dinoflagellates	2
Peridinin	Dinoflagellates	4
Zeaxanthin	Picocyanobacteria, some chlorophytes	1
Canthaxanthin	Filamentous cyanobacteria	1
Crocoxanthin	Cryptophytes	-
Echinenone	Total cyanobacteria	1
Lutein	Chlorophytes	1
Chlorophyll degradation products		
Phaeophytin-*a*	Preservation condition	1
Phaeophytin-*b*	Preservation condition	2
Phaeophorbide a	Grazing, senescence	3
Hydroxyphaeophytin-*a*	Oxidising conditions	-
Purpurin-18-phytl ester	Oxidising conditions in the water column	-
Pyrophaeophytin-*a*	Anoxia	2
Steryl chlorin esters (SCE)	Zooplankton grazing	-
UV absorbing compounds		
Scytonemin	benthic UV radiation	-
Reduced scytonemin	benthic UV radiation	-

Pigments can be classed into four families of compounds: carotenoids, chlorophylls, chlorophyll degradation products (e.g. phaeophytins) and light screening pigments such as scytonemins (Giovannetti *et al*., 2013).

I. Carotenoids

Carotenoids are a large group of pigments constituting over 700 compounds (Britton *et al*., 2004). Over 30 types of algal carotenoids have been reported to function in photosynthesis with many other intermediates, derivative and degraded products (Takaichi, 2011). The two main types of carotenoids are carotenes, such as β-carotene that is present in most algae, and their oxygenated derivates xanthophylls (Kuczynska *et al*., 2017). Carotenes are used by aquatic algae to maximise photosynthetic efficiency (Brunet *et al*., 1993; Hodgson *et al*., 2004). Xanthophylls act as photoprotective pigments to protect cells against excessive light exposure and their production is driven by the xanthophyll cycle (Latowsk *et al*., 2004; Vílchez *et al*., 2011). Some carotenoids are only found in specific algal groups and therefore can be used as taxonomic markers (Takaichi, 2011). An example of this would be alloxanthin, which are found in cryptophytes (Buchaca and Catalan, 2007; Pennington *et al*., 1985; Squier *et al*., 2004). As alloxanthin is derived exclusively from planktonic cryptophytes its presence in high concentrations indicates substantial planktonic primary production (Lami *et al*., 2000).

While fucoxanthin is commonly used as a pigment marker specific to diatoms, it can also be produced by some chrysophytes (Buchaca and Catalan, 2007; Rowan, 1989). Due to chemical instability fucoxanthin often degrades rapidly after deposition, resulting in decreasing sedimentary concentration down a core (Freiberg *et al*., 2011; Reuss *et al*., 2005). Due to their high lability, both fucoxanthin and diadinoxanthin can be sensitive to changes in the water column. As a result they are typically excluded from analysis to minimise the influence of pigment degradation (McGowan *et al*., 2005). However, the presence of fucoxanthin (along with diadinoxanthin) can indicate benthic diatom communities as their high lability makes it unlikely that these pigments are of planktonic origin (Buchaca and Catalan, 2007).

The more stable diatoxanthin is commonly used to indicate past diatom communities (e.g. McGowan *et al*., 2014; Moorhouse *et al*., 2018) with its sedimentary abundance shown to be well correlated with diatom biomass (Bianchi *et al*., 2002). While diatoxanthin is typically used to represent diatom biomass (Buchaca and Catalan, 2007), diatoxanthin is potentially also produced by some dinoflagellates (Olaizola *et al*., 1994; Reuss *et al*., 2005; Rowan, 1989). The contribution of dinoflagellates is also complicated by the fact that their primary pigment marker (peridinin) is very labile and not often found in sediments (Buchaca and Catalan, 2007; Reuss *et al*., 2005). Although diatoxanthin also occurs in some dinoflagellate species, it is often considered as a diatom specific carotenoid, along with fucoxanthin and diadinoxanthin (Kuczynska *et al*., 2017).

Zeaxanthin is one of the major light harvesting carotenoids produced in aquatic environments (Holt *et al*., 2005). Zeaxanthin often has widespread abundance in aquatic sediments and is typically derived from non colonial cyanobacteria, or picocyanobacteria (Krajewska *et al*., 2019). Cyanobacterial pigments are typically very stable and abundances of zeaxanthin in lacustrine sediments have regularly been used to indicate historical cyanobacteria populations (Leavitt and Hodgson, 2001; Squier *et al*., 2004). However, zeaxanthin can also be derived from chlorophytes which can often prevent the identification of which source is driving any change (Hall *et al*., 1997; Squier *et al*., 2004). Chlorophytes produce lutein as their primary carotenoid (Squier *et al*., 2004; Takaichi, 2011). If there is a higher correlation of zeaxanthin to lutein then other cyanobacteria pigments then this may suggest that the source of zeaxanthin is predominantly from chlorophytes (Krajewska *et al*., 2019). If there is strong correlation of both canthaxanthin and echinenone to zeaxanthin then this would indicate a strong contribution of zeaxanthin from cyanobacteria (Deshpande *et al*., 2014).

Filamentous cyanobacteria tend to have a wide range of carotenoids some of which are not found in free-living cyanobacteria (Grant and Louda, 2010). Canthaxanthin has been shown to be a more specific marker for some colonial cyanobacteria such as the filamentous order *Nostocales*, some of which are heterocystous (Freiberg *et al*., 2011; Patoine and Leavitt 2006). As a result, canthaxanthin has been used to represent filamentous taxa and echinenone shown to be a reliable indicator for all cyanobacteria, especially in lakes where zeaxanthin is likely derived from multiple sources (Deshpande *et al*., 2014; Krajewska *et al*., 2019). Additionally, myxoxanthophylls have been suggested to be markers for specific strains of cyanobacteria, such as certain toxic or nitrogen fixing taxa. However these pigments are less stable than the other cyanobacterial carotenoids meaning they are not always detectable in sedimentary samples (Schlüter *et al*., 2004; Leavitt and Hodgson, 2001).

II. Chlorophylls and their degradation products

Chlorophyll is a major pigment used for light harvesting and photosynthesis (Mur *et al*., 1999). As chlorophyll-*a* is present in every algal group it is used as a general proxy for total algal biomass (Louda 2008). As chlorophyll contains N it is prone to biological breakdown through allomerisation (oxidation), demetallation (loss of the Mg), and dephytylation (loss of phytyl chain) (Leavitt and Hodgson, 2001; Porra *et al*., 1997). Due to chemical instability, chlorophyll-*a* often degrades rapidly during the sedimentation process into phaeophytin-*a* (Freiberg *et al*., 2011; Fig. 2.7, Giovannetti *et al*., 2013). However, beyond the surface sediments chlorophyll and its degradation products preserve well in sediments allowing them to be detected through regular HPLC analysis (Carpenter *et al*., 1986; Leavitt, 1993; Leavitt and Hodgson, 2001). The transformation of chlorophylls into their derivatives is regulated by sediment and water column characteristics (e.g. anoxia, stratification, light) and their abundances can indicate lake conditions at the time of deposition (Naylor and Keely, 1998; Hodgson *et al*., 1998).

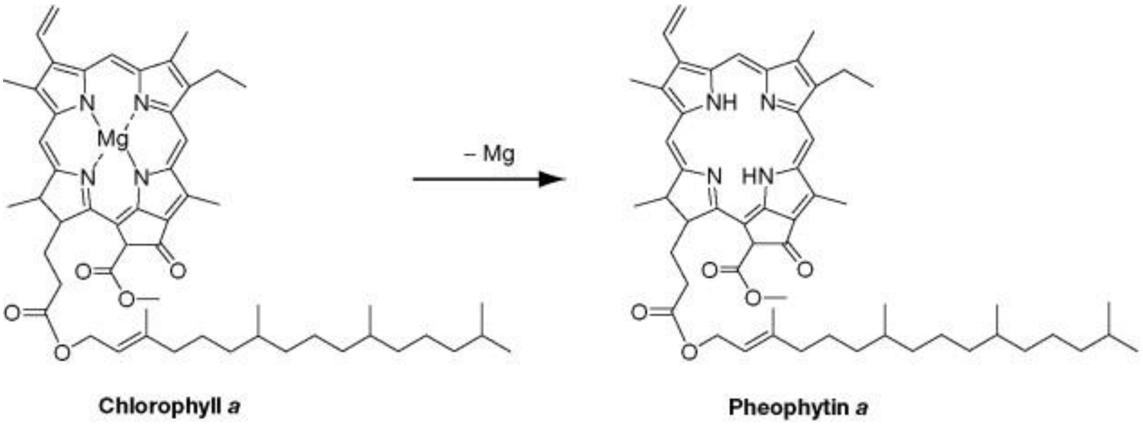

Fig. 2.7 Transformation of chlorophyll to phaeophytin through demetallation (Keely, 2006).

Differences in the ratios of chlorophyll-*a*/pheophytin-*a* can indicate changes in the extent of pigment degradation in water column and the sediment (Deshpande *et al*., 2014). Low ratios of chlorophyll-*a* to its degradation products suggest high levels of degradation that could result from good O_2 conditions, sediment mixing and bioturbation (Deshpande *et al*., 2014; Reuss *et al*., 2005). Therefore changes in these ratios over time can indicate shifts in lake conditions and the post depositional environment (Jeffrey *et al*., 1997; Lami *et al*., 2000; Szymczak-Żyła *et al*., 2017).

Increased primary production may increase pigment preservation through the reduction of O_2 in bottom waters. This can make distinguishing between changes in primary production or preservation conditions difficult (Leavitt, 1993). If the rise in pigment concentrations is greater than the increase in ratios between chlorophyll-*a* and its degradation products then this suggests it is not solely related to diagenetic processes (Deshpande *et al*., 2014).

Chlorophyll oxidation products can often be minor components in sediments, with their widespread occurrence indicating a well oxygenated aquatic environment absent from anoxia (Airs *et al*., 2000; Szymczak-Żyła *et al*., 2017). The major oxidation product of chlorophyll-*a* is usually hydroxyphaeophytin-*a* with the ratio of hydroxyphaeophytin-*a* to the unoxidised phaeophytin-*a* and pyrophaeophytin-*a* used to express O_2 availability (Walker *et al*., 2002). Purpurin-7 phytyl ester and purpurin-18 phytyl ester are oxidative transformation products of chlorophylls formed during the early stages of chlorophyll diagenesis (Airs *et al*., 2000; Naylor and Keely, 1998). Minor amounts of purpurin-18 phytyl ester and purpurin-7 dimethyl phytyl ester indicate oxidising conditions in the water column at the time of deposition (Squier *et al*., 2005). Therefore, the co-occurrence of hydroxyphaeophytins with the purpurins can indicate lakes with fully oxygenated water columns (Naylor and Keely, 1998).

III. Scytonemins

Understanding lake water ultra-violet (UV) conditions is important to be able to fully assess the drivers of aquatic ecological responses. Photosynthetically active radiation (PAR) is sunlight of 400 to 700 nm wavelength that is used by plants and algae in photosynthesis (Chen *et al*., 2015). PAR levels in aquatic environments can vary due to a range of factors including algal biomass, meteorological conditions, ice-cover, DOC and non-organic particles which can scatter incoming radiation (Gao and Xu, 2008; Hodgson *et al*., 2005; Verleyen *et al*., 2005). In aquatic ecosystems, high UV radiation can result in damage to the proteins, lipids, DNA and photosynthetic pigments in microbial cells, largely through oxidative stress which leads to growth inhibition and death (Garcia-Pichel and Castenholz, 1991; Sinha and Hader, 2002; Bancroft *et al*., 2007).

To protect cells against high UV radiation some microorganisms synthesise photo-protective pigments such as scytonemin which is found in extracellular sheaths (Garcia-Pichel and Castenholz, 1991; Sinha and Hader, 2008). Scytonemin is a lipid soluble UV-screening pigment produced by species of cyanobacteria in every major group by genus such as *Nostoc*, *Calothrix*, *Chlorogloeopsis*, *Lyngbya*, and *Chroococcidiopsis* (Garcia-Pichel and Castenholz, 1991; Sinha *et al*., 1998). Scytonemin is thought to be produced exclusively by benthic cyanobacteria and largely absent from planktonic species (Squier *et al*., 2004). As a result, scytonemin is regularly observed in sediments of shallow littoral zones which receive higher UV radiation (Leavitt *et al*., 1997; Cantonati *et al*., 2013).

As scytonemin production increases under elevated UV exposure its abundance can be used to indicate UV radiation intensity (Dillon *et al*., 2002; Brenowitz and Castenholz 1997). To account for changes in productivity that could increase scytonemin production, concentrations are typically compared to concentrations of cyanobacterial carotenoids (e.g. echinenone, canthaxanthin, zeaxanthin) with high ratios indicating high UV radiation (Chen *et al*., 2015; Giovannetti *et al*., 2013). Lake water depth is a major factor that influences scytonemin production as depth of the water column determines how much light reaches the benthic zone (Hodgson *et al.*, 2004; Verleyen *et al.*, 2005). Therefore in lakes which have a stable water level scytonemin is generally used as a proxy for past UV conditions (Leavitt *et al.*, 1997). However, in lakes that observe high water level fluctuations it is likely that the exposure of the lake bed to more UV radiation becomes a dominant driver of scytonemin production (Cantonati *et al.*, 2013).

2.2.3 Geochemical analysis of heavy metals and trace elements

The physical, chemical and biological characteristics of lakes can vary enormously, largely controlled by catchment processes (Davies *et al.*, 2015). These catchment processes can be inferred through sedimentary trace element concentrations as erosion delivers mineral and organic matter to lakes (Oldfield *et al.*, 2003; Yang and Rose, 2005a). The input of eroded material has a controlling influence on trophic status (productivity), redox conditions and sedimentation rates (Bonk *et al.*, 2016). In many lakes sediments are the final sink for many heavy metals and hydrophobic organic contaminants, as they adsorb strongly to eroded mineral matter (Engstrom and Rose, 2013). Therefore, trace elements that are deposited in lake sediments can be used to indicate a range of in-lake and catchment changes.

Elemental analysis can be a particularly useful tool in identifying relative changes in the amount of material derived from a lake catchment (Davis *et al.*, 2015). Indicators of catchment derived inputs include Al, Ti and Fe as they are typically derived from resistant terrestrial minerals and are geochemically stable (Boës *et al.*, 2011). As the concentrations of Al and Ti are high in the Earth's crust, they represent substantial natural terrestrial inputs to lakes from catchment soils through erosion and leaching (Davies *et al.*, 2015; Sarkar *et al.*, 2015). As the catchment provides relatively large quantities of these elements, any changes in atmospherically deposited Al or Ti often have a negligible impact on sedimentary concentrations (Sarkar *et al.*, 2015; Yang and Rose, 2005a).

Input of K has also been shown to be a good indicator of catchment erosion and is typically derived from feldspar bedrock (Morad, 2013). Increases in sedimentary K often correspond with periods of low catchment vegetation cover that leads to increased erosion. During periods of increased catchment vegetation, sedimentary K values are reduced due to the more stable soils (Foerster *et al.*, 2012). Additionally, Mg can be used to indicate inwash from dolomite rocks (Lauterbacher *et al.*, 2011) and Li from silicate bedrocks (Lemarchad et al., 2010). These elements are very stable and insoluble in oxide form and as such they are commonly used as an indicator of allochthonous inputs (Norton *et al.*, 1992; Fedotov *et al.*, 2012).

As weathering is largely influenced by precipitation and temperature, higher concentrations of lithogenic elements can be used to infer enhanced catchment run-off and essentially wetter conditions (Davies *et al*., 2015). Increases in lithogenic elements along with decreases in OC content can be a key indicator of increased catchment erosion as sedimentary OM is diluted by mineral matter (Yang and Rose, 2005a). Although Ti is a more commonly used marker of allochthonous input Al has been found to be just as useful in providing an indicator of catchment erosion and a conservative element against which to normalise changes in other elements (Sarkar *et al*., 2015). However, Al distribution can be affected by pH so Al concentrations may be impacted by acidification in some lakes (Yang and Rose, 2005a).

Sedimentary P concentration is a widely used proxy to indicate changes in external P loading (e.g. Søndergaard *et al*., 2003). Changes in the concentrations of sedimentary P have been shown to coincide with periods of change in land cover and agricultural activity in a lake catchment, which impact P exports (Boyle *et al*., 2014). Internal P dynamics can be impacted by redox conditions, which can be indicated by the presence of Fe and Mn in the sediment profile (Fedotov *et al*., 2012). Reducing conditions are important in nutrient loading as this leads to P species that are bound to Fe oxides being released from the sediment to the water column (Junlong *et al*., 2015). When a lake is well oxygenated insoluble oxides of Fe and Mn readily precipitate in the water and get deposited in the sediment (Naeher *et al*., 2013; Ng and King, 2004). If a lake experiences anoxic episodes, Fe and Mn will appear in their soluble form meaning less is present in the sediment (O'Sullivan and Reynolds, 2005). Mn/Fe ratios have frequently been used to reconstruct past redox conditions as Mn is reduced more rapidly than Fe under anoxic conditions and Fe oxidises more rapidly under oxic conditions (Naeher *et al*., 2013). Therefore, a lower Mn/Fe ratio would indicate reducing conditions and low O_2 availability in bottom waters (Lodenius *et al*., 2008).

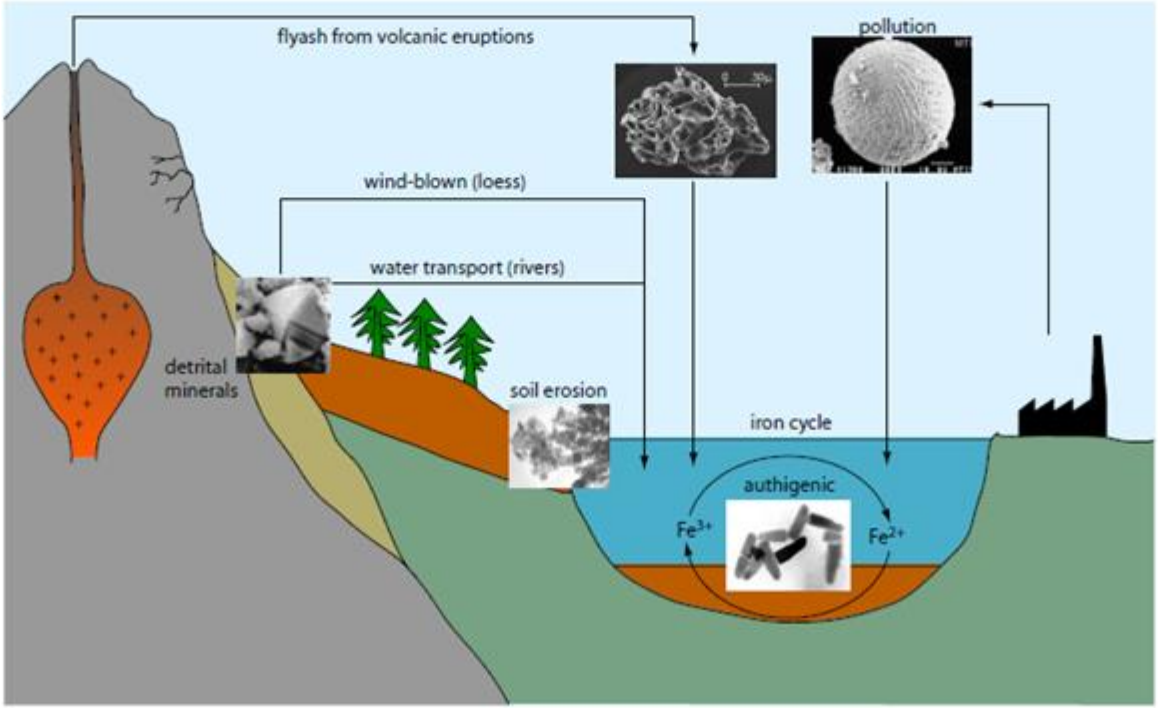

Fig. 2.8 Sources of minerals in lake sediments.

Coal combustion and heavy industry can produce uncombusted mineral particles (often known as fly ash) which contain inorganic components such as heavy metals. These heavy metals can enter lake catchments through atmospheric deposition and impact on lake biogeochemical cycling (Fig. 2.8) (Oldfield *et al*., 2014). As a result, sedimentary concentrations of heavy metals (e.g. Cu, Zn, Cd, Pb) are commonly used indicators of anthropogenic pollution in aquatic environments (Forstner and Wittmann, 1979; Salomons and Forstner, 1984; Sarkar *et al*., 2015; Yang and Rose, 2005a). They have also be used to indicate more specific sources, such as Cu, Pb and Zn mining in the Lake District (Miller *et al*., 2014) with Cr and Ni used to indicate wastewater pollution from the leather industry (Algul and Beyhan, 2020). Heavy metal concentrations can also be affected by the presence of binding sites, changes in oxidation state, changes in solubility and be diluted by high concentrations of $CaCO_3$, organic matter and high sedimentation rates (Lodenius *et al*., 2008; Sarkar *et al*., 2015; Yang and Rose, 2005a). Heavy metal concentrations often correlate due to being derived from the same industrial sources (Lodenius *et al*., 2008). Correlation of metals with the OM content would indicate an organic source whereas correlation with Ti/Al would indicate an association with mineral matter (Yang and Rose, 2005a). In general, there are a wide range of sedimentary elements that can be used to indicate both in lake, catchment and atmospheric changes, with a more extensive assessment described in Davies *et al*. (2015).

2.2.4 Sedimentary chronologies

Accurate sedimentary chronologies are essential to understand the timings of ecological shifts, which can be used to assess the causes of changes in aquatic environments. When investigating anthropogenic impacts on lakes over the recent past, cores are typically sampled to around 1850, which also represents the general limits of ^{210}Pb dating (Battarbee *et al*., 2012). While ^{210}Pb dating can allow for analysis to be undertaken at a high temporal resolution its use if often limited due to its relatively high cost (Engstrom and Rose, 2013). However, the accurate dating of sediment cores is essential to accurately reconstructing the timings of environmental change.

Lake sediments contain the natural radioactive element ^{210}Pb (half-life of 22.26 years) which decays from ^{226}Ra (Battarbee *et al*., 2012). There are two forms of ^{210}Pb that are considered in dating models, supported ^{210}Pb which is derived from *in situ* decay of ^{222}Ra in lake sediment and unsupported ^{210}Pb which results from decayed atmospheric ^{222}Rn which is deposited in lakes (Fig. 2.9). As unsupported ^{210}Pb cannot be measured directly it is calculated by subtracting the supported ^{210}Pb from the total ^{210}Pb activity (Appleby, 2008). Total ^{210}Pb and supported ^{210}Pb are measured indirectly using alpha or gamma spectrometry, assuming they are in equilibrium to ^{210}Po and ^{226}Ra activity respectively (Harle and Heijinis, 2014). The calculated activity of unsupported ^{210}Pb is compared to activity with depth to develop ^{210}Pb chronologies (Noller, 2000).

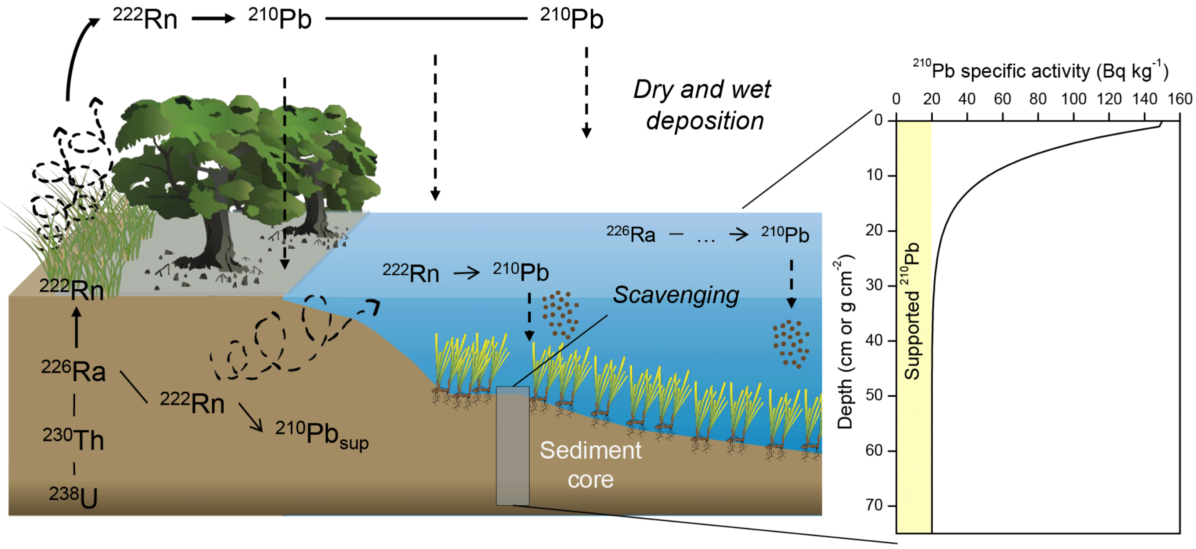

Fig. 2.9 ^{210}Pb input into a lake and idealised ^{210}Pb specific activity profile in sediments (Arias-Ortiz *et al*., 2018).

Using simple models, the fractions between the parent and daughter isotopes can be used to date the sediment (Appleby, 2008). Dating from ^{210}Pb decay requires the estimation of the original ^{210}Pb concentration when it was initially deposited on the sediment surface (Appleby, 2013). The two most common models used are the constant rate of supply (CRS) and the constant initial concentration (CIC) models (Robbins, 1978; Appleby and Oldfield, 1978). While the CRS model is more widely used, changes in precipitation (Appleby, 2001) and sedimentation rates can result in variations of ^{210}Pb delivery to the sediments over time (Engstrom and Rose, 2013). In lakes subject to such environmental changes the CIC model is likely to provide a more accurate dating method (Appleby, 2008). Sediment dating through ^{210}Pb is probabilistic with the standard deviation and uncertainty ranges increasing with depth (Grosjean, 2009).

To validate ^{210}Pb derived chronologies the activities of artificially produced radionuclides (^{137}Cs, ^{241}Am) can also be measured. Increases in these radionuclides relate to nuclear weapons testing, which peaked in 1963, and the Chernobyl disaster of 1986 to provide specific dating markers (Appleby, 2008). However, physical and biological mixing of sediments can also impact radionuclide distributions as ^{137}Cs is particularly mobile, especially in organic-rich sediments (Appleby, 2001; Appleby, 2004). Conversely, ^{137}Cs adsorbs strongly to clay minerals, especially in higher pH and low O_2 environments (Foster *et al*., 2006). As ^{241}Am is considerably less mobile than ^{137}Cs it can help to date sediments where the ^{137}Cs record has been degraded (Appleby *et al*., 1991).

2.3 Summary

This chapter has described the pressures experienced in UK lakes since the industrial revolution. While the impact of many of these pressures have been declining in more recent decades (e.g. acidification, heavy metal pollution) some are still a persistent problem (e.g. eutrophication). Climate change presents a more recent driver of change and although the impacts on lake systems have been widely predicted, the exact effects are less clear often being confounded by other anthropogenic factors. Algae are a commonly used group of organisms that are used to assess ecological impacts from anthropogenic drivers in lakes. Their short generation times and relative simplicity as organisms mean they can be particularly sensitive to change. Palaeolimnology assesses past changes in lake algae through the analysis of photosynthetic pigments that accumulate in the sediments over time. Algal pigments can establish change on both a population and community level enabling a relatively detailed assessment of algal change over time. In conjunction, stable isotopes from organic matter (δ^{13}C, δ^{15}N) can be used along with trace element analysis to indicate the drivers and impacts of past environmental change. The identification and separation of drivers can aid in establishing the impacts of climate change through the utilisation of high resolution dated reconstructions of algal biomass during the 20th century.

3. Materials and methods

This chapter describes the core collection and laboratory methods used in the sediment core analysis. It outlines the loss on ignition, C/N ratios and stable isotopes analyses on organic matter and carbonates. It also describes the sedimentary pigment extraction process along with the subsequent HPLC analysis and quantification. The process for establishing sediment chronologies and the development of the age-depth models will be explored along with the methods for quantification of sedimentary trace elements. The use of instrumental meteorological data with statistical analysis will also be explained. A summary of the laboratory methods used in sediment core analysis is summarised in Table 3.1.

Table 3.1 Summary of the parameters investigated, laboratory analysis performed and sampled resolution.

Investigated	**Parameter**	**Laboratory analyses**	**Sampled resolution**
Algal biomass and community composition	Photosynthetic pigments	HPLC	0.25 cm
Quantity and source of organic matter	Bulk C/N and stable isotopes ($\delta^{13}C$, $\delta^{15}N$)	Mass spectrometry	0.25 cm
Quantity of inorganic matter	Minerogenic and carbonate content	Loss on ignition	1 cm
Catchment inputs and atmospheric pollution	Concentrations of metallic and minerogenic elements	Elemental analysis through ICP-OES	1 cm
Dates sediments were deposited	Isotopes of ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am	Direct gamma assay	14-17 samples per core*

*sediment core samples were pre-scanned for Pb concentrations at 0.25 cm resolution with 14-17 that were deemed the most appropriate for ^{210}Pb dating used for direct gamma assay

3.1 Core collection, sampling and storage

Fieldwork was undertaken in August 2018 to collect sediment cores from the three lakes and tarns. The deepest area of each lake was identified using known bathymetry and water column depths were recorded using a weighted rope with incremental measurement markings. All cores were retrieved using a Pylonex HTH gravity corer (70mm diameter x 50cm length) and locations were recorded using a handheld Global Positioning System (Table 3.2). After extraction the cores were subsampled in the field using the coring extrusion device at a 0.25cm resolution, labelled and sealed in airtight bags. The sediments were stored in a cooled (+4°C) plastic box to prevent pigment degradation and frozen immediately at −25°C on return to the laboratory at the University of York.

Table 3.2 Study site coring details, grey shading indicates core used for pigment, isotope, radiometric and trace element analysis.

Site	Date of coring	BNG coordinates of core location	Water depth where core retrieved (m)	Length of core after extrusion (cm)
Blea Tarn	07/08/2018	NY 29313 04399	6	37.25
	07/08/2018	NY 29318 04394	5.5	36
Sunbiggin Tarn	28/08/2018	NY 67607 07641	8	33.5
	28/08/2018	NY 67609 07640	6.5	34.25
Lake Gormire	31/08/2018	SE 50295 83198	6	45
	31/08/2018	SE 50301 83197	5.5	41

Lithogenic analysis including OM content (%LOI_{550}), carbonate content (%LOI_{950}*1.36) and minerogenic content (100-%LOI_{550}+%LOI_{925}), which are described in section 3.2.1, were used to help determine which core should be chosen for further analysis. The two cores extracted from Blea Tarn and Lake Gormire showed no visible differences in the sedimentological records. As a result, for both lakes, the longer cores were chosen for further analysis. The Sunbiggin Tarn core revealed visible differences between the two cores extracted with an extensive horizon of carbonate and gastropod shell remains in the core taken from greater water depth, which was absent from the other core. Lithogenic analysis indicated that the absence of the carbonate horizon in the core taken from shallower depths was likely due to it being a short temporal record. As a result the core with the carbonate horizon was selected for further analyses.

3.2 Laboratory analysis

3.2.1 Loss on ignition

Loss on ignition (LOI) was used to calculate organic matter, minerogenic content and carbonate content (Heiri *et al.*, 2001) largely to provide information on elemental abundances for organic and carbonate isotope isotopic analysis. Dry bulk densities (g cm^{-3}) for each 0.25cm subsample was calculated by weighing the sediments after freeze drying and dividing the known volume (8.55 cm^3).

Approximately 100mg of dry sediment was ignited at 550°C in a muffle furnace for 4 hours and weighed again after cooling to estimate organic matter content (%LOI_{550}). Following this samples were returned to the furnace at 950°C for 2 hours to calculate carbonate content (%LOI_{950}*1.36). Minerogenic content was calculated as % of residue remaining after ignition at 950°C (100-%LOI_{550}+%LOI_{950}).

3.2.2 Organic matter C/N ratios and stable isotopes

I. Carbon isotope ratios in organic matter

200mg of freeze-dried sediment was added to 250ml glass beakers and treated with 25ml of 5% HCl overnight to remove any carbonates. The beakers were then topped up to 250ml with deionised water and left to settle. The overlying water was then decanted and the rinsing process was repeated another three times to neutralise the pH. On the final decant, the sediment was placed in a drying cabinet overnight at 40°C to minimise the loss of volatile compounds (Kim *et al.*, 2016). When dry the sediments were transferred into Eppendorf tubes and stored in low light conditions until subsampling. Sediment samples were weighed into tin capsules to provide 0.5 mg of organic carbon, based on the TOC content of the sediment, which was estimated using equation 2

$$Sediment\ required\ (mg) = \frac{50}{(\frac{\%LOI_{550}}{2})}$$

Equation 2

Samples were analysed for total organic carbon (TOC), total nitrogen (TN) and $\delta^{13}C_{org}$ at the National Environmental Isotope Facility (British Geological Survey). A Costech ECS4010 elemental analyser (TOC and TN) coupled on-line to a VG Triple-Trap and VG Optima dual-inlet mass spectrometer ($\delta^{13}C_{org}$) analysed the prepared samples. $\delta^{13}C_{org}$ values are reported on the Vienna Pee Dee Belemnite (VPDB) scale and were corrected using within-run laboratory standards (BROC2 and SOILB) that have known values calibrated against the international reference standards NBS 19 and NBS 22. Analytical reproducibility (1σ) for the within-run laboratory standards was <0.05‰ for $\delta^{13}C_{org}$ and <0.5% for TOC and TN. C/N is calculated as the mass ratio of C and N.

II. Nitrogen isotope ratios in organic matter

Freeze dried sediment samples (3-15 mg) were weighed into tin capsules to provide 0.1 mg of N, based on the %N content of the sediment, which was estimated using equation 3

$$Sediment\ required\ (mg) = \frac{9.6}{\%N}$$

Equation 3

Samples from Lake Gormire were analysed for $\delta^{15}N$ by combustion using a ThermoFinnigan Flash 112 elemental analyser coupled on-line via a Conflo III interface to a Delta Plus XL isotope ratio mass spectrometer. Isotope ratios are reported in delta notation versus air (atmospheric N_2) by comparison with laboratory standards (BROC2 and Soil A) calibrated against the international reference materials IAEA-N-1 and IAEA-N-2. Analytical precision based on repeat measurements of the laboratory standards was <0.2 ‰ (1σ).

Samples from Blea Tarn and Sunbiggin Tarn were analysed for $\delta^{15}N$ using an Elementar vario ISOTOPE cube elemental analyser coupled to an isoprime precisION isotope ratio mass spectrometer with an onboard centrION continuous flow interface system. Isotope ratios are reported in δ notation versus air (atmospheric N_2) by comparison with the laboratory standard BROC3, organic analytical standards B2162 (spirulina), B2155 (protein), and B2174 (urea), and the international reference material USGS40 (L-glutamic acid). Analytical precision based on repeat measurements of the laboratory standards was <0.2 ‰ (1σ).

III. Carbon and oxygen isotope ratios from carbonates

Samples from Sunbiggin Tarn (the only marl lake) were processed to remove any reactive organic material by submerging 500mg of sediment in 5% sodium hypochlorite for 24 hours. The sample was then rinsed with deionised water, dried at 40°C, and ground to a fine powder. The prepared samples were weighed to provide ~10 mg of calcite, based on LOI_{950} values, and reacted with anhydrous phosphoric acid overnight in a vacuum at a constant 25°C. The evolved CO_2 was cryogenically separated from water vapour under vacuum and then analysed using a VG Optima dual inlet mass spectrometer. The acid fractionation factor used for calcite was 1.01025, and $\delta^{18}O$ and $\delta^{13}C$ are reported in δ notation as ‰ deviations calculated to the VPDB scale using within-run laboratory calcite standards (MCS and CCS). The values were calibrated using the international reference materials NBS 18 and NBS 19. Analytical precision for the laboratory standards was <0.1 ‰ (1σ) for both $\delta^{18}O$ and $\delta^{13}C$.

3.2.3 Extraction, isolation, analysis and quantification of sedimentary pigments

I. Method for HPLC

Pigment extractions followed the methods described in Meyers *et al*. (2011). 200mg of freeze-dried sediment was taken from every 0.25cm interval and ground in a mortar and pestle. Sediments were transferred to a 5 ml centrifuge tube and immersed in 2ml of acetone under low light conditions to reduce photodegradation. The solution was then sonicated for five minutes to ensure adequate mixing followed by centrifuging at 3000rpm for five minutes. The overlying pigment solution was extracted from the sediment using a glass pipette and transferred to 20ml glass vials wrapped in aluminium foil. This process was repeated until the extract was visibly clear (minimum of four times) to optimise pigment extraction. The pigment extracts were syringed through a 0.2µm PTFE filter to remove any larger particles and evaporated using a vacuum centrifuge, following which they were stored at -20°C until analysis. The dried pigment extracts were re-dissolved in 500µL of methanol and transferred to 2ml glass vials.

II. Separation of pigments in HPLC

The pigment extracts were analysed at the University of York through HPLC using a PerkinElmer Flexar system comprised of a quaternary pump, autosampler, column oven and photodiode array (PDA) detector. The separation method consisted of 90-minute runtimes based on ‘method B’ from Airs *et al*., (2001) using mobile phase solvents of methanol, 0.01M ammonium acetate, acetonitrile, ethyl acetate through two connected Water SPHERISORB 3µm ODS2 columns (4.6x160mm). The solvent gradient stream is described in Table 3.3.

Table 3.3 HPLC solvent separation gradients. From Airs *et al*., (2001).

Time (min)	% ammonium acetate (0.01 M)	% methanol	% acetonitrile	% ethyl acetate	Flow rate (ml min^{-1})
0	5	80	15	0	0.7
5	5	80	15	0	0.7
81	1	32	15	52	0.7
85	5	80	15	0	0.7

HPLC chromatograms were used to identify pigments by comparing the online UV-vis spectra to reported absorbance spectra and retention times (Airs *et al*., 2001). Standards of fucoxanthin, diadinoxanthin and zeaxanthin were also run to establish retention times and aid pigment identification (Fig. 3.1-3).

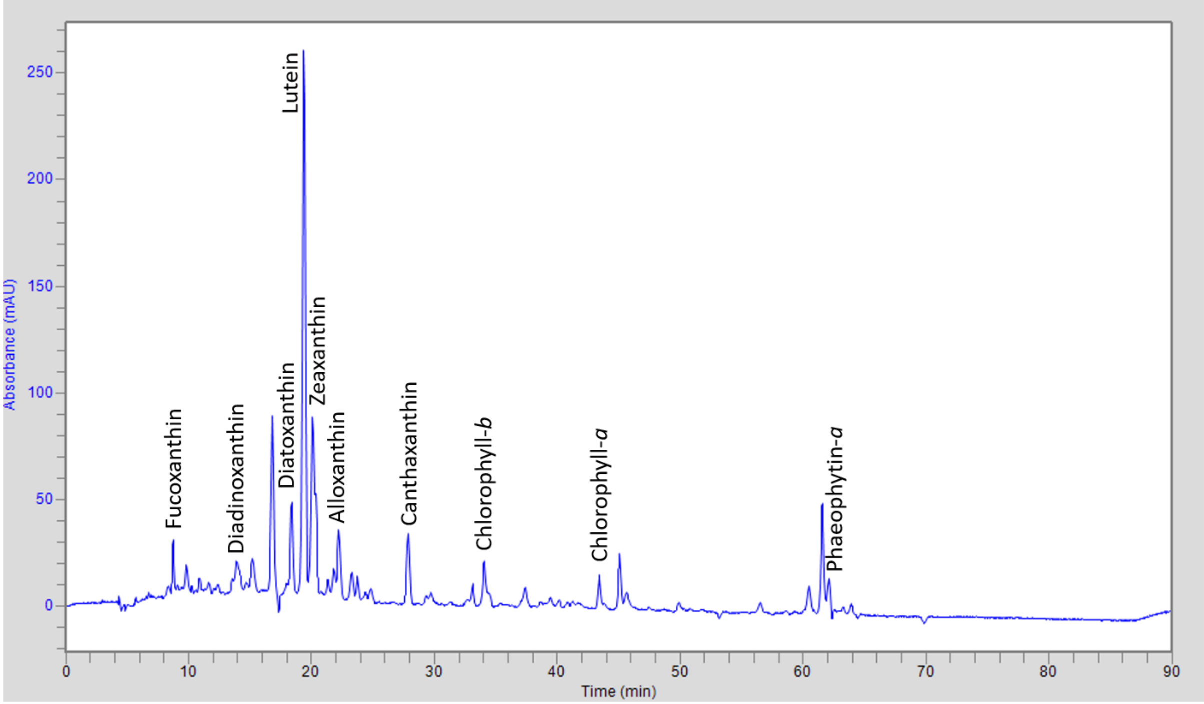

Fig. 3.1 HPLC chromatogram (450nm) with peak identification for Lake Gormire pigment extract.

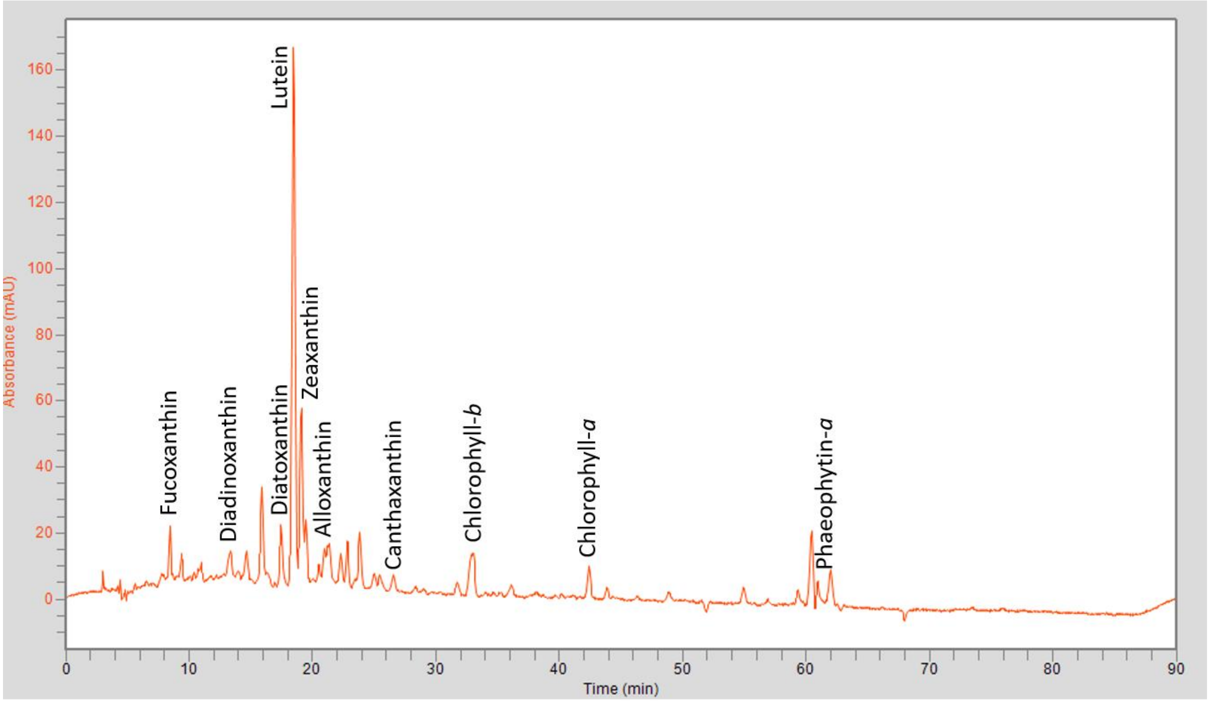

Fig. 3.2 HPLC chromatogram (450nm) with peak identification for Sunbiggin Tarn pigment extract.

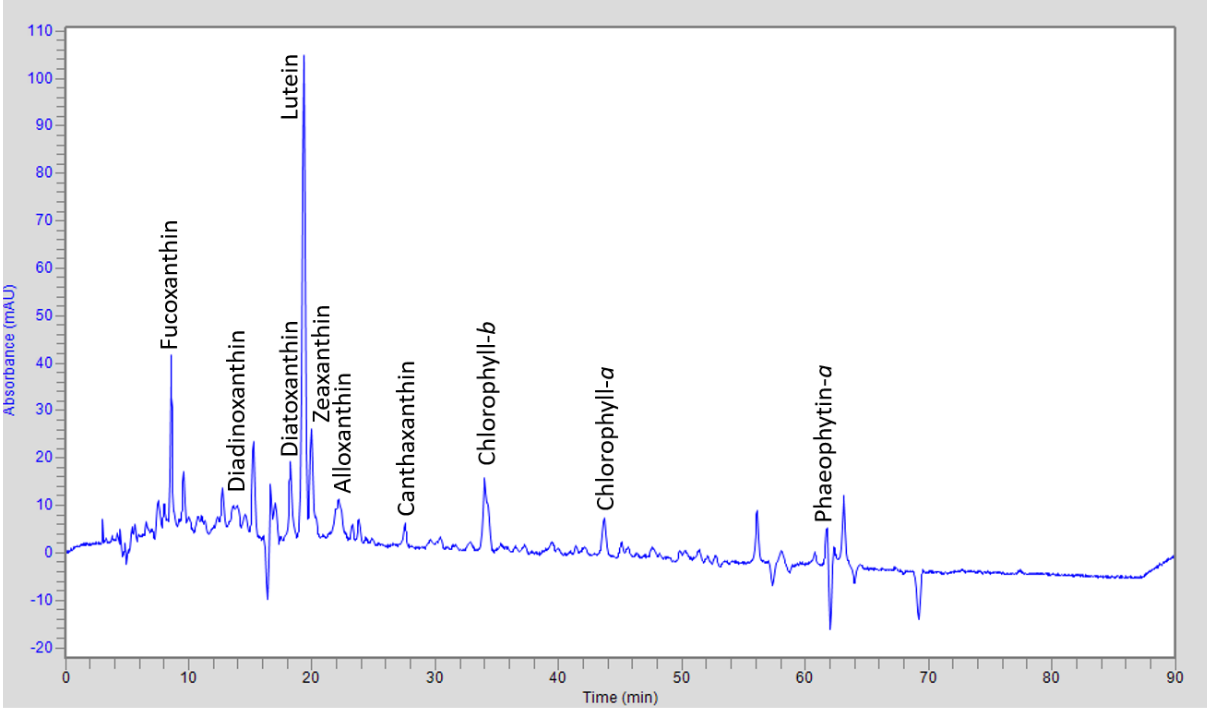

Fig. 3.3 HPLC chromatogram (450nm) with peak identification for Blea Tarn pigment extract.

Pigment standard calibration curves (β-carotene and chlorophyll-*a*) were developed by injecting known quantities of stock solutions into the HPLC to establish the relationship between pigment mass and peak area. As carotenoid absorption in solution follows the Beer Lambert law the carotene calibration curve was used to convert absorbance to concentrations for the identified carotenoid peaks using reported extinction coefficients (Jeffrey *et al.*, 1997b). Concentrations were then converted to nmoles of pigment to account for differences in molecular mass between different pigments. Pigment concentrations, nmolar, were then expressed per organic content of the sediment, to account for dilution and degradation of organic matter (nmole pigment g^{-1} organic weight sediment), using equation 4.

$$\text{Concentration of pigment} = \frac{(nmole\ of\ pigment\ in\ extract * \frac{TV}{IV})}{(EM * \frac{\%OC}{100})}$$

Equation 4

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

Pigment preservation conditions were calculated as the ratio between chlorophyll-*a* and phaeophytin-*a* (Leavitt and Hodgson, 2001) with the UV index representing the ratio of scytonemin to echinenone, representing total cyanobacteria.

Changes in the relative abundances of cryptophytes (alloxanthin), chlorophytes (lutein), diatoms (diatoxanthin) and cyanobacteria (zeaxanthin + canthaxanthin + echinenone) over time were calculated by expressing them as a percentage of the sum of these pigments.

Analytical precision based on repeat measurements of the laboratory standards was >95%.

3.2.4 Quantification of sedimentary trace elements

To quantify specific metal concentrations in sediments, most analytical techniques require the extraction of metals to an aqueous solution (Sneddon *et al.*, 2006). The ISO 11466.3 method is commonly used and involves the digestions of sediment with mixtures of 12 M HCL and 17 M HNO_3 in a 3:1 ratio which is known as aqua regia (Peña-Icart *et al.*, 2011). Freeze dried sediment (0.25 g) was digested in 250 ml pyrex flasks with 10ml of aqua regia for 24 hours as described in Peña-Icart *et al*. (2011). Sediments were digested on a hotplate (130°C for 15 minutes) before filtering through ashless Whatman 41 filter paper and diluted to 25 ml with 0.17 M HNO_3 and transferred to volumetric flasks. Samples were diluted 50:50 with ultra-pure water to reduce acidity and transferred to plastic centrifuge tubes for storage at 4°C until processed.

Aqueous samples were analysed for 16 elements (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Zn) using a Thermo Scientific iCAP 7000 Plus Series ICP-OES at the University of York. Samples were run in triplicates and mean concentrations were quantified using within-run laboratory standards (Certipur ICP multi-element standard solution 111355). Concentrations were expressed per sediment weight (µg element g^{-1} sediment) using equation 5.

$$Elemental\ concentration = \frac{ppm\ of\ element\ in\ solution}{extracted\ sediment\ weight\ (g)} * 100$$

Equation 5

Detection limits were calculated by repeated measurements of procedural blanks and precision (which was generally >95%) by repeated measurements of selected solutions of known concentrations.

3.2.5 Sedimentary chronologies

I. ^{210}Pb dating laboratory analyses

Subsamples of freeze-dried sediment (~500mg) were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay in the Environmental Radiometric Facility at University College London, using an ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. ^{210}Pb was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope ^{214}Pb following three weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662keV and 59.5keV (Appleby *et al.*, 1986). The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self-absorption of low energy gamma rays within the sample (Appleby *et al.*, 1992).

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

The CRS model was used to determine the chronologies of Blea Tarn and Lake Gormire due to the non-monotonic variation in unsupported ^{210}Pb activities. However, for Sunbiggin Tarn the CRS modelled date for the base of the core suggested the sediments were older than the ^{137}Cs and ^{241}Am records. Due to the highly variable sedimentation rate recorded in this core it was assumed that the CRS model was overestimating age. As a result, the final CRS chronologies were corrected using ^{137}Cs and ^{241}Am records to indicate 1963 weapons testing. Due to the limitations of ^{210}Pb dating, sediment chronologies were extrapolated from the final ^{210}Pb derived date to the base of the Blea Tarn and Lake Gormire sediment cores. This was done through using the deepest calculated sedimentation rate and working downcore to estimate the age of the entire sediment core.

Sedimentation accumulation rates (g cm^{-3} yr^{-1}) were calculated for each core by dividing the dry bulk density (g cm^{-3}) of the sediment by years per cm (yrs^{-1}cm^{-1}).

3.3 Instrumental meteorological data and statistical analysis

Dated pigment concentrations (chlorophyll-*a*, lutein, zeaxanthin, diatoxanthin, canthaxanthin, alloxanthin) were compared against meteorological data to investigate the links to algal biomass using multiple linear regression. Annual and seasonal means of maximum daily temperature and mean monthly precipitation data was obtained from the UK Meteorological Office's weather monitoring station network as freely available online records (Met Office, 2021a; Met Office, 2021b). The closest monitoring station to Lake Gormire, around 30 miles north-east in Whitby, has been recording daily temperature and precipitation since 1961 and is displayed as monthly means. The weather monitoring station of Newton Rigg was used for both Blea Tarn (20 miles south-west) and Sunbiggin Tarn (18 miles south-east) as the closest long-term weather monitoring station for these lakes, recording temperature and precipitation from 1960. To corroborate the results of the instrumental meteorological data an additional dataset was used, the HadUK-Grid climate dataset. The HadUK-Grid dataset interpolates *in situ* observations to produce high resolution grids of temperature change for the whole of the UK (Hollis, 2019). The estimated daily mean air temperature for the 5km^2 grids that covered each lake, and their catchments, was analysed from 1960 and compared to the pigment concentration data using regression analysis.

For the instrumental data, there were incomplete records for several of the monthly temperature records in the Whitby dataset, outside of the summer months. Therefore, summer temperatures were used for analysis of the sedimentary pigments at Lake Gormire. For Blea Tarn and Sunbiggin

Tarn, annual and seasonal temperatures were used as the Newton Rigg dataset contained unbroken records for all the monthly means. Winter precipitation was selected for the regression analysis, representing the period of greatest absolute quantities and relative change for both the primary meteorological records.

Principle component analysis (PCA) was used to transform the multiple response variables onto a two-dimensional biplot. The sedimentary pigments and trace element data were normalised by transforming concentrations into z-scores using equation 6.

$$Zscore = \frac{x - \mathrm{mean}}{\mathrm{std}}$$

Equation 6

Z-scores represent each datapoint as the number of standard deviations away from the mean. PCA was performed on the normalised data using PAST (version 4.03). The zonation of the data was established based on visual inspection to represent the key periods of change in the sedimentary records. PCA axis 1 and PCA axis 2 scores were used to summarise the main trends in sedimentary pigments and trace element concentration data.

4. Lake Gormire

This chapter presents the results and interpretations for the data generated from the Lake Gormire sediment core. It will discuss a timeline of events and explore the causes for the identified changes, along with an assessment of the impact of 20th century climate warming.

Fig. 4.1 Photograph of Lake Gormire taken from the south-west bank facing the cliff and woodland to the north-east of the catchment, May 2018.

4.1 Background

4.1.1 Historical land cover and vegetation

Palynological evidence suggests that from ca. 1100–600 BC the catchment of Lake Gormire contained a dense woodland consisting primarily of oak (*Quercus*) and elm (*Ulmus*). From 600 BC–AD 800 there was a rapid decline in tree and shrub pollen with increasing grass and cereals suggesting deforestation (Oldfield *et al.*, 2003). Between AD 800–AD 1200 trees and shrubs made almost a complete recovery, although the woodland is less dense than during the Romano-British period, with Birch (*Betula*) replacing elm (Oldfield *et al*., 2003). The most recent period (AD 1200–AD 1970) showed more deforestation with a decline in trees and shrubs and increased pollen from aquatic plants, ferns, cereals and grasses up to the 19th century.

The increases in aquatic pollen (*Sparganium*-type then *Myriophyllum alterniflorum* and *Equisetum*) during the periods of deforestation indicate the development of a reedswamp and submerged aquatic communities (Oldfield *et al*., 2003). The establishment of reedswamp communities could have occurred through increased erosion creating shallower lake margins and supplying soil associated nutrients to the lake (Fisher *et al*., 2003). The period of minimum woodland cover in the Lake Gormire catchment is likely to have ended around the 1950s. Sustained increases in sedimentary birch pollen were recorded up until the 1970s, which represents the most recent palynological data (Fisher *et al*., 2003). While the lake catchment has experienced periods of deforestation, the woodland in the lower parts of the catchment is likely to have survived at least 600 years, potentially since Romano-British times (Oldfield *et al*., 2003).

During the 21st century, the catchment has been dominated by deciduous woodland (79.8% of catchment area; Fig. 4.2) comprising birch (*Betula pendula*), oak (*Quercus*), sycamore (*Acer pseudoplataus*), elm (*Ulmus glabra*) and ash (*Fraxinus excelsior*). The rest of the catchment is predominantly grasslands (19.2%) with a range of flora typical of acidic conditions with bluebell, wood sorrel, moschatel broad buckler-fern and bracken (Morton *et al*., 2011). Above the woodland lies an area of heather and bracken dominated moorland on the edge of the Hambleton Hills (Oldfield *et al*., 2003; Fig. 4.2).

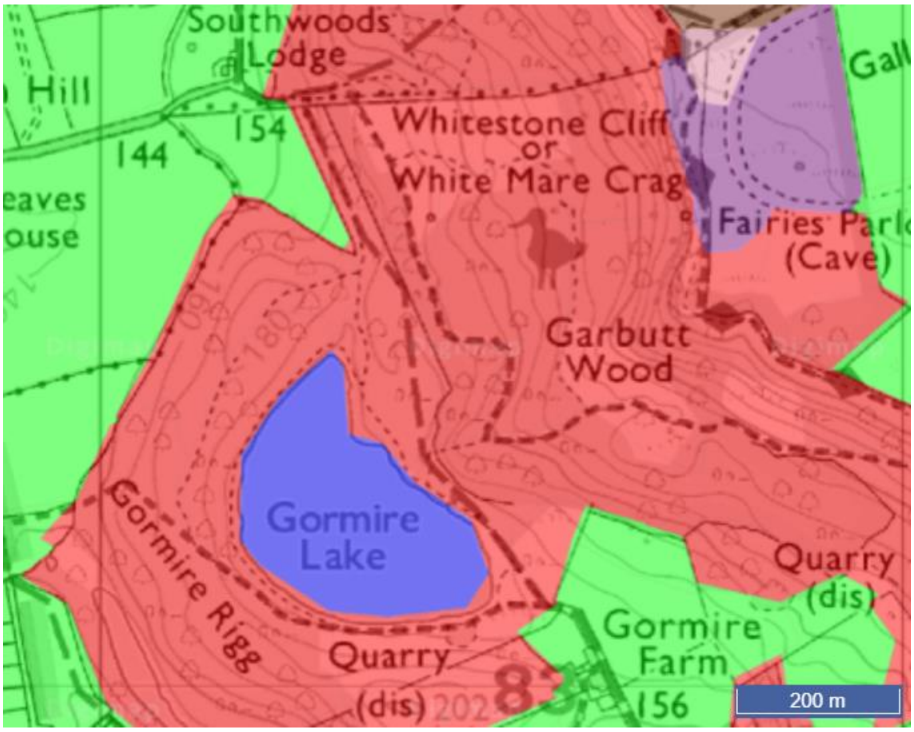

Fig. 4.2 Land cover map of Lake Gormire catchment showing areas of woodland (red), grassland (green) and heather (purple) and heather grassland (pink).

The lake margins have good macrophyte development around the shore, in particular on the eastern margin (Oldfield *et al*., 2003). This relatively small area of reedswamp and fen has a rich macrophyte community containing water mint (*Mentha aquatica*), common skullcap (*Scutellaria galericulata*), lesser marshwort (*Apium inundatum*), marsh speedwell (*Veronica scutellate*) and common spotted orchid (*Dactylorhiza fuchsia*) (Natural England, 2010). The lake is also an important site for tufted loosestrife (*Lysimachia thyrsiflora*), a rare species of wetland plant in England which has declined regionally due to a loss of suitable wetland habitats since the 1960s (Preston *et al*., 2002). However aquatic flora is sparse, which has been attributed to the geographical isolation of Lake Gormire, with *L. uniflora* the only characteristic species recorded in the lake (Smith, 2010). Due to the macrophyte community, Lake Gormire was designated as a Site of Special Scientific Interest (SSSI) for botanical conservation in 1954 with the woodland surrounding the lake also incorporated into the SSSI in 1985 (Natural England, 2010). Today the lake catchment forms a large part of the Garbutt Wood Nature Reserve which is managed by the Yorkshire Wildlife Trust.

4.1.2 Water quality and monitoring

Palaeolimnological research suggests that since AD ~1600 deforestation in the catchment of Lake Gormire resulted in a period of elevated inputs of catchment material (Oldfield *et al.*, 2003). Since the second half of the 20th century, a recorded decline in sedimentary C/N suggests that algal productivity may have increased, potentially a result of enhanced nutrient loading from the catchment (Fisher *et al.*, 2003). There have been rapid increases in sedimentary Cu, Zn, Hg, Pb, Cd, Fe and S during the mid-19th century indicative of anthropogenic pollution through atmospheric deposition (Oldfield *et al.*, 2003; Yang and Rose, 2005b).

Lake Gormire is one of the few natural bodies of water of any size in North Yorkshire and is also unusual for the region due to its relatively low alkalinity (mean of 387 µEq L^{-1}). The lake was ecologically assessed in 2010 by Natural England with unfavourable conditions recorded. The sparse aquatic flora, especially with depth, suggested that the lake suffered from periods of turbidity although there were no signs of pollution (Smith, 2010). In response to these findings Natural England commissioned a water quality survey in March 2013, with some of the key parameters displayed in table 4.1.

Table 4.1 Mean water quality parameters for Lake Gormire from March 2013 (White, 2013).

Parameter	**value**
Water temperature (°C)	3.5
pH	7.7
Dissolved oxygen saturation (%)	106
Dissolved oxygen (mg L^{-1})	14.1
Nephelometric Turbidity Units (NTU)	2
Specific conductance (µS/cm)	116
TAN (mg L^{-1})	0.35
Nitrate (mg L^{-1})	0.17

Reactive orthophosphate in surface waters was measured as 0.02 mg L^{-1} between 2008 and 2009 (Environment Agency, 2008) categorising Lake Gormire as a mesotrophic lake (O.E.C.D, 1982). Nitrate concentrations were measured at 0.2 mg L^{-1} over the same period which would give a nitrate:phosphate (N:P) concentration ratio of 10, or a molar ratio of 15, indicating that P concentrations are not a limiting factor. A N:P ratio of 16 (known as the Redfield ratio) is associated with optimal growth conditions with respect to nutrient availability (Redfield, 1958).

4.1.3 Weather and climate

The mean annual daily maximum temperature at Whitby (~30 miles NE from Lake Gormire) was 13.4°C during the 2010s, with a maximum summer (June – August) daily temperature of 19.6°C. The mean annual monthly precipitation was 56.6 mm with 61.3 mm in the winter (December – February) months (Met Office, 2021a). Due to the steep catchment surrounding Lake Gormire, it experiences substantial orographic rainfall with a mean precipitation of 825 mm yr^{-1} (Fisher *et al*., 2003). Based on observations, the lake regularly freezes over in the winter months, likely due to a combination of low temperatures, high level of shading from the forested catchment and very calm waters (Fig. 4.3). Whilst the timing of the thaw is uncertain, photographic records since 2010 indicate that the thaw typically occurs between the middle and end of February.

Fig. 4.3 Photograph of Lake Gormire completely frozen taken from the top of the cliff in the north-east of the catchment, January 2011.

Mean daily maximum temperatures have increased from 11.6°C between 1962-1989 to 13.1°C between the period of 1990-2018. Similarly, mean summer daily maximum temperatures have increased from 17.1°C (1962-1989) to 19.0°C (1990-2018) (Fig. 4.4). Consequently, warming has resulted in the five warmest summers on record all occurring during the 21st century. The warmest summer on record was 2006 which had a mean daily maximum temperature of 20.7°C followed by 2003 (20.6°C), 2018 (20.5°C), 2013 (20.4°C) and 2010 (19.7°C). One other period of warmth occurred in 1975 (Fig. 4.4) and this is followed by the well documented heatwave of 1976 which was ~2°C higher than the 1970s average. This period of warmth was relatively short lived and was followed by the coolest summer on record in 1977 of 15.8°C.

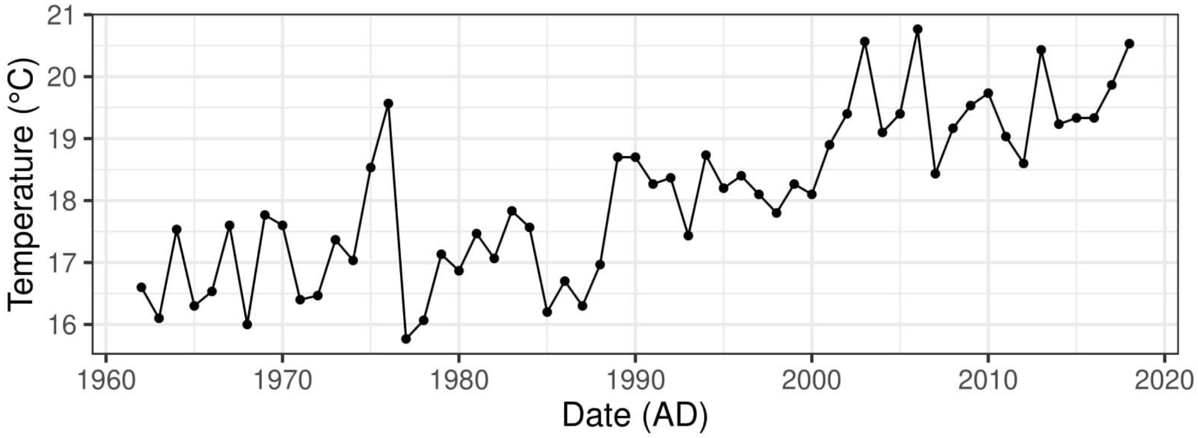

Fig. 4.4 Mean daily maximum summer temperature at Whitby weather station (Met Office, 2021a).

Mean monthly winter rainfall has been 30% higher since the start of the 21st century (57.3mm) compared to the period of 1962-1989 (44.0mm)(Fig. 4.5). Four of the five wettest winters have all occurred in the 21st century, with the wettest occurring in 2016 (95.7mm) followed by 2004 (91.1mm), 2010 (90.8mm), 1977 (88.1mm) and 2014 (84.4mm). The 2010s also had some of the greatest interannual variations in winter precipitation. The range between the means of the three wettest and three driest winters (58.8mm) is higher in the 2010s than in any other decade.

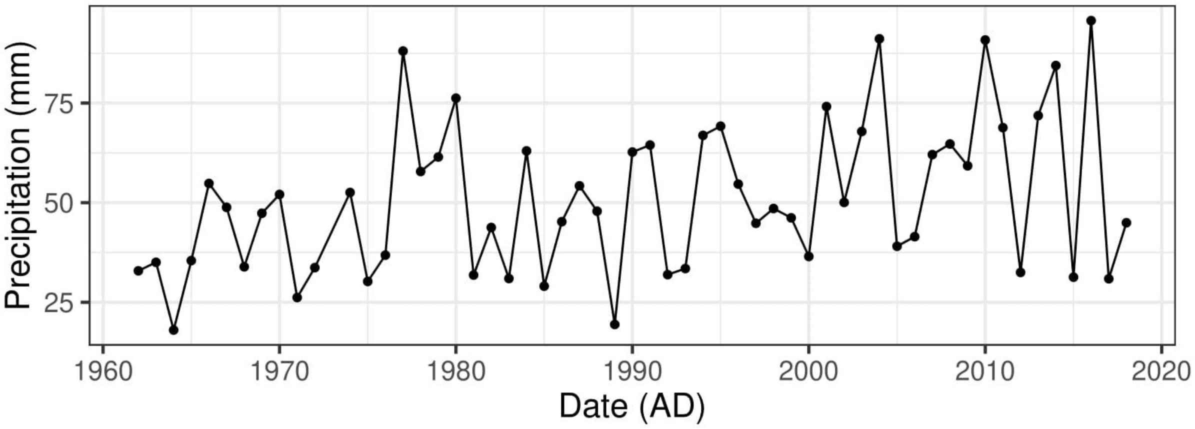

Fig. 4.5. Monthly mean winter rainfall at Whitby weather station (Met Office, 2021a).

4.2 Results

4.2.1 Sediment chronology

Total ^{210}Pb activity reached equilibrium with supported ^{210}Pb activity at a depth of 30 cm (Fig. 4.6a). Overall unsupported ^{210}Pb activities decline irregularly with depth, suggesting changes in sedimentation rates. However, in the section from sediment surface to 14.63 cm, unsupported ^{210}Pb activities decline more or less exponentially with depth, indicating a relatively uniform sedimentation rate in this section. A dip of unsupported ^{210}Pb activity at 20.13 cm suggest an increased sedimentation rate (Fig. 4.6b). ^{137}Cs activities show a broad peak with relatively high values between 9.38 cm and 12.13 cm. Detected low ^{241}Am activities might suggest fallout from nuclear bomb testing. However, separated low ^{241}Am activity points are not sufficient for dating (Fig. 4.6c).

Due to the non-monotonic variation in unsupported ^{210}Pb activities, the chronologies were calculated using the Constant Rate of Supply (CRS) model. The CRS dating model places 1963 at around 15.13 cm and 1986 at 11.13 cm, suggesting the site may have been affected by the fallout derived from the Chernobyl accident in 1986. The CRS ^{210}Pb dating model suggests that there are some small fluctuations in sedimentation rates before the 1950s, with a peak in the 1930s reaching a sedimentation rate of 0.033 g cm^{-2} yr^{-1}. Since the 1960s, sedimentation rates have been relatively stable, with a mean at 0.015 g cm^{-2} yr^{-1} (Fig. 4.7).

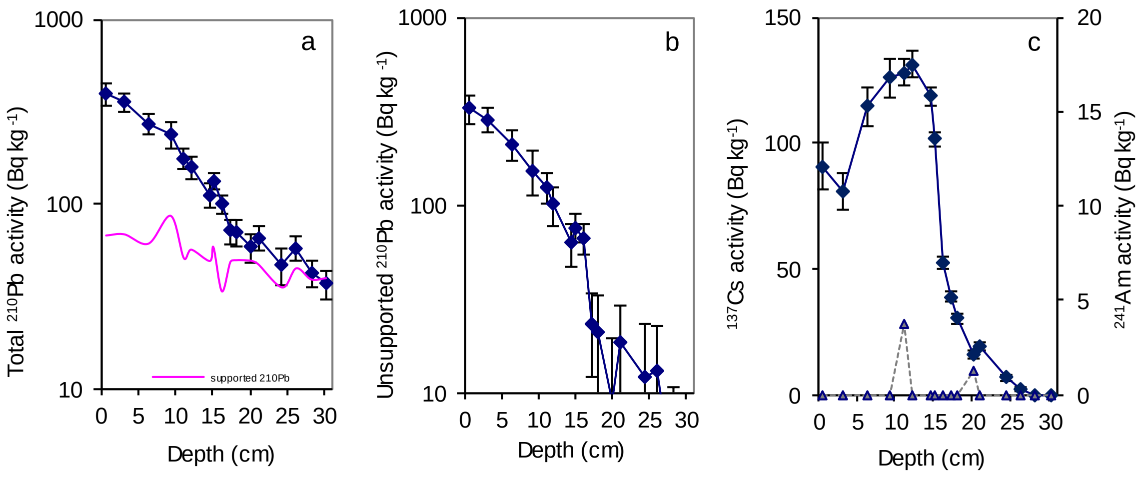

Fig. 4.6 Fallout radionuclide concentrations in the core taken from Lake Gormire, showing (a) total ^{210}Pb (blue line) and supported ^{210}Pb (pink line), (b) unsupported ^{210}Pb, and (c) ^{137}Cs (solid line) and ^{241}Am (dashed line) concentrations against depth.

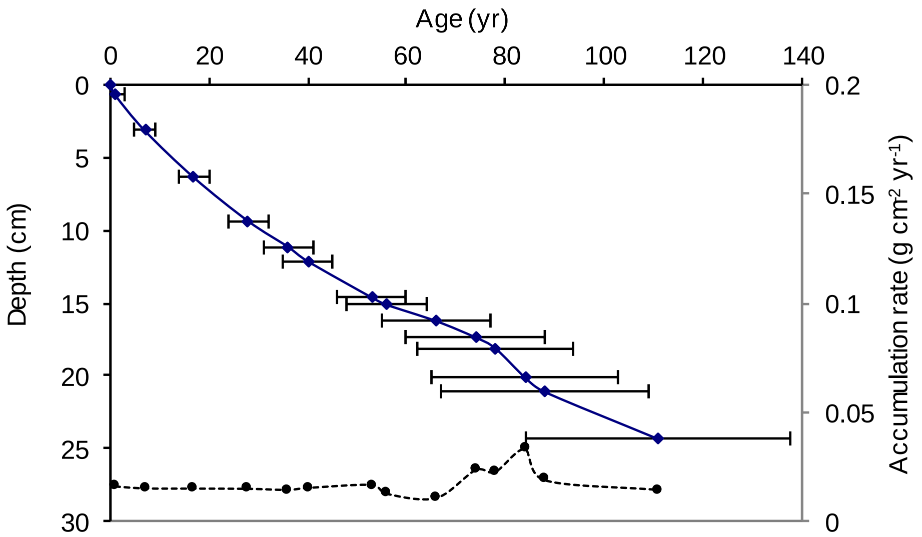

Fig. 4.7 Radiometric chronology of the core taken from Lake Gormire, showing the CRS model ^{210}Pb dates and sedimentation rates. The solid line shows age, the error bars represent model uncertainty while the dashed line indicates sedimentation rate.

While absolute ages are used in the following text, they represent the CRS model’s estimated age with uncertainty increasing with depth. Dates prior to 1907 were estimated based on the sedimentation rate calculated from the deepest ^{210}Pb dating point (24.38 cm). Therefore uncertainty in the estimated ages of the sediments are likely to be greater for samples deeper than 24.38 cm.

4.2.2 Sediment lithology

OM content decreases from 40.1% in the early 18th century to 30.9% by the 1750s and 20.7% by the middle of the 19th century (Fig. 4.8a). OM increases during the 20th century to 38.7% in 1982, reaching a peak of 51.7% in 2018. Minerogenic content increases during the 18th century to 75.2% in 1790 and remains relatively stable until the end of the 19th century when it starts to decline. The decline in minerogenic content of the sediments continues during the 20th and 21st century to 45.1% in 2018 (Fig. 4.8b). Carbonate content remains relatively stable during the 18th and 19th centuries with 3.6% in 1743 and 3.9% in 1886 (Fig. 4.8c). Carbonate content increases from the start of the 20th century to 5.8% in 1960 and then declines for the rest of the century with 3.5% in 2012.

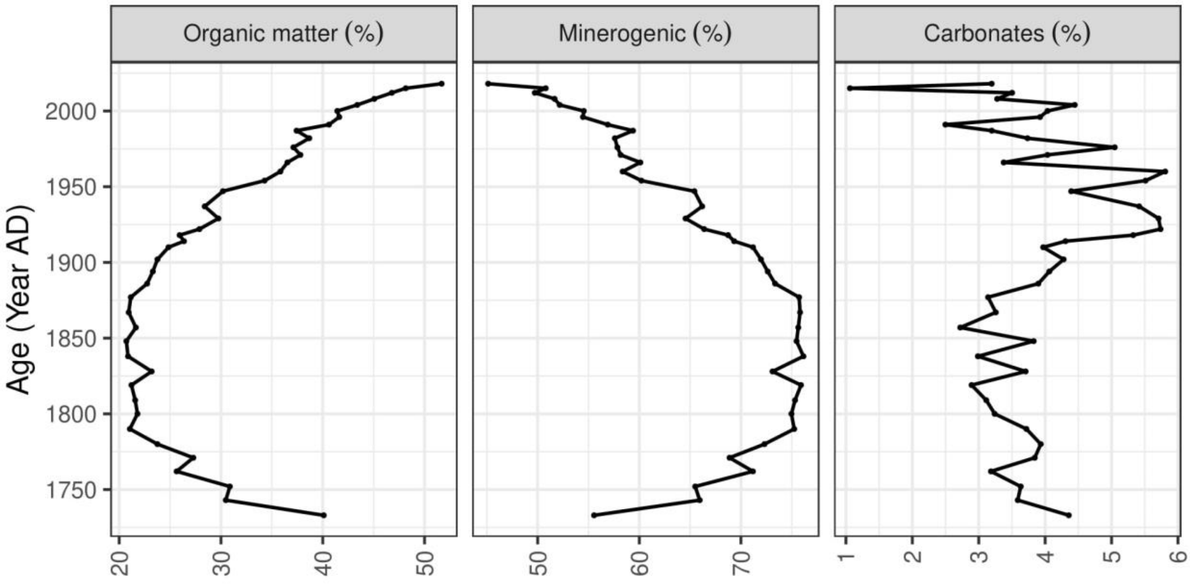

Fig. 4.8 Main sedimentary parameters from loss on ignition analysis: organic matter content (a), minerogenic content (b) and carbonate content (c) for the Lake Gormire sediment core.

4.2.3 Sedimentary trace elements

The concentrations of lithogenic elements (Al, Li, Mg, K) all show similar trends, increasing from the 1750s to a peak in the 1880s (Fig. 4.9). They broadly decline from the start of the 20th century to the present and by the turn of the 21st century, sedimentary concentrations of lithogenic elements had returned to levels detected during the 18th century. The element Fe steadily increases from the start of the 18th century to the start of the 20th century, concentrations reach 48.0 mg g^{-1} sediment in 1934 after which they decline to the 21st century with a relatively rapid increase in surface sediments to 48.8 mg g^{-1}. Heavy metals (Cd, Cu, Zn) all follow broadly similar trends with relatively stable concentrations until the start of the 20th century when they start to increase relatively rapidly. Concentrations peak during the second half of the 20th century with a slight decline during the 21st century. Pb follows similar trends except it increases during the 19th century and starts to decline in the 1980s, from a peak of 267.5 µg g^{-1} in 1973. Sedimentary concentrations of Pb decline consistently through the rest of the 20th century, with 182.9 µg g^{-1} in 2017. The other heavy metals (Cr, Ni) diverge somewhat from each other, with Cr having relatively stable concentrations during the majority of the time period, Ni experienced slight increasing concentrations from the 18th century. After a period of elevated Ni concentrations around the turn of the 21st century with 53.1 µg g^{-1} in 2001, concentrations decline. Both Cr and Ni share a distinct and rapid spike in concentrations around 1814 where concentrations more than double from 1806.

P remains relatively stable during the 18th century before a period of increasing concentration between the 1830s and 1840s with 1.74 mg g^{-1} sediment in 1840. After a relatively rapid decline, sedimentary concentrations return to similar values as those at the start of the 18th century where they remain until the ~1970s when P starts to increase. From the middle of the 1980s, P concentrations stabilise with a slight period of decline around the turn of the 21st century before a rapid increase during the 2010s with 5.30 mg g^{-1} in the most recent surface sediments. Mn shares some similarities to P, however concentrations broadly increase from the middle of the 19th century up until the 1980s where concentrations stabilise with 195.9 µg g^{-1} in 1986. After a slight decline, Mn rapidly increases from the 2010s to 724.9 µg g^{-1} in the surface sediments. Ba also broadly increases from the middle of the 19th century after relatively stable concentrations. There is a more rapid increase in sedimentary Ba with a more rapid increase in concentration around the turn of the 21st century, accelerating to the present. Ca mirrors the trends in minerogenic content, with a decline during the 18th century and increasing concentrations from the second half of the 20th century. Na concentrations remain relatively stable up until the 1980s after which they increase. This is followed by a more rapid rise from the start of the 21st century and a reduction during the 2010s. PCA axis 1 (44.1%) and PCA axis 2 (29.0%) scores account for 73.1% of the total variance in the trace elements dataset (Fig. 4.10). There were strong positive correlations between Pb, Zn, Cu, Cd and Ni along PCA axis 1 with a divergence along PCA axis 2 for Al, Mg, Li and K.

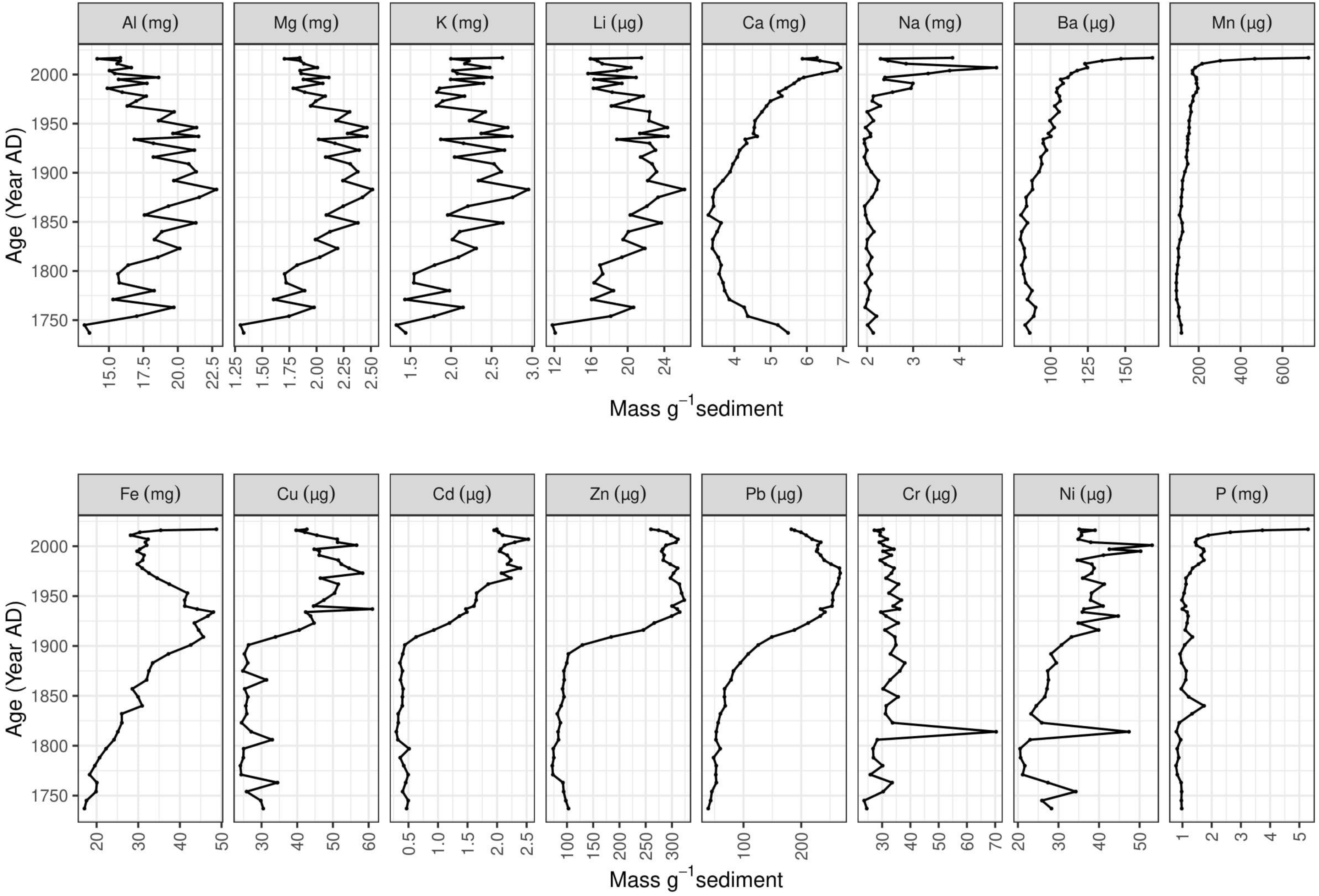

Fig. 4.9 Lake Gormire sedimentary trace elements.

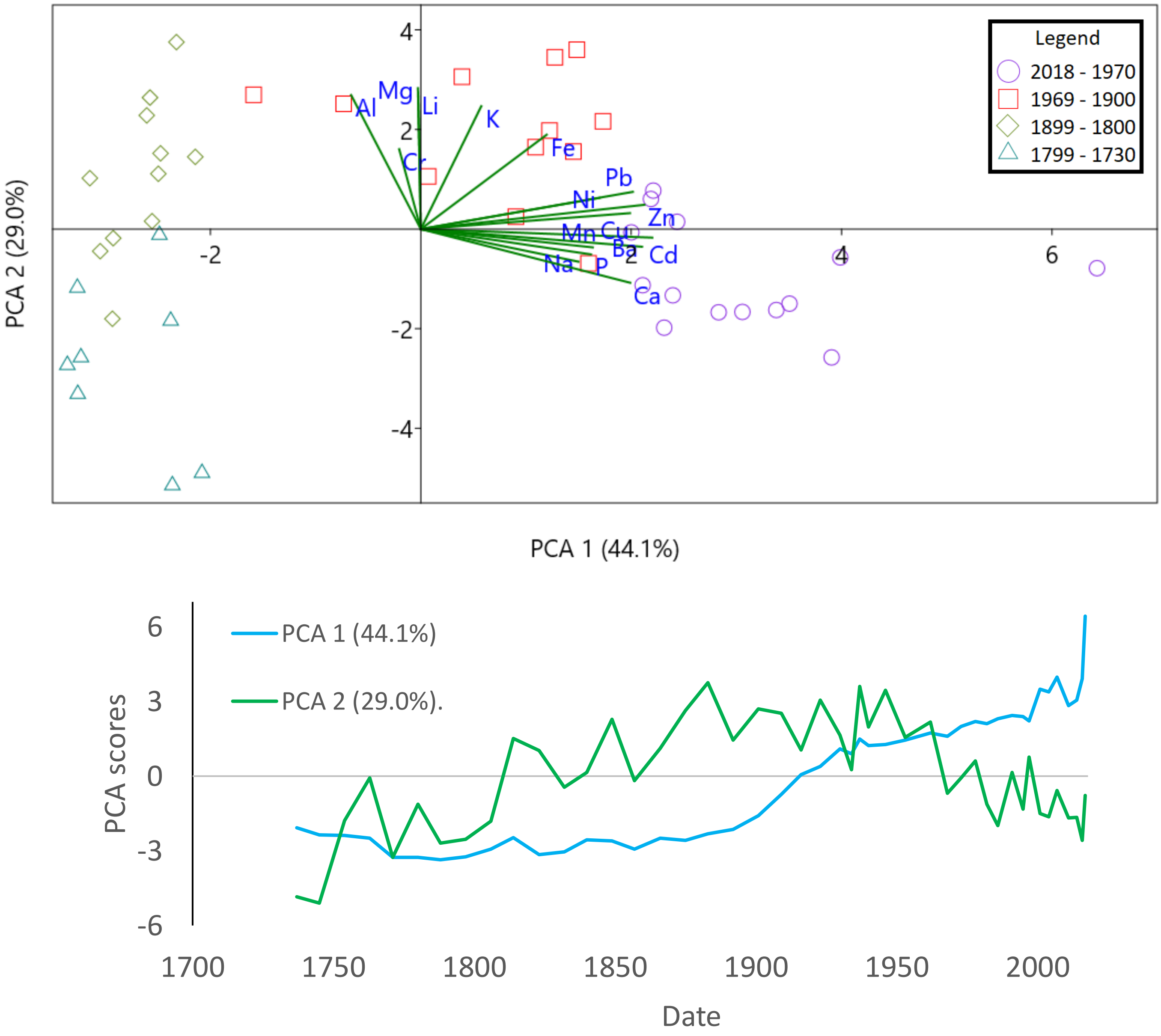

Fig. 4.10 Biplot and graph of PCA score change over time for sedimentary trace element concentrations in Lake Gormire.

4.2.4 Sediment C/N mass and stable isotopes ($\delta^{13}C$, $\delta^{15}N$)

Sedimentary %C and %N values decrease relatively rapidly around the middle of the 18th century, with %C declining from 22.0% in 1743 to 14.1% in 1754 (Fig. 4.11a). The decline in %C and %N is more gradual during the rest of the 18th century and then becomes relatively stable during most of the 19th century. During the 20th century %C and %N consistently increase, with %C returning to values experienced in the early 18th century and %N exceeding them during the 21st century. C/N values generally decline over time from a mean of 13.1 in the 18th century to 9.9 in the 21st century. The declining C/N trend is reversed from the end of the 19th century before stabilising during the middle of the century with values ~10.5. During the 21st century C/N returns to the previous low values of the late 19th century (<10). Values of $\delta^{13}C_{org}$ change considerably through the core maintaining <−28‰ in the first half of the 18th century and increasing to −26.1‰ by the start of the 19th century. $\delta^{13}C_{org}$ values maintain >−25‰ during most of the 19th century with considerably more stable values from the 1820s. $\delta^{13}C_{org}$ decreases consistently from the start of the 20th century with a mean of −28.3‰ during the 21st century. $\delta^{15}N$ broadly declines over time from a mean of 3.8‰ in the 18th century to 1.9‰ in the 21st century with some fluctuations. During the 18th century $\delta^{15}N$ ranges from 3.2‰ in 1739 to 4.3‰ in 1782 with a very similar range in $\delta^{15}N$ during the 19th century (1.0‰). $\delta^{15}N$ consistently declines during most of the 20th century, reaching a low of 1.7‰ in 2011.

4.2.5 Sedimentary pigments

Chlorophyll-*a* concentrations are relatively low at the base of the core with 41.8 nanomole (nmole) g^{-1} OC, broadly increasing over time to 108.3 nmole in 1892 (Fig. 4.11c). There are two notable episodes of increased chlorophyll-*a* between these periods. There is a short-lived spike in concentrations to 184.9 nmole in 1814 and longer period of increased chlorophyll-*a* concentrations during the second half of the 19th century with 170.4 nmole in 1885. Chlorophyll-*a* increases more rapidly during the 20th century, accelerating from the 1970s. Phaeophytin-*a* generally increases during the 18th and 19th centuries. There are considerable variations during the 20th century, but overall concentrations remain largely stable with a mean of 995.4 nmole. Therefore, preservation conditions (chlorophyll-*a*/phaeophytin-*a*) generally follow the trends in chlorophyll-*a*. Chlorophyll *b* largely follows the trends in chlorophyll-*a* but with a more prominent period of increase during the 19th century. Lutein, zeaxanthin and alloxanthin concentrations all broadly follow the same trends with two major periods of increased concentrations one during the second half of the 19th century and the second from 1970. Canthaxanthin and echinenone concentrations broadly follow the same trend except there is a relatively greater increase during the second half of the 19th century with higher concentrations of canthaxanthin during the 1870s (mean 75.7 nmole g^{-1} OC) than at any other time recorded in the core. The increase in canthaxanthin and echinenone during the 20th century is relatively muted, but in line with many of the other carotenoids, showing increases through to the 21st century. The UV index broadly follows the trends in %C with declines during the first half of the 18th century, relative stability during the 19th century and an increasing trend during the 20th century. The UV index shows considerable variability through the core with periods of no detectable concentrations, something that is shared with alloxanthin and diatoxanthin. Diatoxanthin concentrations also follow a similar trend to %C (and by extension UV index) with declines in the 18th century followed by a more gradual decline during most of the 19th century (Fig. 4.11b). The second half of the 19th century represents a period of increased fluctuations in diatoxanthin, with years of no detectable concentrations alongside years of elevated concentrations. The diatoxanthin increase during the 20th century is in line with the other primary pigments. PCA axis 1 (79.3%) and PCA axis 2 (10.9%) scores account for >90% of the total variance in the pigment dataset (Fig. 4.12). The PCA biplot shows that all pigments are positively correlated to each other with the relatively small divergence of echinenone and canthaxanthin on PCA axis 2 reflecting the relatively greater increases in these pigments during the second half of the 19th century.

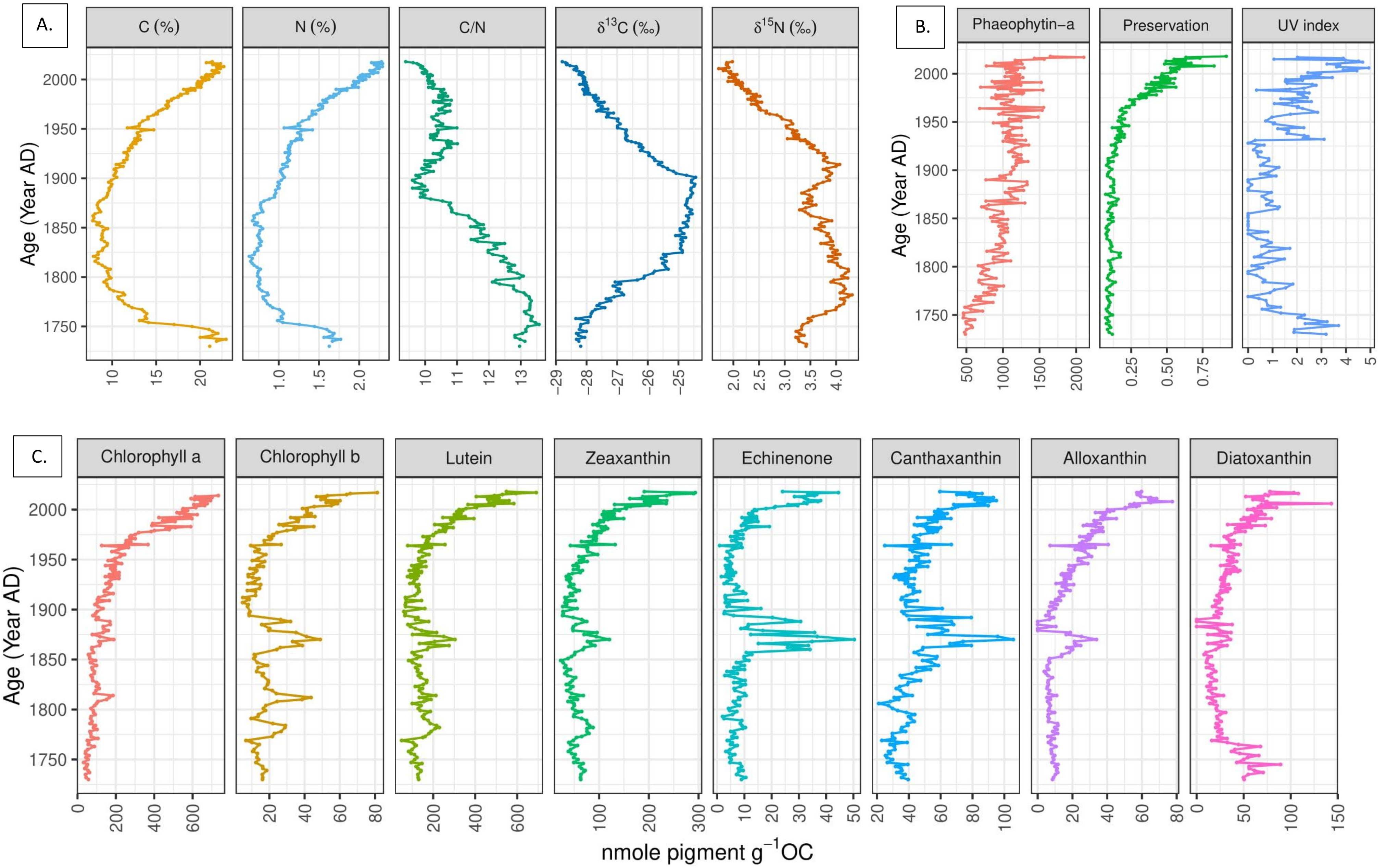

Fig. 4.11. Changes in Lake Gormire bulk organic C, N and their isotopes (A), preservation condition and UV index (B), sedimentary chlorophylls and carotenoids.

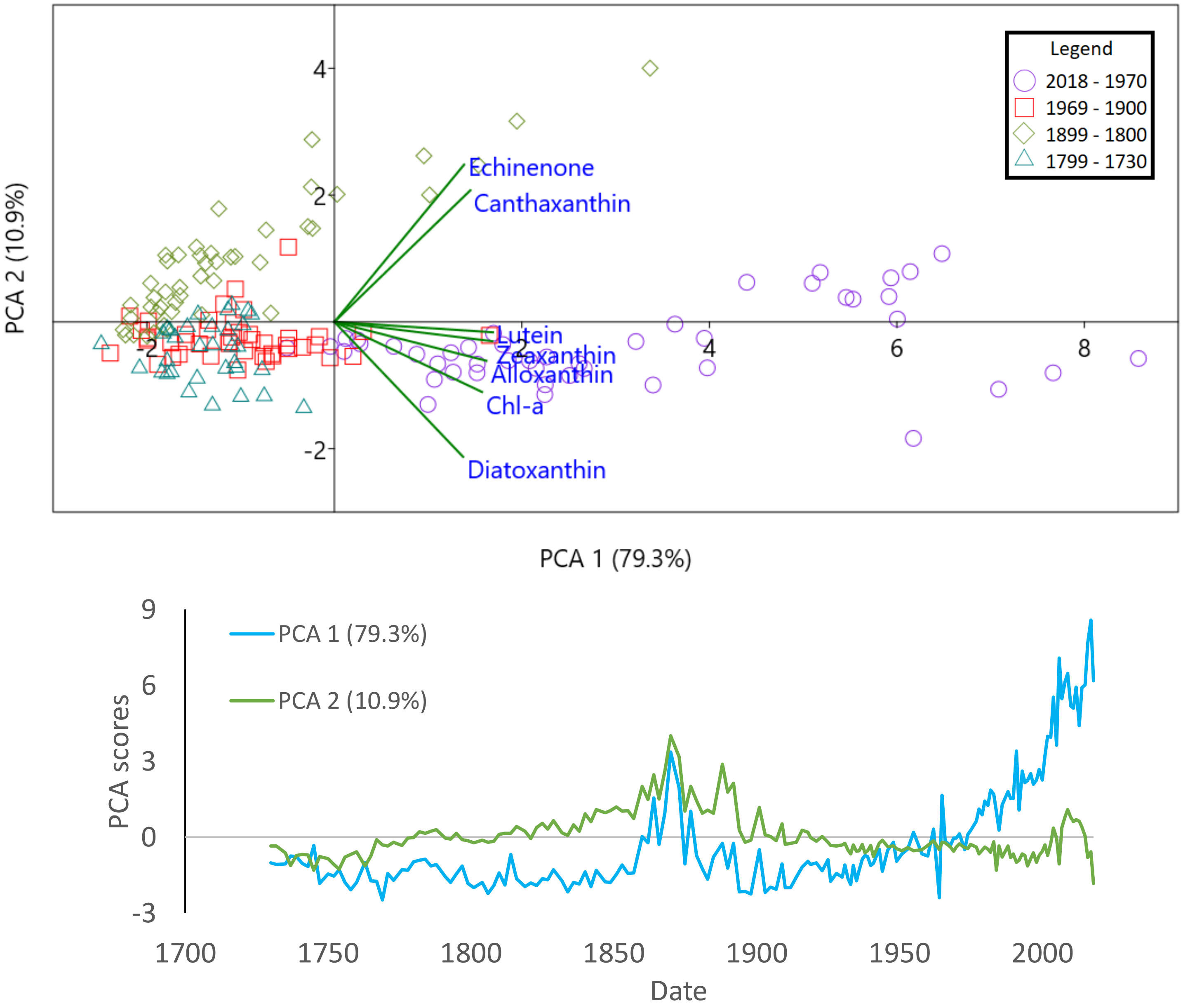

Fig. 4.12 Biplot of PCA scores and graph of change over time for sedimentary pigment concentrations in Lake Gormire.

4.2.6 Regression analysis of meteorological data and sedimentary pigment concentrations

Temperature was shown to be a moderately strong and highly significant predictor for all sedimentary pigment concentrations (Fig. 4.13, $p<0.0001$, $n=52$). The residuals for each of the linear regression models were randomly distributed indicating that the errors were independent, validating the assumptions of the models (Fig. 4.14). Precipitation was shown to be a weaker but significant ($p<0.05$) predictor of sedimentary concentrations of lutein, zeaxanthin and alloxanthin with canthaxanthin concentrations ($r^2=0.21$, $p<0.0001$) being the most significantly influenced by winter precipitation. Diatoxanthin and chlorophyll-*a* concentrations were not impacted by precipitation. Multiple linear regression with temperature and precipitation showed negligible improvements in r^2 values for most pigments with canthaxanthin, and to some extent alloxanthin, the only exceptions (Table 4.2).

Table 4.2 Regression analysis statistics (r^2, p value) of sedimentary pigment concentrations at Lake Gormire with meteorological data from Whitby. Figures in bold $p<0.0001$ ($n=52$).

Pigment	*Temperature*	*Precipitation*	*Temperature + Precipitation*
Diatoxanthin	**0.40**	0.06 (p=0.09)	**0.42**
Lutein	**0.52**	0.10 (p=0.025)	**0.55**
Zeaxanthin	**0.48**	0.13 (p=0.01)	**0.52**
Canthaxanthin	**0.36**	**0.21**	**0.48**
Alloxanthin	**0.46**	0.18 (p=0.002)	**0.54**
Chlorophyll-*a*	**0.41**	0.03 (p=0.20)	**0.41**

To corroborate the results from the Whitby weather monitoring station, changes in sedimentary pigment data was also analysed with average daily maximum air temperatures (^{o}C) derived from the HadUK-Grid climate dataset for the 5 x 5 km modelled grid covering the Lake Gormire catchment (Table 4.3).

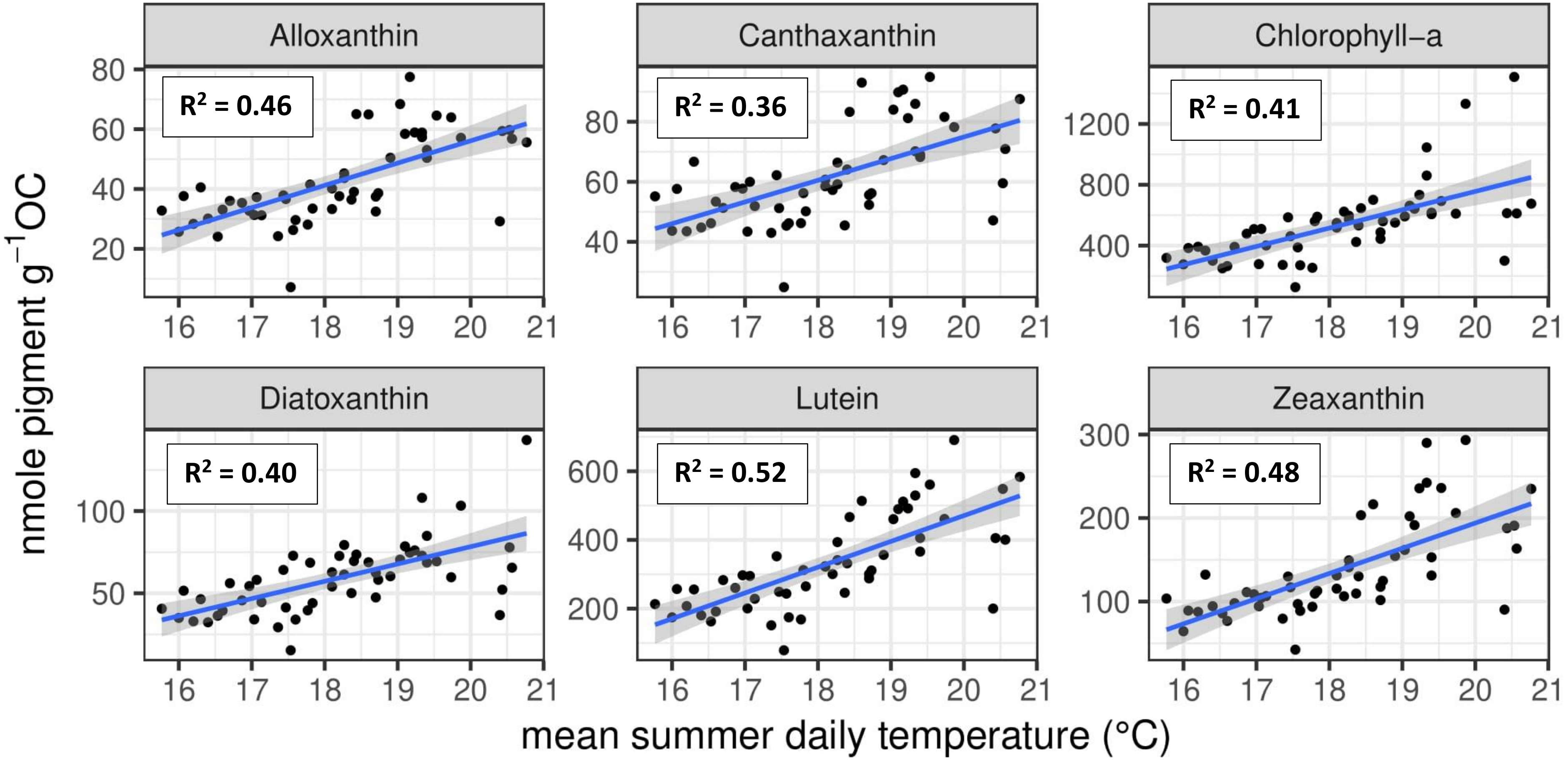

Fig. 4.13 Regression analysis of dated sedimentary pigment concentrations and temperature recorded at Whitby weather station.

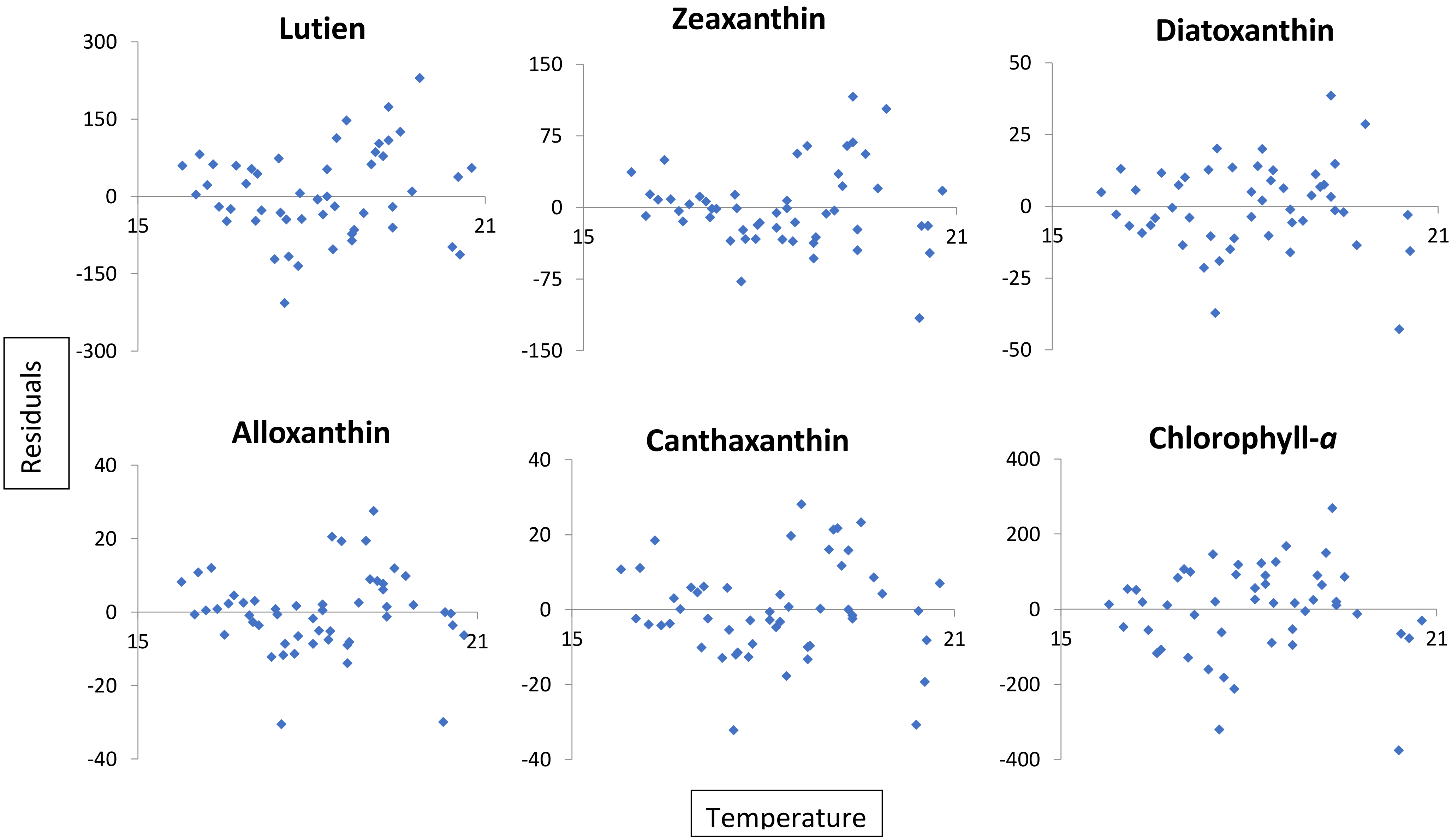

Fig. 4.14 Residuals of regression analysis between mean maximum daily summer temperatures at Whitby weather station and sedimentary pigment concentrations in Lake Gomire.

Table 4.3 Regression analysis statistics (r^2, p value) of sedimentary pigment concentrations with annual daily maximum temperature for the Lake Gormire $5km^2$ grid from the HadUK-Grid climate dataset. Figures in bold $p<0.0001$ (n=52).

Pigment	*Temperature*
Diatoxanthin	**0.40**
Lutein	**0.45**
Zeaxanthin	**0.37**
Canthaxanthin	**0.37**
Alloxanthin	**0.29**
Chlorophyll-*a*	**0.40**

The relationship between sedimentary pigment concentrations and temperature from 1962 is comparable to Whitby data with all pigments having a moderate to strong (r^2 = 0.29 – 0.45) and highly significant ($p<0.0001$) relationship to annual temperatures. As both datasets show similar results this would indicate that the Whitby dataset is likely to well represent temperature changes experienced at Lake Gormire

4.3 Interpretation

4.3.1 $\delta^{13}C$ indicating different C sources

The shift to lower %C, C/N and higher $\delta^{13}C_{org}$, during the 18th century likely represents an increasing supply of degraded organic material being washed in from the catchment (Hammarlund, 1993; Lacey *et al*., 2018). Increases in allochthonous inputs are supported by the trends in the lithogenic elements (e.g. Al, K, Mg and Li) indicating an enhanced delivery of catchment material being washed into the lake during the 18th and 19th centuries. An increased input of inorganic material would dilute the relative quantities of organic matter in the sediments thereby lowering %C (Fisher *et al*., 2003). Therefore the trends in %C, at least in the lower portion of the core, appear to be largely a result of dilution. Considering the catchment of Lake Gormire is predominantly woodland, such an increase in allochthonous inputs likely represents some deforestation in the catchment.

The continued decline in C/N and %C during the 19th century represents the period of maximum catchment erosion, with Lake Gormire dominated by allochthonous inputs during the 19th century (Fig. 4.15). While the decrease in C/N is most likely caused by increased degraded OM inputs from the catchment, it may have been further lowered by an increase in algal productivity. An increase in allochthonous inputs would likely have provided the lake with an enhanced supply of nutrients which can stimulate algal growth (Oldfield *et al*., 2003; Sparber *et al*., 2015).

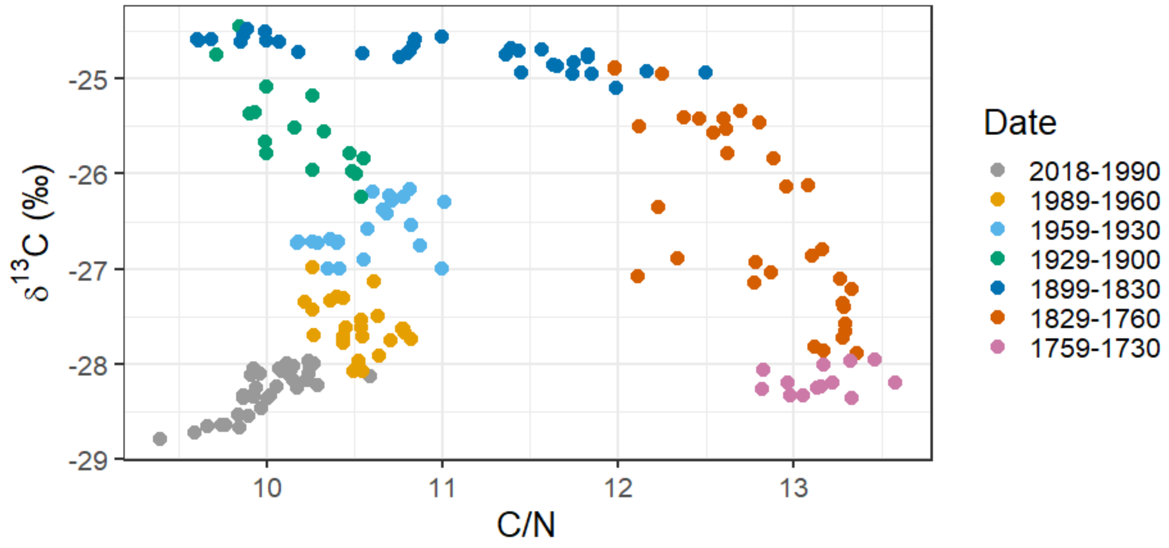

Fig. 4.15 Cross-plot of $\delta^{13}C_{org}$ and C/N for the Lake Gormire sediment core.

The start of the 20th century is defined by increasing %C and declining $\delta^{13}C_{org}$ and increasing algal pigments, indicative of increasing algal biomass (Fig. 4.16). The shift in $\delta^{13}C_{org}$ is relatively rapid with a decline of ~1‰ from 1901 to 1910 and ~3‰ by 1962. In addition, increasing %C, the low C/N values of the 20th century (mean=10.3) suggesting a lake with sediments increasingly dominated by algal material (Lacey *et al*., 2018). Considering C/N values had a mean of 13.1 during the 18th century, this change in C/N indicates a lake which has transitioned over time to one of increasing algal dominance.

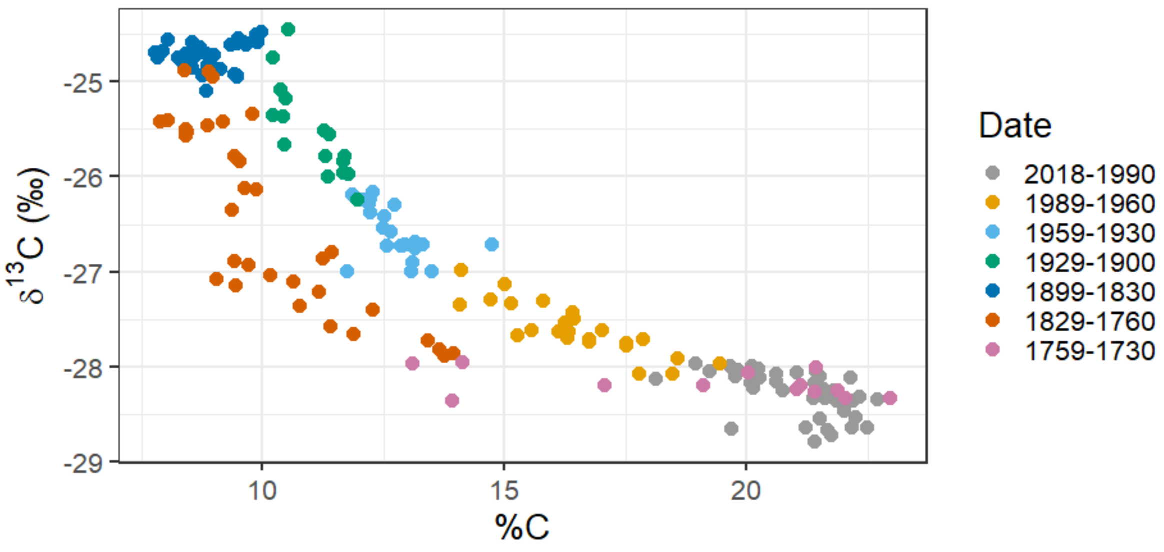

Fig. 4.16 Cross-plot of $\delta^{13}C_{org}$ and %C for the Lake Gormire sediment core.

From the 1970s, %C increases more rapidly and C/N starts to decline along with the continued transition to lower $\delta^{13}C_{org}$. This indicates that the increasing algal productivity in Lake Gormire may have accelerated since the 1970s. While C/N ratios do start to decline slightly from the 1970s the decline becomes more apparent during the 1990s. By the 21st century it appears that Lake Gormire had transitioned to a system which is highly dominated by phytoplankton, with sedimentary organic matter indicative of algal material (Meyers, 2003).

The decrease in $\delta^{13}C_{org}$ could also be caused by the global reduction in the $\delta^{13}C$ of atmospheric CO_2, which has declined up to 2‰ since the 19th century (Keeling *et al.*, 2017). The reduction in the $\delta^{13}C$ of atmospheric CO_2 is predominantly the result of fossil fuel combustion, known as the Suess effect (Verburg, 2007). Considering the $\delta^{13}C_{org}$ values for Lake Gormire have not been corrected for the Suess effect, it is possible that sedimentary $\delta^{13}C$ has been impacted by a reduction in atmospheric $\delta^{13}C$. However, most of the change in atmospheric $\delta^{13}C$ has occurred since the 1960s (Verburg, 2007). By contrast, Lake Gormire has experienced a rapid decline in $\delta^{13}C_{org}$ from ~1900. Additionally, the magnitude of change in $\delta^{13}C_{org}$ in Lake Gormire is ~4.4‰ since 1900, more than double the expected shift of the Suess effect and therefore, it is not the dominant driver of changes in the $\delta^{13}C_{org}$ record.

4.3.2 $\delta^{15}N$ indicating different sources of N

The initial increase in $\delta^{15}N$ during the 18th century is likely to be related to catchment inputs which would increase the supply of ^{15}N to the lake. $\delta^{15}N$ values experience a relatively minor decline from 4.2‰ in 1780 to 3.8‰ in 1842. During this period C/N values decline more rapidly (Fig. 4.17). This period of slight decline in $\delta^{15}N$ could represent a number of processes, including changes in mineralisation, nitrification and denitrification rates (Woodward *et al.*, 2012) or represent the increase in proportion of N_2 fixing cyanobacteria which can act to lower $\delta^{15}N$ values (Patoine *et al.*, 2006). However, markers for filamentous cyanobacteria (canthaxanthin) and total cyanobacteria (echinenone) remain relatively low during this period. Typically, cyanobacteria represent <10% of the algae community in British lakes, with even lower proportions of potentially N-fixing *Nostocales* (Jones *et al*., 2004). Therefore, $\delta^{15}N$ values are unlikely to be influenced by N fixation in many lakes.

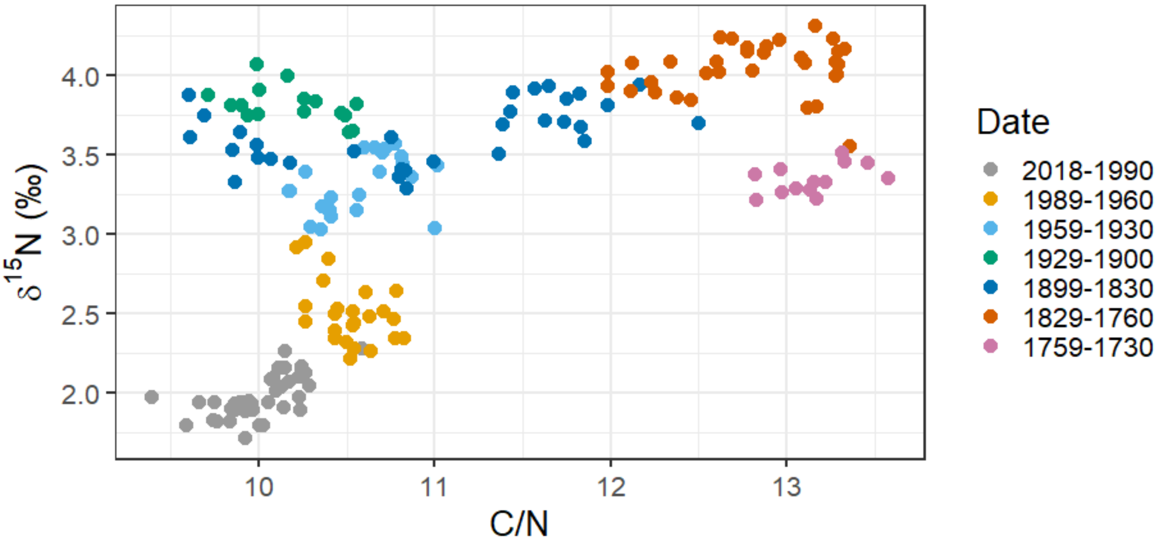

Fig. 4.17 Cross-plot of $\delta^{13}C_{org}$ and C/N for the Lake Gormire sediment core.

A more rapid decline in $\delta^{15}N$ (and C/N) during the second half of the 19th century from 3.8‰ in 1851 to 3.4‰ in 1864 is recorded and probably reflects a period of enhanced algal productivity. This decline in $\delta^{15}N$ may represent an increase in nutrients being delivered to the lake, stimulating aquatic productivity. Organic soils from woodlands were shown to have $\delta^{15}N$ of −3.3‰ to 2.6‰ across China (Sheng *et al*., 2014) and in Rothiemurchus Forest, Scotland soils were recorded as having a $\delta^{15}N$ of 2.1‰ (Weber *et al*., 2008). Therefore, this period of decline in $\delta^{15}N$ values in Lake Gormrie, may represent the increase in degraded catchment material being transported to the lake.

An increase in mineralised organic matter (e.g. ammonium) during this period would also explain the increase in algal productivity during the second half of the 19th century. The decline in $\delta^{15}N$ during this period may also be directly related to a relative increase in autochthonous material. As with C, algae preferentially uptake lighter isotopes of N resulting in algal dominated OM being depleted in ^{15}N (Woodward *et al*., 2012). While declining C/N values support that this was a period of enhanced algal biomass, %C and $\delta^{13}C_{org}$ remain relatively stable with only a slight increase in %C towards the end of the 19th century. It is likely that the second half of the 19th century was still a period of high catchment inputs. Therefore, while algal biomass may have increased, the continual high quantities of allochthonous material entering the lake may have muted any signal of autochthonous productivity.

The second half of the 19th century recorded both increased algal biomass and high catchment-derived input and is supported by the lower $\delta^{15}N$ values at the end of the 19th century. C/N values stabilise and start to increase, indicating that the period of enhanced algal biomass may have ended. Simultaneously, $\delta^{15}N$ values increase and return to values similar to observed those during the first half of the 19th century. Therefore, $\delta^{15}N$ values may be responding primarily to the changes in relative inputs of autochthonous and allochthonous material, rather than being driven by changes in other lake processes such as denitrification which can result in higher sedimentary $\delta^{15}N$ values (Talbot, 2001).

The shift to lower $\delta^{15}N$ during the 20th century occurs during the 1920s, around 25 years after $\delta^{13}C_{org}$ starts to decline with $\delta^{15}N$ reducing from ~3.8‰ to 1.9‰ by 1998 (Fig. 4.18). This likely indicates that the C pool is more sensitive to changes in OM supply, with $\delta^{15}N$ comparatively buffered. The delayed response of $\delta^{15}N$ could represent the greater resilience of the lake to $\delta^{15}N$ change, with greater quantities of OM required to exceed the buffering capacity of the $\delta^{15}N$ pool, compared to $\delta^{13}C$. The strong correlation between $\delta^{15}N$ and $\delta^{13}C_{org}$ from 1926 to the end of the 20th century ($r^2=0.95$, $p<0.0001$) highlights how $\delta^{15}N$ and $\delta^{13}C_{org}$ are both responding to a change in the source of organic matter. Declining $\delta^{15}N$ along with $\delta^{13}C_{org}$ can be indicative of increasing algal biomass (Reuss *et al*., 2010; Woodward *et al*., 2012). This is supported by a concurrent increase in %C during the 20th century, although it should be noted that a recovery from deforestation is also likely to be influencing sedimentary OM from around the middle of the 20th century (Oldfield *et al*., 2003).

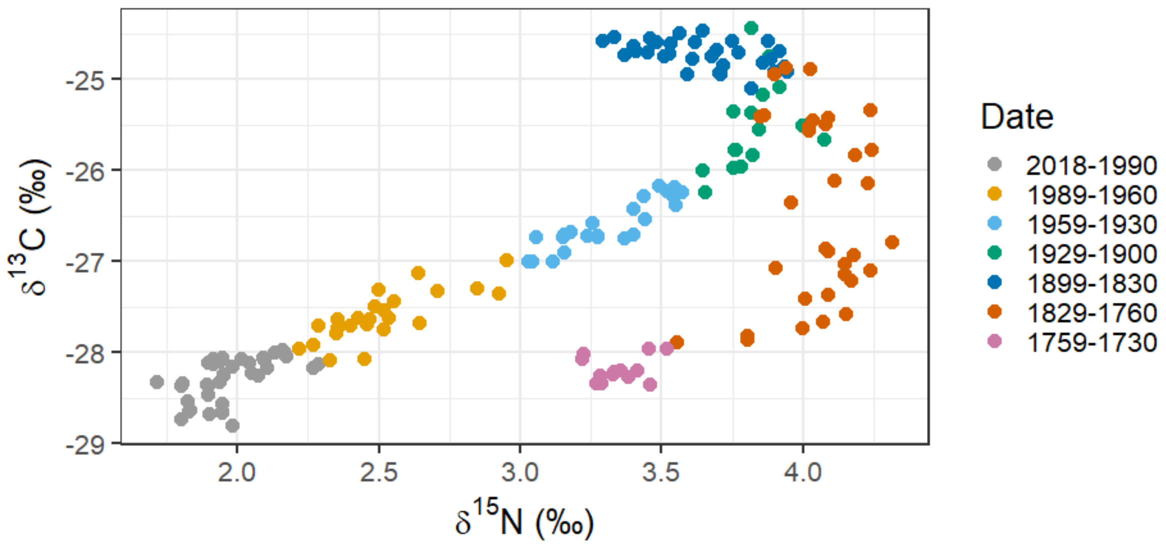

Fig. 4.18 Cross-plot of δ^{13}C$_{org}$ and δ^{15}N for the Lake Gormire sediment core.

The trends in the C and N profiles indicate that the increases from the start of the 20th century represents a different driver of change, rather than just being a reversal of the declines in the 18th century (Fig. 4.19). Whilst the 20th century increase is defined by higher %N, which is indicative of protein-rich cellulous poor algal material (Meyers, 2003), the decline during the 18th century had relatively lower %N. This indicates that from the 18th century, the predominant driver of change to the sedimentary organic material in Lake Gormire has shifted from catchment-dominated inputs to autochthonous lake algal productivity.

There is strong evidence to indicate that woodland recovery started in the 1950s (Oldfield *et al.*, 2003). Prior to this point, δ^{15}N had already been declining for ~25 years and δ^{13}C$_{org}$ for around 50 years. Therefore, it seems unlikely that a recovery from deforestation was predominantly driving the shift to lower δ^{13}C$_{org}$ and δ^{15}N during the first half of the 20th century. Additionally, the increase in δ^{15}N that occurred around the period of likely deforestation was ~0.9‰, in line with the decline between 1925 and 1950 (~0.8‰) representing the period before woodland recovery had begun. The period following the start of woodland recovery recorded a decline in δ^{15}N by a further ~1.2‰ by the start of the 21st century. The trends in δ^{15}N illustrate that while deforestation appears to have had a notable impact on δ^{15}N values in the past, the changes in δ^{15}N since the 20th century are unlikely just to be a reversal of the increase following deforestation, especially considering the timing and magnitude of changes in δ^{13}C$_{org}$, which occurred even earlier in the 20th century. However, it is possible that woodland recovery had initiated before it became detectable in the 1950s. During the first half of the 20th century C/N increases slightly to the 1930s and then stabilises to the end of 1960s. The increase in C/N during the first three decades of the 20th century may represent the start of woodland recovery, as even relatively small amounts of high C/N material being transported to the lake can have a detectable impact on sedimentary C/N (Lacey *et al*., 2018). While this was a period of declining catchment inputs, as inferred by the lithogenic sedimentary elements concentrations, allochthonous inputs were still relatively high with only slight reductions from the peak inputs of the 1880s which is summarised by the PCA axis score 2 for the trace elements data (Fig. 4.12).

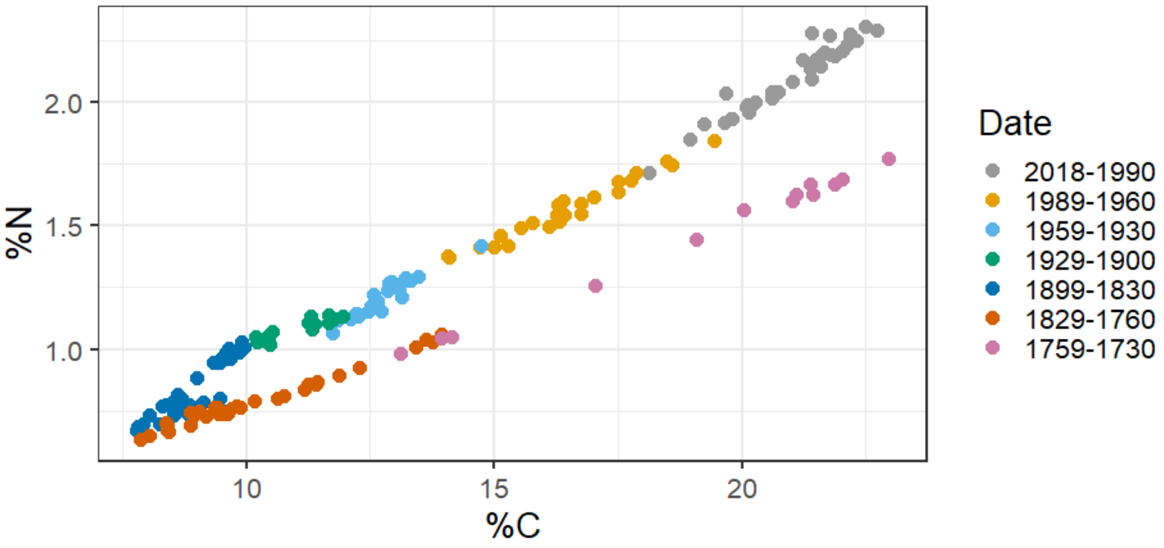

Fig. 4.19 Cross-plot of %N and %C for the Lake Gormire sediment core.

In addition to environmental and anthropogenic changes, diagenetic processes can also impact sedimentary δ^{15}N values, along with C/N. This is due to the selective loss of lighter N compounds which increase C/N while decreasing δ^{15}N over time (Gälman *et al*., 2008). Diagenesis of sedimentary OM can increase δ^{15}N by 1-2‰ within the first 50 years after burial, after which values stabilise (Brahney *et al*., 2014). Therefore, some of the δ^{15}N changes experienced since the second half of the 20th century may be driven by diagenesis. The difference between the historic and modern low δ^{15}N values (3.2‰ and 1.7‰, respectively) are within the range of changes that can be impacted by diagenesis. The suggestion that diagenesis has impacted sedimentary δ^{15}N values at Lake Gormire is also supported by the concurrent decline in δ^{15}N with C/N and %N, which indicates that isotopically light N compounds are being preferentially transformed. However, this trend only becomes apparent from ~1990 and is relatively small. The rate of C/N change from diagenesis is highest within 5 years after deposition after which change is much slower (Gälman *et al*., 2008). As a result, changes are not usually of sufficient magnitude to affect larger scale change in source over time (Meyers and Ishiwatari, 1993). The suggestion that the impact of diagenesis is relatively minor is also supported by the ~1‰ decline in $\delta^{15}N$ between 1926 and 1965. Considering these sediments were deposited >50 years ago it seems unlikely that diagenesis is a driving the $\delta^{15}N$ changes during this time period. Although there is indication that diagenesis has impacted $\delta^{15}N$ in the most recent sediments (~20 years after deposition) it is only likely to be having a minor or negligible impact over longer timescale. This is supported by the strong correlation between $\delta^{15}N$ and $\delta^{13}C_{org}$ values during the 20th century, as $\delta^{13}C_{org}$ values are typically not changed by diagenetic processes (Hodell and Schelske, 1998; Meyers and Lallier-Verges, 1999).

4.3.3 Total algae (chlorophyll-*a*, phaeophytin-*a*)

There is an inverse relationship between chlorophyll-*a* (Fig. 4.20) and %C ($r^2=0.42$, $p<0.0001$) during the 18th century. This indicates that an increase in allochthonous inputs during the 18th century, driven by deforestation, may have had some stimulative impact on algal biomass in Lake Gormire. A stimulation of lake algae is supported by the sum of chlorophyll-*a* and phaeophytin-*a* which show a progressive increase from 520.0 nmole in 1750 to 1203.8 nmole in 1806 (Fig. 4.21). The relationship between chlorophyll-*a* and %C breaks down during the 19th century in Lake Gormire ($r^2=0.0045$, $p=0.66$). This suggests that the impact of deforestation, and associated increased nutrient supply, had become less important to algal productivity which is supported by the slight declines in total algae during the first half of the 19th century (Fig. 4.21). Allochthonous inputs becoming a less important driver of change may reflect the catchment becoming N limited during this period, which is typical of a woodland recovering from deforestation (Fenn *et al*., 1998). Recovering forest vegetation removes a large quantity of N and reduces leaching of N into lakes. As a result algae in lakes with forested catchments can be consistently N limited (Hayes *et al*., 2015). N limitation during the second half of the 19th century is supported by the canthaxanthin concentrations, which indicate higher, potentially N-fixing, filamentous cyanobacteria during parts of the 1870s than at any other point in the time series. Additionally, there is a period of increased sedimentary P concentrations during the 1830s and 1840s. This could represent a period of increased P loading to the lake, as concentrations are higher than at any point prior to 2011, and likely represents the naturally higher P contents of the surface sediments. Notably this period did not occur with a corresponding increase in algal biomass which indicates that P availability may not be the driver behind algal biomass during this period.

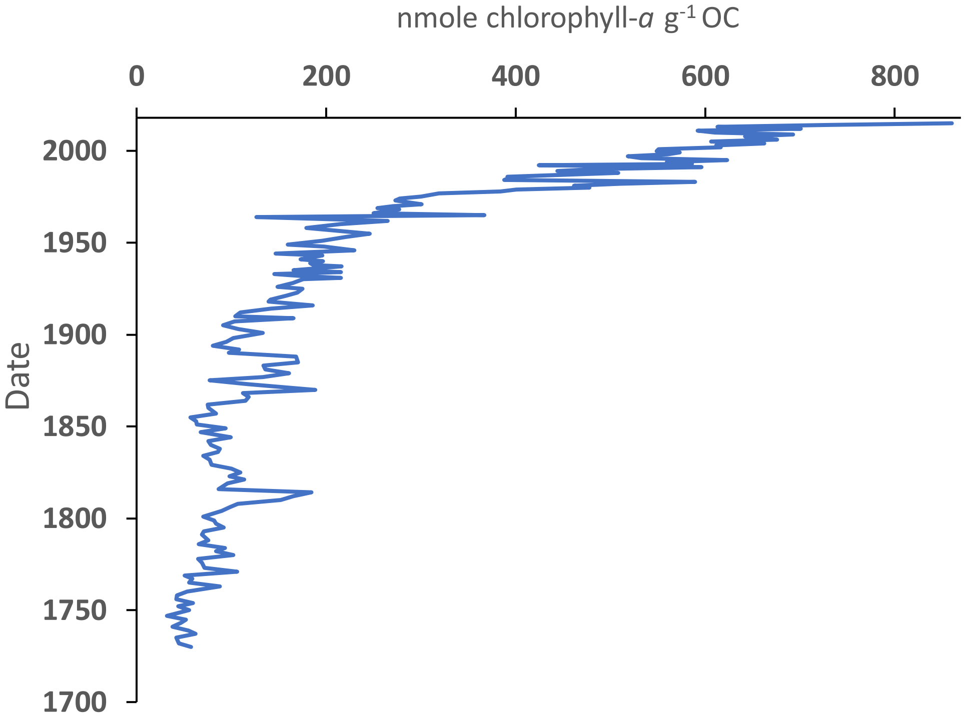

Fig. 4.20 Concentrations of chlorophyll-*a* from Lake Gormire sediment core.

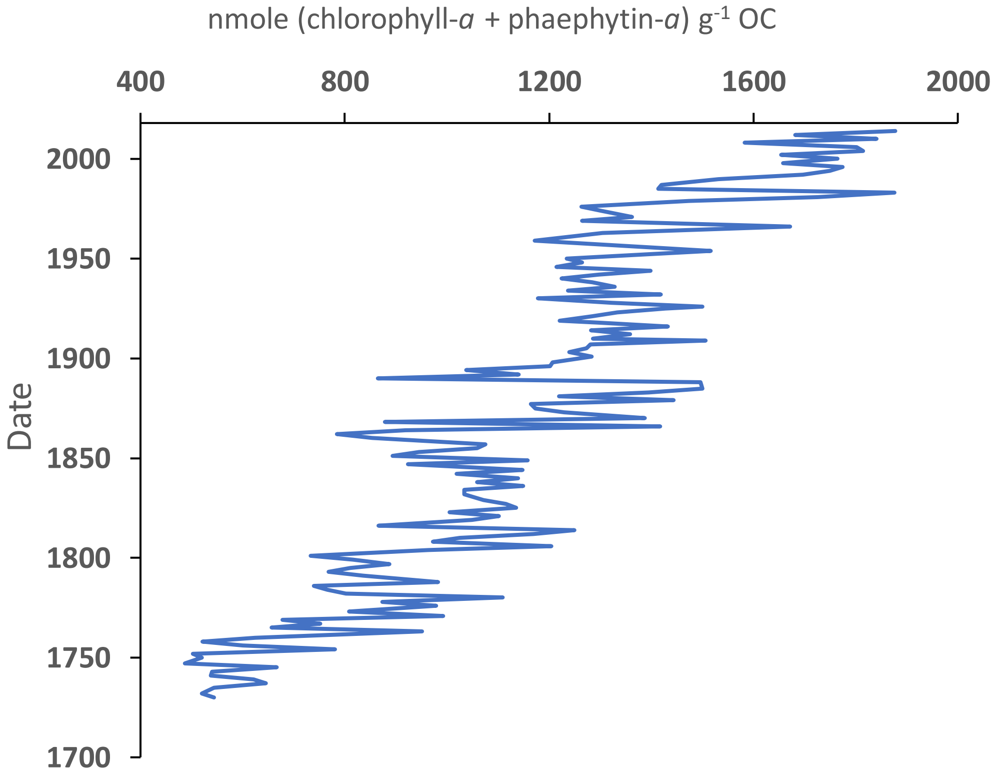

Fig. 4.21 Concentrations of chlorophyll-*a* and phaeophytin-*a* from Lake Gormire sediment core.

There were, however, two notable periods of increases in total algae (chlorophyll-*a* and phaeophytin-*a*) elsewhere in the 19th century, 1810-1814 and 1864 -1888 which had peak concentrations of 1249.1 and 1500.7 nmole respectively. These periods are defined by their rapid increase (and subsequent decline) and short duration for both chlorophyll-*a* and phaeophytin-*a*. They may represent a pollution event, possibly atmospheric considering the lack of streams and the small catchment. Pollution as the cause is supported by the sharp increase in sedimentary Cr and Ni recorded in 1814, elements that were used for inorganic pigments and leather tanning processes during the 19th century (Guertin *et al.*, 2005). Considering the lack of streams to Lake Gormire, how Cr and Ni entered the lake is uncertain. It is possible that the lake has a groundwater source but there is currently no evidence to support this. Conversely, the period of 1864 to 1888, does not appear to be related to an anthropogenic source. Concentrations of lithogenic elements (Al, K, Mg and Li) all peak during the 1870s and 1880s indicating a period of maximum catchment erosion. Precipitation records show that the 1870s and 1880s contained some particularly wet years, with three out of ten of the wettest years on record occurring between 1872 and 1882; 1872 being the wettest year since at least 1766 (Wigley *et al*., 1984). Although sediment dating uncertainty is relatively large during this period, it remains a possibility that extreme wet weather enhanced catchment inputs to Lake Gormire during this period. These periods of enhanced chlorophyll-*a* concentrations in the 19th century do not appear to have impacted %C or $\delta^{13}C_{org}$ values. The reason for the lack of change in the bulk organics data is likely due to the overwhelming influence of allochthonous inputs on diluting the in-lake components during this period.

There is another period of increase in total algal biomass from the start of the 20th century, with sedimentary chlorophyll-*a* concentrations more than doubling to 265.3 nmole in 1962. There is high positive correlation between chlorophyll-*a* and %C (r^2=0.91, p<0.0001) and with $\delta^{13}C_{org}$ (r^2=0.75, p<0.0001) from the start of the 20th century. This supports the interpretation that increasing algal biomass since the start of the 20th is driving the changes in sedimentary $\delta^{13}C_{org}$ and C/N values in Lake Gormire. The negative relationship between chlorophyll-*a* and %C in the 18th century supports the interpretation that the %C and $\delta^{13}C_{org}$ during the 20th century is not simply a reversal of the change experienced in the 18th century. While the $\delta^{13}C_{org}$, C/N and %C data during the 18th century are primarily driven by increasing catchment inputs, the change in the 20th century appears to be primarily driven by increasing algal biomass.

Atmospheric pollution is also another potential cause for changes in algal biomass. There are relatively rapid increases in some heavy metals (e.g. Cd, Cu and Zn) around the same time algal biomass starts to increase, at the beginning of the 20th century. While these elements are important micronutrients (Sunda, 2012) their toxicity at higher concentrations means any increases often result in negative impacts on ecosystems (Xu *et al*., 2016). Considering sedimentary Cu concentrations were higher in 1916 than 2016 it seems unlikely that these metals have a net positive impact on algal growth. Supporting this, many of these heavy metals peak and either stabilise or start declining from the 1970s while algal biomass starts to accelerate in growth. The divergence between heavy metal concentrations and algal biomass indicate that they were unlikely to have contributed towards the changes in algal biomass from the start of the 20th century. While the increase in algal biomass and heavy metal concentrations may be coincidental, it is likely that they reflect the sensitivity of Lake Gormire to changes in the catchment. Increases in atmospheric pollution would readily be transported to the lake via catchment erosion of soils.

Sedimentary pigments (including chlorophyll-*a*) can also be impacted by changes in preservation. The preservation condition (the ratio of chlorophyll-*a* to phaeophytin-*a*) increases during the 20th century (Fig. 4.11b) however the high correlation between chlorophyll-*a*, %C and $\delta^{13}C_{org}$ from the start of the 20th century indicates that variations in chlorophyll-*a* are likely to be driven by changes in algal biomass. In many lakes, higher preservation conditions may be a consequence of increased chlorophyll-*a* deposition, or changes in the proportion of planktonic vs benthic production, rather than changes in preservation (Buchaca and Catalan, 2007). This is supported by the increasing phaeophytin-a concentrations from the second half of the 20th century (Fig. 4.11b). In addition, the presence of high concentrations of hydroxyphaeophytin-*a* and purpurin-18-phytyl ester throughout the entire time series indicates the consistent availability of oxygen in the water column. The presence of these pigments indicates that the lake has not suffered from extensive periods of anoxia that would improve pigment preservation. Another indication that preservation of chlorophyll-*a* is not driving these trends is due to the increasing water clarity during the 20th century. An increase in water clarity should increase the photo-oxidation of chlorophyll-*a* and vice versa (Leavitt and Carpenter, 1990). As a result, it is likely that chlorophyll-*a* is preserved more efficiently in lakes with low water clarity (McGowan *et al*., 2018; Sobek *et al*., 2009). However, it would be expected that a reduction in light availability would have a much greater impact on chlorophyll-*a* production, through restricted photosynthetic activity. This is indicated by the periods in the 19th century with particularly low UV index corresponding to low sedimentary pigment concentrations. Therefore, whilst a relative increase in chlorophyll-*a* concentrations does indicate increased preservation during the 20th century, it is most likely driven by increased *in situ* production.

Improvements in water clarity may also contribute towards the observed increase in algal biomass. There has been a clear increase in UV index during the 20th century, which by the 21st century had returned to values similar to the start of the 18th century (Fig. 4.11b). However, lakes that experience increasing phytoplankton biomass typically also have more turbid waters. It is likely that the dominant driver of water clarity has been catchment inputs as demonstrated by the close correlation of the UV index to %C. While there is evidence that allochthonous inputs have declined during the 20th century, it is unlikely that water clarity today is comparable to when the relative proportions of diatoms and submerged macrophytes in the lake was higher. This is supported by the lithogenic element concentrations (e.g. K, Mg, Li), which although they have declined during the 20th century, still remain relatively high at similar concentrations to the first half of the 19th century. There is a more rapid decline in Al, compared to the other lithogenic elements, although this may reflect a recovery from acidification. Al solubility is inversely correlated to pH and so increasing soil pH may have reduced the leaching of Al to the lake, relative to other elements (Kryzevicius *et al*., 2019). The muted decline in lithogenic elements has occurred despite the catchment woodland recovery from the middle of the 20th century, which would be expected to reduce catchment erosion (Oldfield *et al*., 2003). However, any reduction in catchment erosion from increased tree cover may be offset by any increases in precipitation and rainfall intensity. There has been a shift towards enhanced rainfall at Whitby, in particular during winter months with an increase ~20mm month^{-1} between the 1960s and 2010s (Fig. 4.5). Despite concentrations of lithogenic elements remaining relatively high during the 20th century, the UV index continued to increase. By the start of the 21st century, the UV index is higher than during the early 18th century, representing minimal catchment inputs prior to deforestation. Therefore, while it is likely that water clarity has improved during the 20th century, there may be additional drivers of the increase in UV index.

Some of the increase in water clarity maybe attributed to enhanced water level fluctuation (WLF) in the summer months (Baker and Hilt, 2015). This is supported by the generally increasing sedimentary Na concentrations since the 1980s (Ma *et al*., 2016). Enhanced WLF will increase the salinity of lakes, especially those of closed lakes as water loss concentrates the chemical constituents of the lakewater. An enhanced reduction in water level during the summer would likely improve underwater light conditions and increase the area of the benthic zone that can support photosynthetic activity (Baker and Hilt, 2015; Sparber *et al*., 2015). An improvement in water clarity would typically benefit lake macrophytes, as opposed to phytoplankton but in Lake Gormire submerged macrophytes are rare. Therefore, an increase in temperature may have enhanced WLF during the 20th century contributing towards enhanced algal productivity at Lake Gormire.

The highly significant correlation between sedimentary chlorophyll-*a* concentrations and summer temperatures during the second half of the 20th century indicate that Lake Gormire may be particularly sensitive to short term (seasonal) weather variations. Therefore it seems likely that 20th century climate warming has played a role in increasing algal biomass in Lake Gormire, particularly since the 1970s. As Lake Gormire is a relatively small and shallow lake it is likely to respond more directly to short term variations in weather than larger deeper lakes (Arvola *et al*., 2010). This is due to the lower heat storage capacity of small lakes, which typically results in rapid freezing in the winter months and conversely enhanced warming in the summer (Shuter *et al*., 1983). The quick response of smaller lakes to changes in weather will translate to the algal community (Adrian *et al*., 1999). The sensitivity of Lake Gormire to weather conditions may be reflected by the clear and short lived decline in chlorophyll-*a* (and of all other carotenoids) around 1964 to 126.5 nmole. Taking the uncertainty associated with radiometric dating into account, it is possible that this data point reflects the year of 1963 which was the coldest winter experienced in 200 years nationally, and when the lowest mean winter temperatures were recorded at Whitby. Other years of extremely low minimum winter temperatures (e.g 1881, 1895) are also periods of notably low algal biomass indicating the role that temperature may be playing in determining annual algal biomass. Particularly low winter temperature during 1963 would likely have resulted in extensive ice cover which would have had an impact on primary production, including reducing the length of the growing season for spring blooming taxa such as diatoms (Reuss *et al*., 2010). Therefore, it would be expected that particularly cold years would result in the suppression of algal growth. Notably, while being the coldest winter in around 200 years, total algal biomass remained higher in the 1960s than during some warmer parts of the 19th century. This likely reflects the range of factors that can influence lake algal biomass, as by the 1960s there are indications of improvements in water clarity and changes in nutrient supply. Additionally, while the winter of 1964 was extremely cold, temperatures had increased substantially by the spring and were typical of the 1960s. Therefore, whilst the spring growing season may have been severely restricted, conditions for summer taxa may have still allowed large populations to develop.

4.3.4 Diatoms (diatoxanthin)

Diatoxanthin shows a relatively rapid decline from 89.2 nmole at the start of the 18th century to 32.5 nmole in 1767 (Fig. 4.22). There is a close correlation between diatoxanthin concentrations and %C ($r^2=0.73$, $p<0.05$) which could be interpreted as diatoms being a major source of OM to lake sediments (Wang *et al*., 2013). However, the decline %C during the 18th century is likely to be due to increased dilution of lake OM by allochthonous inputs. This is supported by diatoxanthin also being well correlated to the UV index ($r^2=0.53$, $p<0.05$), which in turn is correlated to %C. The decline in UV index during the 18th century likely reflects the increase in catchment inputs. The disturbance of afforested catchments can enhance the release of DOC and particulate organic carbon (POC) to lakes with the reduction in light penetration limiting production of some benthic taxa (Karlsson *et al*., 2009).

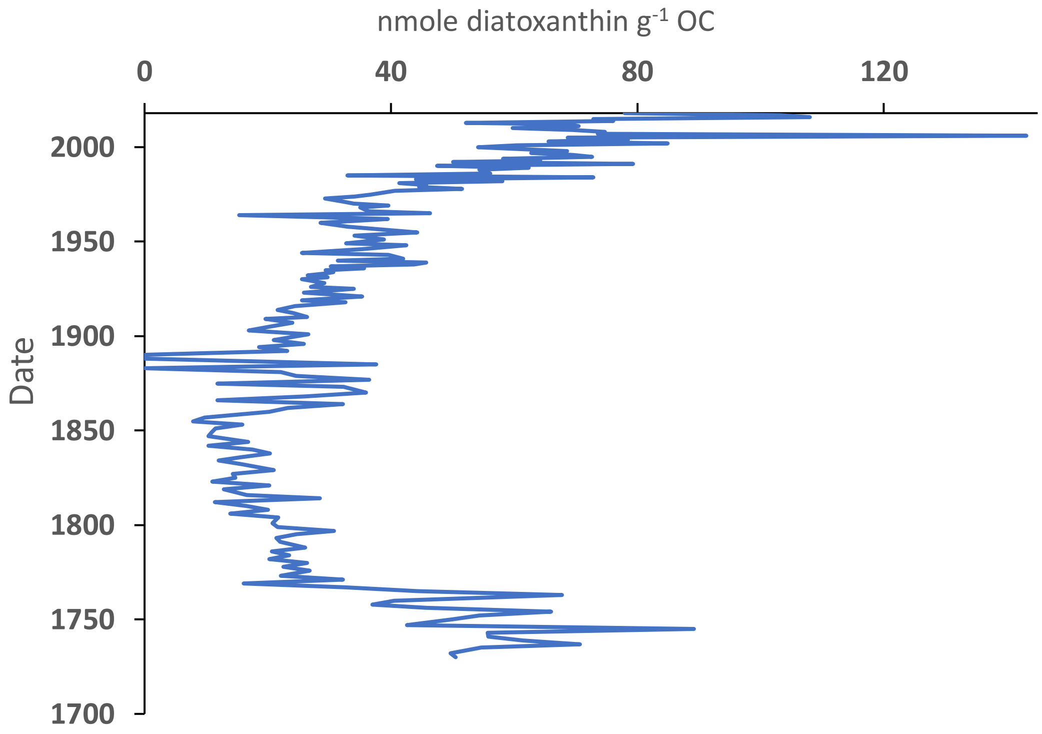

Fig. 4.22 Concentrations of diatoxanthin from Lake Gormire sediment core.

The possibility that the diatoms in Lake Gormire are predominantly benthic is supported by the continuous presence of the more labile diatom pigments (fucoxanthin and diadinoxanthin). Preservation of these pigments typically indicates diatoms growing on or close to the sediment surface which would reduce the opportunity for degradation before sedimentation (Buchaca and Catalan, 2007). In some lakes fucoxanthin will only be present in the surface sediments, which would suggest a substantial level of degradation (McGowan *et al*., 1999). Fucoxanthin loss typically increases with the depth of travel from its source to the sediments (Leavitt, 1993). Therefore, the consistent presence of fucoxanthin through the core probably means that Lake Gormire has always had a relatively large population of benthic diatoms.

Diatoms appear to respond to two periods of increased total algal biomass during the 19th century (1810-1814 and 1864 -1888). However, the single and relatively small spike in concentrations around 1814 to 28.5 nmole indicates that the increase in heavy metals in these years had only a marginal impact on diatom biomass. The period of increase from 1864 -1888 is slightly more prominent, increasing to 37.7 nmole in 1885, but is more muted compared to most other algal groups. While there is a small increase in the UV index during this period, it remains much lower than during the 18th century. This probably still reflects poor water clarity during this period which would severely restrict diatom growth. The impact of water clarity is likely highlighted further by the high variability of diatoxanthin concentrations during this period. Whilst there was some stimulation of diatom biomass there were also some years with no detectable diatoxanthin concentrations (1883, 1888 and 1890) indicating very low diatom populations in the lake. These years of very low diatom biomass occurred along with very low water clarity, with no detectable concentrations of the UV screening pigment scytonemin during these years. This again supports the suggestion that diatom populations in Lake Gormire are strongly controlled by water clarity. Low water clarity is likely a result of the 1870s and 1880s being the period of maximal catchment erosion to the lake.

Although there is uncertainty around the precise dating of sediments, the years where no detectable concentrations of diatoxanthin were recorded were also particularly cold. As recorded by the Central England Temperature Index, four out of ten of the coldest years on record occurred in the 1880s and the coldest on record in 1892 (Parker *et al*., 1992). Such cold temperatures would likely have supressed diatom growth and resulted in ice cover in Lake Gormire during the winter months. Ice cover may be particularly extensive in Lake Gormire, when temperatures are cold enough, considering the lake has little to no flow and is protected from the winds by woodland and the large cliff on the NE bank. Due to the considerable shading that the trees and cliff provide, direct solar input to the lake is likely to be restricted in the winter months. Therefore, ice cover in Lake Gormire during this cold period could have been extensive and relatively long lasting for a temperate lake.

Diatom biomass increases from the start of the 20th century, to 84.8 nmole in 2002, with a strong correlation to chlorophyll-*a* ($r^2=0.73$, $p<0.0001$), along with %C. The concurrent increase in diatoxanthin, chlorophyll-*a* and %C highlights the difference with the decline in diatoms during the 18th century, as chlorophyll-*a* increased. Therefore, it is likely that from the start of the 20th century there is a greater contribution of diatoms to the sediments. While diatoxanthin consistently increases during the first half of the 20th century, the concentration of fucoxanthin remains stable from 1918 to the 1970s (Fig. 4.23). It is possible that this indicates a relative increase in pelagic taxa, which would be expected to lead to comparatively less fucoxanthin due to the higher travel distances from diatom cells to the sediment. It could also represent a decline in chrysophytes, as these taxa can also produce fucoxanthin (Rowan, 1989). However, considering the uniform increase in algal biomass in all taxa during the 20th century this seems unlikely. Another diatom-derived pigment (diadinoxanthin) shares the same periods of increase in the 19th century as diatoxanthin and the gradual increase since the start of the 20th century. There are some divergences between diatoxanthin, diadinoxanthin (and fucoxanthin), in particular during the 18th century. These divergences can be partly explained by the fact that diatoxanthin can also be derived from dinoflagellates (Rowan, 1989) with the lake having been documented to contain populations of *Ceratium hirundinella* (Scott, 1948). The divergences will also likely be reflective of the relatively high lability of diadinoxanthin (and fucoxanthin) compared to the comparatively stable diatoxanthin.

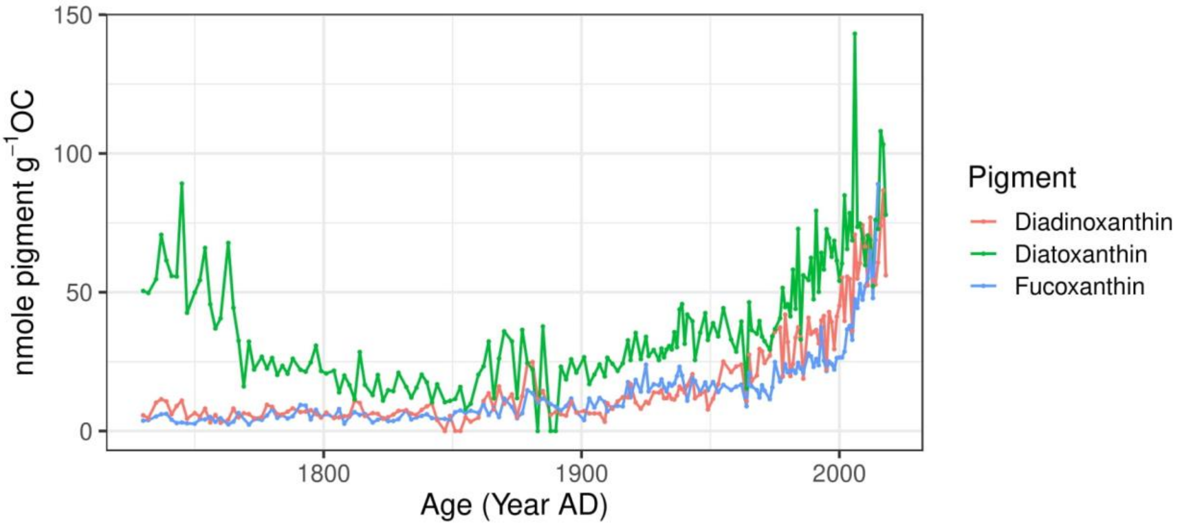

Fig. 4.23 Concentrations of diatom derived pigments from Lake Gormire sediment core.

The significant correlation between diatoxanthin concentrations and summer temperatures indicates an impact of climate change on diatom biomass, in particular since the 1970s. In general, warmer temperatures experienced in Lake Gormire will have multiple beneficial impacts on diatoms such as increased growth rates and extended growing seasons. Higher temperatures will also increase nutrient availability through higher recycling rates and greater internal loadings (Jeppesen *et al*., 2005; Jeppesen *et al*., 2009). However, diatoms will still be restricted by Si availability, which may be limiting the impact of climate change as 60% of the diatoxanthin variation in the regression model was not explained by temperature (Billen *et al*., 2001; Kong *et al*., 2021). For Lake Gormire, the geomorphology of the catchment means the allochthonous inputs are readily delivered to the lake. Along with the lack of outflows, this may mean that Si availability in Lake Gormire is naturally high. In such an environment, these factors may allow for the development of even larger diatom blooms in the future.

4.3.5 Cryptophytes (alloxanthin)

Cryptophyte biomass slowly but consistently declines from the start of the 18th century, to around 40% by the middle of the 19th century with alloxanthin concentrations of 6.4 nmole in 1840 (Fig. 4.24). This is followed by a large (5 times) increase in alloxanthin concentrations from the start of the 1850s, to 33.8 nmole in 1870. This is a greater change than any other algal group during this period, indicating that cryptophytes had benefitted disproportionately from an environmental change. The community shift towards higher cryptophyte abundances likely reflects greater organic inputs to the lake during this period. Cryptophytes are often abundant in lakes that receive high DOC inputs (Lepisto and Rosenstrom, 1998). This is due to the ability of cryptophytes to employ mixotrophy where organic carbon (such as DOM and DOC) is utilised as an energy source (Jansson *et al.*, 2000; Jones, 2000). They are also adapted to low light conditions as their motility means they can migrate to parts of the lake with more favourable light exposure (Gervais, 1997; Katechakis *et al.*, 2005). Therefore, the stimulation of cryptophytes may be related to an increase in organic matter influx from the catchment (Burkholder *et al.*, 2008; Stevenson *et al.*, 2016) and benefitted by the generally low water clarity during this period (Fig. 4.11b).

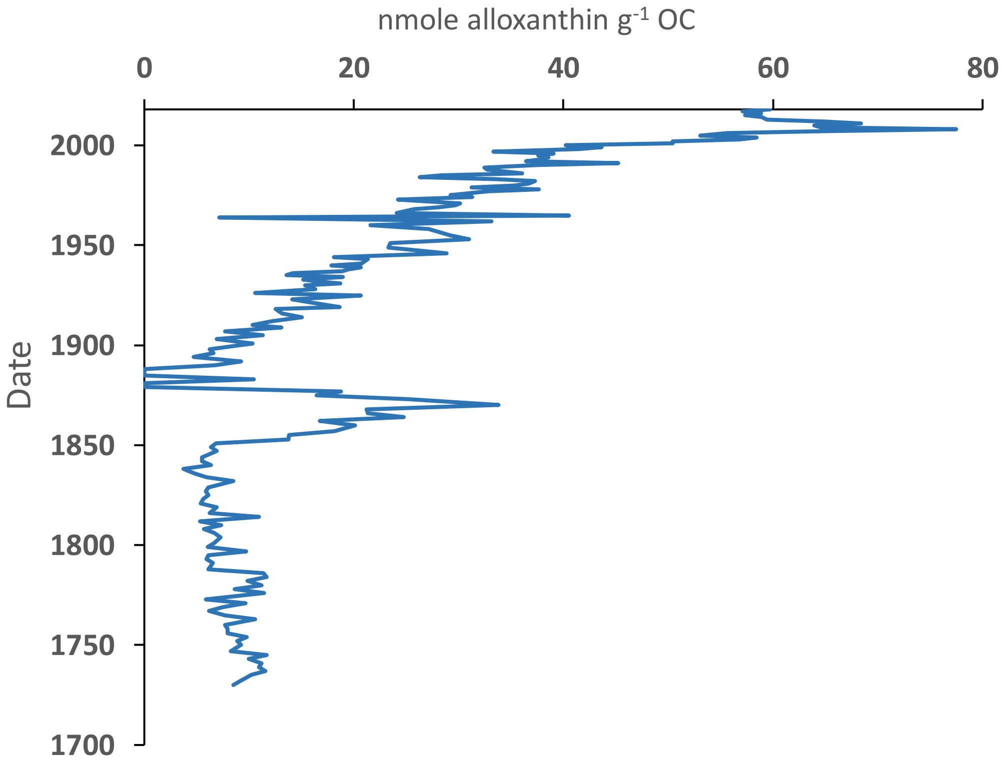

Fig. 4.24 Concentrations of alloxanthin from Lake Gormire sediment core.

Cryptophytes experience a rapid decline towards the end of the 19th century, with undetectable concentrations of alloxanthin in 1879-1881 and 1885-1888. Along with diatoms, cryptophytes are the only algal group in which concentrations reach undetectable levels during this period. Therefore, cryptophyte and diatoms are most likely impacted by the same environmental driver, which is reinforced by the fact that both are typically spring blooming taxa (Feuchtmayr *et al*., 2012). Longer periods of ice cover would be expected to impact the development of planktonic communities during cold periods, especially spring blooming taxa (Wang *et al*., 2013).

While alloxanthin declines to undetectable levels around the same time as diatoxanthin there is only one year where both pigments are undetectable (1888), with the other years alternating between the presence/absence of these pigments. The alternation between cryptophyte and diatom presence may reflect competition between the two taxa under variable and unsettled conditions, which could favour one algal taxa (or habitat) over the other (McGowan *et al*., 2005). The wet periods of the 1870s and 1880s may have contributed towards promoting cryptophyte populations when cold winters restricted their growth. Increases in precipitation will enhance catchment erosion and transportation of nutrients to the lake (Werritty, 2002). Therefore, wet conditions can lead to an increase in lake water nutrient availability. The importance of precipitation driven increases in allochthonous inputs for cryptophytes is highlighted by the regression analysis presented in section 4.2.6. Precipitation alone accounted for ~18% of the variability in sedimentary alloxanthin concentrations from the 1960s, second only to canthaxanthin concentrations. While temperature appears to be a more dominant driver of cryptophyte biomass, the role of precipitation may be more important for cryptophytes than many other algal taxa.

Cryptophytes appear to experience a greater decline during the extremely cold winter of 1963 than any other algal group to 7.2 nmole. Again, this may reflect the impact that an extended period of ice cover has on these spring blooming taxa. Alloxanthin concentrations during this year are almost four times less than the mean concentrations in the 1950s. This is compared to diatoxanthin concentrations which are ~2.5 times lower than the 1950s mean. The greater decline in cryptophyte biomass, likely because of the extreme cold, may reflect a greater impact on these planktonic taxa compared to benthic diatoms.

Cryptophyte biomass increases consistently during much of the 20th century to 40.2 nmole in 1999. This trend is common amongst all algal groups, highlighting a general shift in lake conditions towards a higher tropic state. From the second half of the 20th century, increased temperatures have likely enhanced cryptophyte biomass in Lake Gormire, along with all other taxa. The most rapid increase in cryptophyte biomass in recent years occurs at the start of the 21st century to 77.5 nmole in 2008. Pigment concentrations increase by 50% between the 1990s and the following decade, with a 40% increase in lutein (chlorophytes). However, there is a much more muted increase in total algal biomass during the same period (14%), indicating a community shift towards greater planktonic dominance in Lake Gormire.

4.3.6 Chlorophytes (lutein and chlorophyll-*b*)

As two key pigments of chlorophytes, changes in lutein and chlorophyll-*b* concentrations are closely associated ($r^2=0.89$, $p<0.0001$). A notable spike occurs around 1814 which, although not present in lutein (Fig. 4.25), is prominent in chlorophyll-*b* and most likely represents a brief period of enhanced chlorophyte biomass following anthropogenic pollution indicated by elevated levels of Cr and Ni. Nickel has been shown to have a stimulating effect on the growth of the chlorophyte *Botryococcus braunii* (Song *et al*., 2012). Considering the prominent increase in chlorophyll-*b* and the lack of corresponding increase for most other pigments (except chlorophyll-*a*), the impact of this pollution event may have been more pronounced for chlorophytes.

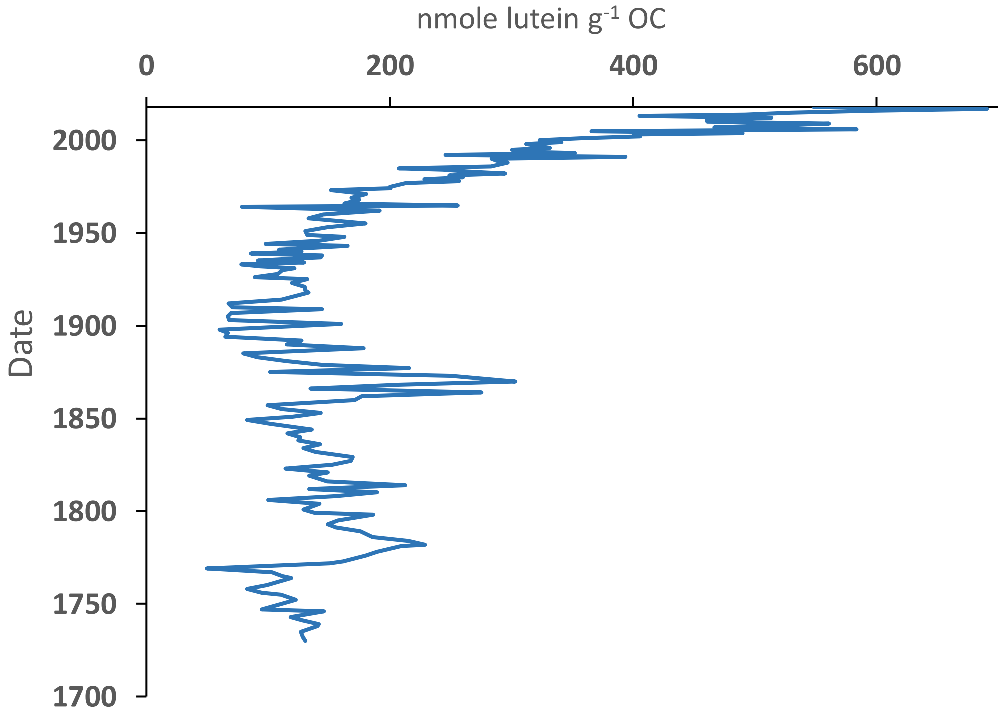

Fig. 4.25 Concentrations of lutein from Lake Gormire sediment core.

Chlorophytes appear to comprise a major proportion of the algal community in Lake Gormire, due to the relatively high concentrations of lutein compared to canthaxanthin (Fig. 4.11c), alloxanthin and echinenone (Oleksy *et al*., 2020). A dominance of chlorophytes typically indicates a high nutrient loading, often from elevated release rates from sediments which continuously resupply the photic zone (Jensen *et al*., 1994). As Lake Gormire has a closed basin, there will be minimal loss of nutrients through flushing and high internal loadings (Kilinc and Moss, 2002). In addition, the productive woodland that surrounds Lake Gormire, coupled with the steep profile of the catchment, will likely deliver substantial quantities of terrestrial nutrients to the lake. While the large chlorophyte population in Lake Gormire may be indicative of a relatively high 'background' supply of nutrients to the lake, increases in chlorophyte biomass may indicate periods of further nutrient enrichment. As indicated by the strong relationship between summer temperature and lutein concentrations, warming may be a driver of these trends. This is highlighted by the timing of the increase in chlorophyte biomass, from the start of the 20th century, representing a key transition from the Little Ice Age (15th – 19th centuries) into a period of sustained climate warming from the 20th century. Overall, the large increase in chlorophytes during the 20th century indicates that Lake Gormire has shifted to a system dominated by algae, with lutein concentrations increasing to 341.2 nmole in 1999. The dominance of chlorophytes may also reflect the macrophyte status of the lake which is currently poor, with very few modern assemblages and only sparse areas of submerged macrophytes.

It is also possible that light availability has impacted chlorophyte biomass change, especially considering the relatively large changes in the UV index during the 20th century. However, increased chlorophyte biomass during the 19th century occurred during a period of minimal water clarity. The increase in chlorophyte biomass during the second half of the 19th century is comparatively lower than that of other algal groups (e.g. cryptophytes, cyanobacteria). This indicates that chlorophytes inhabiting Lake Gormire may have been restricted compared to other low light tolerant taxa. The impact of light availability may also be reflected by a relatively rapid decline in lutein during the 1760s, reaching the lowest concentrations in 1769. The period of minimal chlorophyte biomass occurs when the UV index rapidly declines, with undetectable concentrations of the UV screening pigment scytonemin. The decline in alloxanthin to 49.7 nmole in 1769 is relatively short lived as it is followed by a period of increase, more than doubling by the start of the 1780s.

4.3.7 Cyanobacteria (echinenone, zeaxanthin, canthaxanthin)

While echinenone (total cyanobacteria; Fig. 4.26) and zeaxanthin (picocyanobacteria; Fig. 4.27) concentrations remain relatively stable during the 18th century, canthaxanthin (filamentous cyanobacteria; Fig. 4.28) increases. From the 1750s there was a period of ~100 years where filamentous cyanobacteria became relatively more dominant in Lake Gormire. This may indicate that the lake had relatively low nutrient availability during this period, which would favour N-fixing taxa. N-fixing cyanobacteria dominance can be a common occurrence for lakes in forested catchments, as the extensive vegetation removes large quantities of N before it can be transferred to the lake (Hayes *et al.*, 2015).

From the 1850s there were large increases in echinenone (>400%) to 50.3 nmole in 1870 (Fig. 4.26). The relatively rapid increase in total cyanobacteria biomass during the second half of the 19th century is indicative of an increase in nutrient availability (Rigosi *et al.*, 2014). This was a period of especially high allochthonous inputs, likely enhanced by particularly wet years and anthropogenic catchment activity. While echinenone is strongly correlated to canthaxanthin overall ($r^2 = 0.70$, $p<0.0001$), the increase in zeaxanthin of 169% and canthaxanthin by 80% during the 19th century is relatively muted (Fig. 4.27-8). This indicates that the increase in cyanobacteria is driven mainly by colonial non-heterocystous cyanobacteria during this period.

Non-heterocystous cyanobacteria can often respond strongly to increased nutrient availability, in particular over N_2-fixing cyanobacteria due to the lower energy efficiency of utilising atmospheric N_2 (Finlay *et al.*, 2010; Herrero *et al.*, 2004). Cyanobacteria were also likely further favoured by the low light conditions of Lake Gormire during this period. Cyanobacteria generally have higher growth rates than other types of algae when light conditions are low, such as in turbid conditions (Mur *et al.*, 1999). Therefore, the low water clarity may have given cyanobacteria a competitive advantage during the second half of the 19th century.

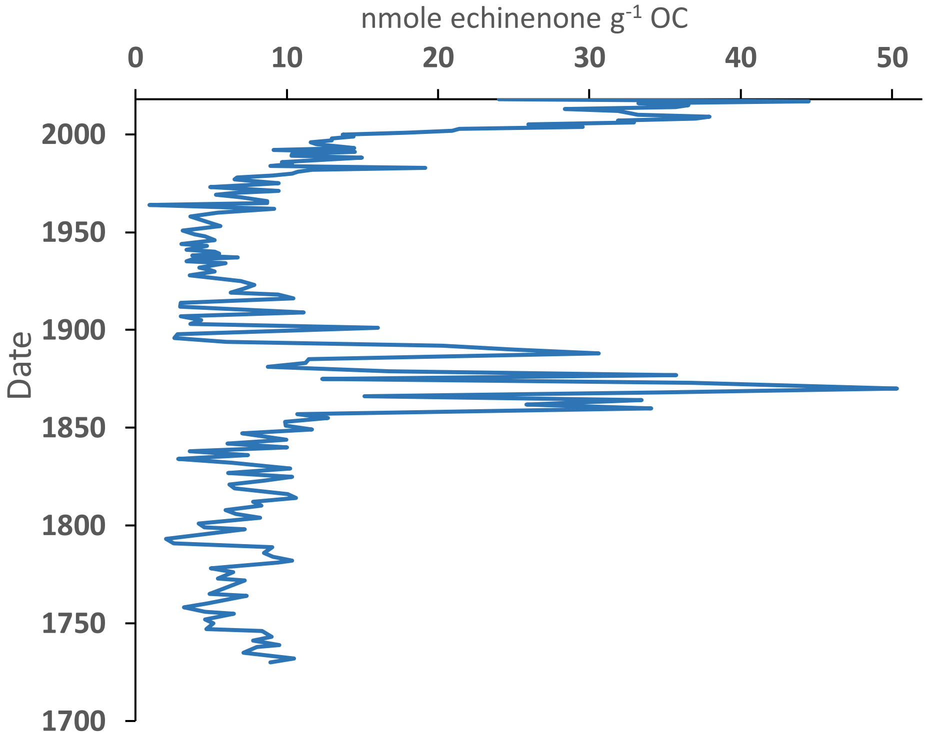

Fig. 4.26 Concentrations of echinenone from Lake Gormire sediment core.

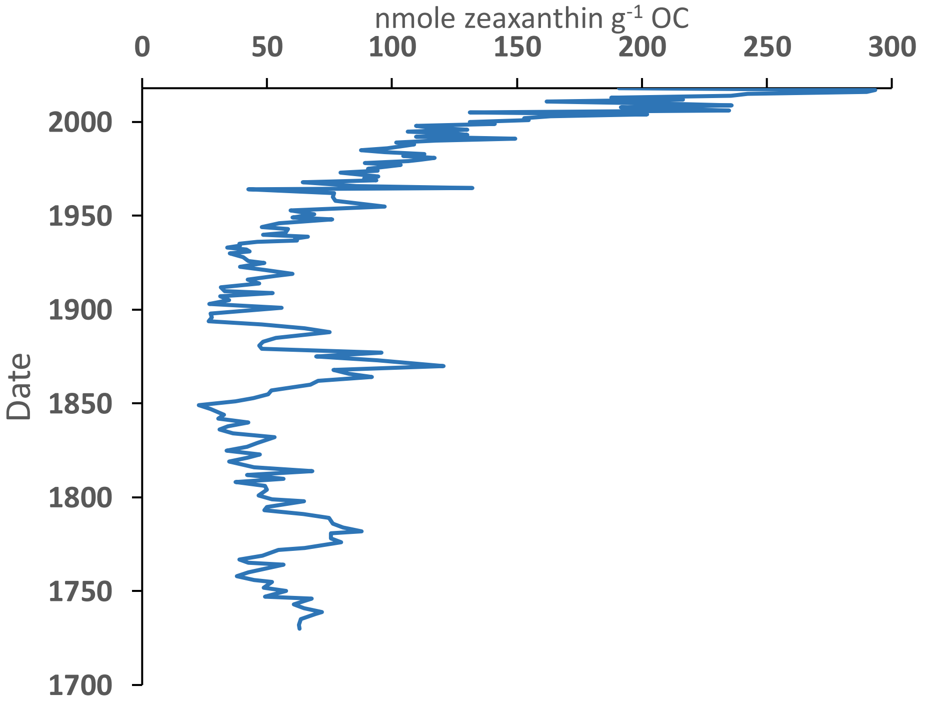

Fig. 4.27 Concentrations of zeaxanthin from Lake Gormire sediment core.

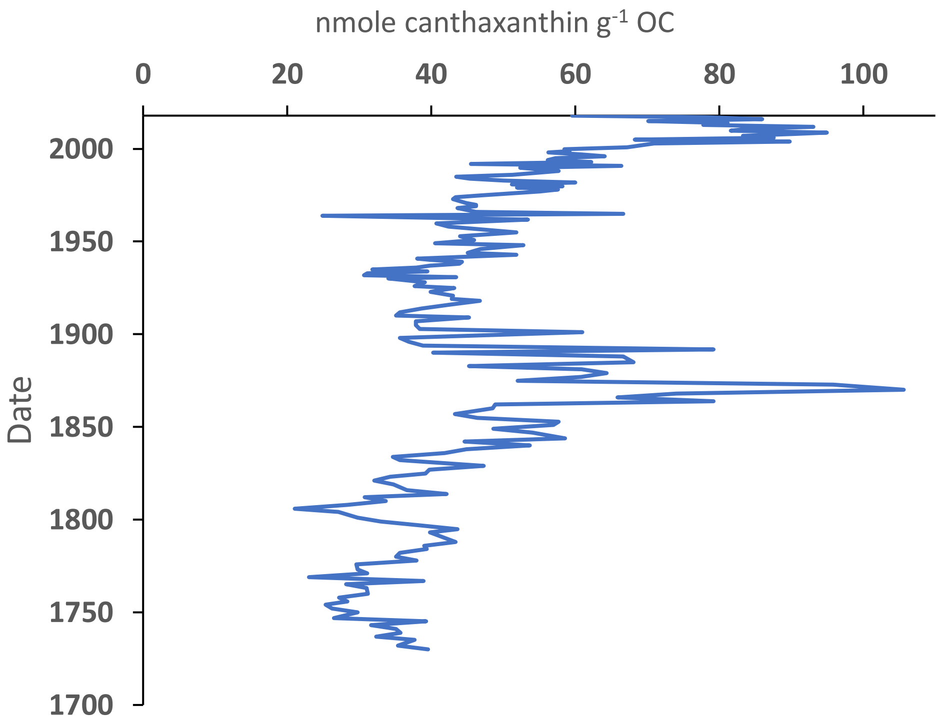

Fig. 4.28 Concentrations of canthaxanthin from Lake Gormire sediment core.

From around the start of the 20th century there is shift in the relationship between zeaxanthin and echinenone, representing all cyanobacteria. While there were relatively greater increases in echinenone (and canthaxanthin) during the 19th century, zeaxanthin experienced a greater increase in the 20th century. This divergence likely represents a shift in the cyanobacteria community to a relatively more picocyanobacteria-dominated assemblage (Romero-Viana *et al.*, 2010). While the increase in total cyanobacteria is relatively muted in the 20th century, it is still a period of increasing cyanobacteria abundances with echinenone concentrations increasing to 38.0 nmole in 2009.

The cause of the change in cyanobacteria community in Lake Gormire may be reflected by the increasing UV index during the 20th century, in particular since the 1930s. Typically, cyanobacteria are thought to be better adapted to low light conditions although there can be considerable variability between species (Huisman *et al.*, 1999). For picocyanobacteria, high light penetration can enable them to grow in the deeper layers of the water column, where nutrient availability is higher (Romero-Viana *et al.*, 2010). Therefore, the improving light conditions during the 20th century may have reduced the competitive advantage of some low light tolerant taxa and benefitted picocyanobacteria. As a result, improving light conditions in Lake Gormire during the 20th century may have contributed towards the shift towards greater picocyanobacteria and their dominance in the cyanobacteria community.

Whilst zeaxanthin is regularly used as the pigment marker for picocyanobacteria (e.g. Bianchi *et al*., 2000; Hobbs *et al*., 2021; Romero-Viana *et al*., 2010) it can also be produced by some chlorophytes (Brown and Jeffrey, 1992). It is notable that there is a stronger correlation of zeaxanthin to lutein (r^2=0.93, p<0.0001) compared to canthaxanthin (r^2=0.56, p<0.0001) and echinenone (r^2=0.55, p<0.0001). This was also reported by Deshpande *et al*. (2014) from sediment cores take from Lac Saint-Augustin, an urban lake in Canada. They attributed the stronger relationship of zeaxanthin and lutein to a substantial production of zeaxanthin by chlorophytes. Considering the relatively high biomass of chlorophytes in Lake Gormire, as inferred by high lutein concentrations, chlorophytes may also be producing zeaxanthin, potentially obscuring the picocyanobacteria signal. However, there is strong correlation between most of the algal pigments in Lake Gormire, especially since the start of the 20th century, for example alloxanthin (r^2=0.81, p<0.001) and chlorophyll-*a* (r^2=0.77, p<0.001). The concurrent increase in pigments indicates that the strong relationship between zeaxanthin and lutein may be more reflective of the concurrent increases in cyanobacteria and chlorophyte biomass, rather than indicating an overwhelming contribution of zeaxanthin by chlorophytes. Therefore, while it is possible that the use of zeaxanthin as a marker of cyanobacteria may be somewhat confounded by a high chlorophyte population it is still likely to be the best marker for picocyanobacteria (Krajewska *et al*., 2019; Stal *et al*., 2003).

Since the start of the 20th century there have also been concurrent increases in cyanobacteria and diatom derived pigments, for the first time in the sedimentary record. This may reflect an increased trophic status of the lake during the 20th century, with broad increases in lake algae. The 153% increase in zeaxanthin concentrations between 1901 and 1999 (141.1 nmole) is higher than the increase in chlorophyte (113%) and diatom (130%) derived pigments (Fig. 4.27). In comparison there was a 422% increase in cryptophyte derived pigments over the same time period. While it is difficult to assess the dominance of a particular taxa in a lake based on sedimentary pigments alone, it does not appear that picocyanobacteria have become increasingly dominant during the 20th century. A shift towards cyanobacteria dominance is commonly predicted to arise from enhanced nutrient loading and temperature (e.g. Johnk *et al*., 2008; Reynolds, 2006). However, while cyanobacteria have traditionally been considered as faster growing under higher temperatures, chlorophytes can have very similar growth rates when nutrient supply is sufficient (Bogard *et al*., 2020 Lurling *et al*., 2013). There can also be considerable variability in growth rate and optimum conditions between specific species of cyanobacteria. Therefore, cyanobacteria will not necessarily dominate through elevated nutrients and temperature.

As indicated by the significant correlation between summer temperatures to canthaxanthin and zeaxanthin pigments, climate change is likely an important driver of this increase, at least in the second half of the 20th century. Cyanobacteria typically have a high optimum growth temperature, greater than many other algae (Kosten *et al*., 2012). Therefore they would be expected to respond strongly to increases in temperature. While there is a significant correlation between temperature and filamentous cyanobacteria biomass, the increase in the 20th century is relatively muted. However, there are more rapid increases in canthaxanthin concentrations from the start of the 21st century to 38.0 in 2009. While temperature is an important driver, regression analysis indicates that winter precipitation has a greater impact on canthaxanthin concentrations compared to the other algal pigments, explaining >20% of the variation. The 21st century has been a period of particularly warm summers along with wet winters. The impact of wet winters is likely reflected by the concentrations of some of the lithogenic elements (K, Li) which stopped declining and possibly increased slightly from the end of the 1990s despite the recovery of the woodland. Therefore, relatively high catchment inputs may have produced more favourable conditions for filamentous cyanobacteria during this period. There is indication that water clarity has stopped improving with some declines in the UV index in the most recent decades. A more variable, or a slight reduction, in water clarity may benefit some low light tolerant taxa of cyanobacteria. Notably, this more rapid increase in filamentous cyanobacteria also occurs concurrently with the more rapid increase in cryptophyte, another taxa which typically benefits in lower light conditions, while the light sensitive diatoms appear to have declined slightly.

4.4 Discussion

4.4.1 Zone 1 (1730 - 1799)

This period is defined by indicators of increasing catchment inputs, with a rapid reduction in %C, UV index, increases in $\delta^{13}C_{org}$, $\delta^{15}N$ and lithogenic elements (e.g. Al, Li, Mg, K). This is likely reflective of a period of deforestation in the catchment which is consistent with the findings of Oldfield *et al*. (2003) and Fisher *et al*. (2003). They attributed increased catchment erosion to periods of deforestation in the upper parts of the catchment, with the lower parts of the catchment estimated to be at least 600 years old (Oldfield *et al*., 2003). The deforestation is indicated by a notable decline in tree and shrub pollen along with increases in relative abundance of pollen from aquatic plants, cereals and grasses. These pollen are typical indicators of forest clearance and farming. In other parts of England, this pre-industrial period (1500-1850) was a time of particularly intensive ploughing and deforestation. In Blelham Tarn, these activities resulted in increased catchment erosion and inwash of minerogenic material, which corresponded with declines in %C and %N (Moorhouse *et al*., 2014; Pennington *et al*., 1976). Therefore, periods of deforestation are often reflected by a decrease in the OC content of lake sediments (Fisher *et al*., 2003).

O'Reilly *et al*. (2005) found that sedimentary $\delta^{15}N$ values in Lake Tanganyika, Africa increased consistently with other indicators of deforestation (e.g. pollen assemblage change, sedimentation rates). The increase in $\delta^{15}N$ resulted from the increase in overland flow which transported greater quantities of soil-associated N compounds to the lake. Therefore, the increase in sedimentary $\delta^{15}N$ at Lake Gormire from the 1760s to 1780s likely reflects an increase in allochthonous inputs to the lake following a period of deforestation. The timing of the increase in $\delta^{15}N$ would suggest that the impact of deforestation progressed for several decades after the initial event. This is consistent with the findings of Ochia *et al*. (2015), who found that in Bishaguso-ike reservoir, Japan the erosion of catchment soils and organic matter increased for 15 years after deforestation. This was driven by an increased exposure of bare soils to heavy rainfall, which transported enhanced quantities of terrestrial OM to the lake.

The years between 1730 and 1799 is also accompanied by a shift towards gradually lower C/N. Degraded soil material can have relatively low C/N with Lacey *et al*. (2018) reporting C/N values of 11.5 for the soils of the grasslands in the catchment and 11.9 of the soils from the inflow to Rostherne Mere in Cheshire (UK). In comparison, C/N for the woodland soils was 35.4, representing the difference in C/N between fresh and degraded OM. This supports the suggestion that for Lake Gormire the source of the increase in catchment material is not from the immediate vicinity but higher up in the catchment away from the surrounding woodland (Oldfield *et al*., 2003). In general, the period of 1730-1799 is defined by a rapid decline in %C and C/N with increasing $\delta^{13}C_{org}$ and catchment derived materials, which is consistent with a deforestation event analysed by Oldfield *et al*. (2003) and Fisher *et al* (2003).

The decline in C/N may also reflect the increasing algal biomass following the period of deforestation, which is accompanied by minor increases in chlorophyll-*a* concentrations. Oldfield *et al*. (2003) and Fisher *et al*. (2003) suggested that periods of deforestation had led to enhanced aquatic productivity, likely through increased soil associated nutrients being washed into the lake. This probably led to a progressive increase in trophic state over time (Fisher *et al*., 2003).

A decline in C/N and $\delta^{13}C_{org}$ stability also occurred in Rostherne mere from 1994. Lacey *et al*., (2018) reported that in Rostherne Mere, the lake had experienced substantial eutrophication from a sewage treatment works which was closed in 1991. However, the continual decrease in C/N values to the present day indicates how nutrient concentrations had remained high in the lake, even years after the diversion of effluent. High nutrient concentrations were attributed to internal nutrient loading maintaining high nutrient concentrations. The continual decline in C/N values at Rostherne Mere highlights how algal productivity can still be stimulated by high levels of internal loading long after the external supply has been reduced. Therefore, for Lake Gormire, deforestation of some parts of the catchment may have caused a stimulation in algal growth even after the activities which had increased nutrient exports had ended. During the 18th century there are minor increases in chlorophyll-*a* concentrations along with a progressive decline in C/N. Therefore the progressive decline in C/N may be reflective of both the continual influx of catchment material and an increasing algal biomass in the lake.

Lake Gormire is a closed basin lake, and therefore nutrients are not readily flushed out but can accumulate over time. Brooks *et al*. (2001) investigated the small (6.4 ha) closed basin kettle hole of Betton Pool, Shropshire to infer past P concentrations. Lake water P increased gradually since 1850 until 1974 when P increased more rapidly, with the increase since the 1970s likely representing anthropogenic eutrophication from diffuse sources. Prior to the 1970s, increasing lake water P at Betton Pool was likely a natural occurrence. Due to long water retention time (WRT), incoming P from the catchment is not flushed out and this has resulted in the P pool gradually increasing over time (Kilinc and Moss, 2002). This enhanced P pool can result in substantial quantities of P being re-released from the sediments in summer months (Jeppesen *et al*., 2009; Søndergaard *et al*., 2003). In such lakes it is likely that algal blooms can be sustained through the recycling of nutrients within the lake system long after initial allochthonous inputs occur (Heisler *et al*., 2008). In Whitemere, Shropshire cyanobacteria blooms have been a long-term natural phenomenon of this closed basin lake (McGowan *et al*., 1999). A high level of recycling and reduced nutrient loss, coupled with periods of enhanced allochthonous input means that closed basin lakes can develop high levels of algal biomass (Heisler *et al*., 2008; Reuss *et al*., 2010).

The impact of a high WRT was also indicated by Moorhouse (2016), who demonstrated that there was a clear positive correlation between the extent of algal community change and WRTs in lakes within the English Lake District. This was attributed to lakes with high WRTs being relatively more impacted by nutrient loading while maintaining favourable conditions for bloom forming taxa to develop. Therefore, lakes such as Lake Gormire should be highly susceptible to any changes in nutrient loading. Considering nutrient loading is the key driver for determining algal biomass in most lakes (Kosten *et al*., 2012), it is most likely that deforestation during the 18th century resulted in a progressive increase in algal biomass.

There has been a clear deterioration in light conditions as a result of the period of deforestation. In temperate lakes, light is often considered to be the sole limiting factor in winter and early spring (Sommer *et al*., 1986). The impact of light availability on diatom biomass was reported by Hu *et al*. (2014) in Moon Lake, Tibet, where the lowest diatom pigment concentration occurred during the Little Ice Age when light availability was severely restricted by extensive ice cover. For Lake Gormire, diatoms appear to be the only taxa supressed by the increase in catchment inputs during this period. There is a concurrent but gradual increase in total algal biomass which could represent a shift in community composition following catchment disturbance. Compared to cyanobacteria, many of which are well adapted to grow in low light conditions (Kosten *et al*., 2012), many diatom species are not adapted to grow in turbid waters with *Cyclotella* shown to grow poorly under low light conditions (Lotter and Bigler, 2000)**.** Diatoms typically dominate benthic habitats and their growth can be limited by turbid waters, whereas cryptophytes are typically pelagic and along with chlorophytes and cyanobacteria can be present in benthic and pelagic habitats (Buchaca and Catalan, 2007). Therefore, under conditions of rapidly deteriorating light conditions, benthic diatoms would be expected to be disproportionately impacted.

4.4.2 Zone 2 (1800 - 1899)

The 19th century represents the period of maximal erosion and allochthonous inputs to Lake Gormire. While catchment inputs have resulted in a decline in C/N values at Lake Gormire since the start of the 19th century, for the lakes in the Windermere catchment C/N values increased from 1800 to 1900. The increase was suggested to be due to increased allochthonous OM deposition from land disturbance, including deforestation (Moorhouse, 2016). Considering land disturbance is likely to have contributed to the C/N decline at Lake Gormire during this period there is a clear difference between these lakes. Catchment characteristics can have a large impact on the composition of sedimentary organic matter (Maberly *et al*., 2013). Therefore, it can be expected that C/N would respond differently between lake catchments to similar drivers of change.

During the first half of the 19th century there is a notable increase in canthaxanthin concentrations while most other algal pigments decline or show little trend. Similarly, Hobbs *et al*. (2021) reported increases in canthaxanthin in Anderson Lake, USA during the 1950s and 1960s. Concentrations were higher than during the last ~250 years and were attributed to agricultural activity. As in Lake

Gormire, there was a shift away from picocyanobacteria (indicated by zeaxanthin) that were prevalent prior to the 1900s. While zeaxanthin declined following the end of farming of the catchment in the 1970s, canthaxanthin remained high to the present day (Hobbs *et al*., 2021). Therefore, the period of eutrophication probably initiated a shift to the dominance of N_2-fixing cyanobacteria, even after nutrient loading had declined. It is likely that the period of enrichment gave some filamentous taxa a competitive advantage that allowed them to dominate the lake (Paerl and Otten, 2013). This is likely to also have been occurring in Lake Gormire, following deforestation, as there is a consistent increasing trend for canthaxanthin (filamentous cyanobacteria) in the first half of the 19th century while zeaxanthin declines.

While there is a shift towards more filamentous cyanobacteria during the first half of the 19th century, there is more broad increase in algal biomass during the second half of the 19th century, supported by the declining C/N and increased algal pigments. There is evidence of an increase in algae from ~1850, however the lack of response in $\delta^{13}C_{org}$ and %C indicates that continually high catchment erosion may be the over-riding driver of these signals. Stevenson *et al*. (2016) found that for Irish lakes in plantation woodlands, forest planting was a major factor regulating the growth of cryptophytes and to a lesser extent cyanobacteria. In lakes where woodland exceeded 50% of the catchment land cover, forest plantation had a substantial impact on algal abundance and community composition. There was a two- to six-fold increase in pigments from cryptophytes (alloxanthin) and a 39 – 116% increase in cyanobacteria (canthaxanthin), likely due to increased fertiliser use on the expanded forestry area. While the community shifts reported by Stevenson *et al*. (2016) are in line with the changes observed in the Lake Gormire record, the period of increased algal biomass in Lake Gormire occurs ~100 years before the wide application of fertilisers for forestry (Nieuwenhuis *et al*., 2007). Therefore, it is unlikely that the increase in algae in Lake Gormire from the 1850s is due to fertilisation of the catchment. However, an increase in organic matter from the catchment during this period (>75% forested) could have stimulated cryptophyte growth through enhanced inputs of OM from the catchment. Oldfield *et al*. (2003) noted the start of an increase in *Pinus* pollen from 1770, which was attributed to the beginning of forestry plantations that were common in the North of England during the second half of the 19th century. Therefore, it is possible that the increase in filamentous cyanobacteria pigments (along with other algal groups) were related to forestry activity in the catchment that could have increased nutrient loading to the lake.

The dominance of cryptophytes and cyanobacteria in Lake Gormire during the second half of the 19th century is also likely also related the low water clarity at the time. Across a range of lakes in Europe and South America Kosten *et al*. (2012) found that a higher shade index correlated with a higher proportion of cyanobacteria. Additionally, an increase in shade tolerant cyanobacteria (e.g *oscillatoriaceae*) can cause an increase in turbidity that favours their competitive advantage (Scheffer *et al*., 1997). This suggests a positive feedback loop where a lake becomes progressively more turbid as cyanobacteria biomass increases. While there were increases in canthaxanthin, there were greater increases in echinenone which suggest that the increase is driven by non-heterocystous cyanobacteria. In Wascana Lake, Canada, experimental addition of NH_4^+ favoured the growth of colonial non-heterocystous cyanobacteria, chlorophytes and cryptophytes, with the poor growth of N_2-fixing cyanobacteria and diatoms (Donald *et al*., 2011). The increase in these taxa mirrors the trends experienced in the late 19th century in Lake Gormire and may suggest that the second half of the 19th century was a period of increased NH_4^+ transport to the lake via enhanced input of degraded catchment material. Increased NH_4^+ loading is also supported by the changes in $\delta^{15}N$ at the time which likely reflect greater proportions of mineralised organic matter entering the lake. An increase in nutrients could have resulted from the particularly wet conditions during this time period. Five out of ten of the wettest years on record occur between 1848 and 1882 (Wigley *et al*., 1984), which encompasses the period of enhanced algal biomass in Lake Gormire. At Easedale Tarn, periods of increased catchment-derived nutrient inputs have been associated with an increase in cryptophyte populations. The increased nutrients were attributed to high rainfall frequency events enhancing catchment erosion (Moorhouse, 2016).

Typically, chlorophytes respond strongly to nutrient additions due to their high maximum growth rates and nutrient uptake rates (Fernandez and Galvan, 2007). Due to their ability to respond strongly to all forms of N (Donald *et al*., 2011) chlorophytes can be superior competitors in high nutrient environments (Litchman *et al*., 2007). However, chlorophytes do not appear to have become dominant in Lake Gormire during the period. Bogard *et al*. (2020) showed that in experimental treatments, cyanobacteria dominate in all N loads except with the highest treatments (which is unlikely to be reflective of the vast majority of lakes) where chlorophytes dominated. Oleksy *et al*. (2021) found that benthic chlorophytes reacted strongly to N additions, even when N concentrations are relatively high. Additions of both N and P in field experiments resulted in the dominance of chlorophytes and significant increase in total algal biomass, with P alone having a negligible impact. Additionally, the strong response of chlorophytes to N availability was also found through the experimental additions of N and N+P to two lakes in the French Alps. Chlorophytes responded strongly to N alone indicating N availability to be the controlling factor of chlorophyte growth (Lepori and Robin, 2014). The lack of dominance by chlorophytes may reflect a moderate increase in nutrient loading during the second half of the 19th century, along with the low water clarity of the time. Such conditions would be better suited for low light adapted taxa such as cryptophytes and cyanobacteria.

Considering the second half of the 19th century represents some particularly cold and unsettled conditions towards the end of the Little Ice Age, adverse conditions may have contributed to the decline in all algal taxa. In temperate lakes, diatoms are typically spring blooming taxa (e.g. Feuchtmayr *et al*., 2012; Reavie *et al*., 2016; Shatwell and Köhler, 2019; Townsend *et al*., 1992). As a result, the length of the spring growing season can impact diatom populations (Thackeray *et al*., 2008). Extended ice cover would have reduced the time available for diatoms to proliferate, as ice thaw is often the major trigger for diatom bloom development in lakes (Shatwell *et al*., 2008). Planktonic taxa (e.g. *Cyclotella*) typically grow poorly in colder conditions and under periods of enhanced ice cover (Hu *et al*., 2014; Lotter and Bigler, 2000). Therefore, it is likely that diatom populations in Lake Gormire were impacted by a combination of low water clarity and water temperature during the late 19th century. The reduced growing season through extended ice cover coupled with particularly high catchment erosion would likely result in particularly unfavourable conditions for diatoms during this period. However, it also likely contributed towards the general decline in algal taxa towards the end of the 19th century.

4.4.3 Zone 3 (1900 - 1969)

Increased algal dominance is a common occurrence in English lakes during the 20th century, coinciding with lower sedimentary $\delta^{13}C_{org}$ (e.g. Fielding *et al*., 2020; McGowen *et al*., 2012; Moorhouse *et al*., 2014). Abrupt changes to lower $\delta^{13}C_{org}$ values were also recorded in Erlongwan maar, China with a decline of 4.2‰ during the 19th century (Wang *et al*., 2013). As with Lake Gormire, Erlongwan maar is a closed basin lake in a relatively small catchment, surrounded by woodland. The decline in $\delta^{13}C_{org}$ at Erlongwan maar lake during the 19th century is similar to the magnitude of change experienced in Lake Gormire, with $\delta^{13}C_{org}$ values declining ~3.8‰ over a similar length of time. These shifts were attributed to a change in diatom community composition, towards more planktonic taxa at the end of the Little Ice Age. Benthic algal taxa (−26‰) were found to have higher $\delta^{13}C$ values than planktonic taxa (−32‰) with an average difference of ~6‰ (Doi *et al*., 2009; France, 1995). Following the Little Ice Age TOC increased indicating relatively more productivity in Erlongwan maar lake with low $\delta^{13}C_{org}$ and C/N. While some of these findings are consistent with what was experienced in Lake Gormire there is no direct evidence that the 20th century increase in diatoms was a result of an increase in planktonic taxa. However, considering the concurrent increase in other planktonic taxa (e.g. cryptophytes) from the start of the 20th century it seems likely that this was a period of general increase in pelagic phytoplankton.

Woodland recovery could explain some of the decline in $\delta^{13}C_{org}$ and $\delta^{15}N$ values from the start of the 20th century, reflecting an increase in catchment productivity. At Blelham Tarn sedimentary $\delta^{13}C_{org}$ declined along with an increase in permanent grassland, agricultural land and woodland cover in the catchment (Moorhouse *et al*., 2016). An increase in agricultural and woodland cover would have increased catchment productivity, which will have led to lower $\delta^{13}C_{org}$ values as a result of DIC with lower $\delta^{13}C$ being delivered to a lake (Maberly *et al*., 2013). In Bishaguso-ike reservoir, Japan $\delta^{15}N$ (along with $\delta^{13}C_{org}$) declined for at least 35 years after deforestation (Ochia *et al*., 2015). These declines likely reflect a decreasing contribution of soil OM, which had significantly higher $\delta^{15}N$ values than the sediments ($\delta^{15}N_{soil}$ = ~3, $\delta^{15}N_{sediment}$=~0). The decrease in soil OM suggests a gradual recovery of catchment vegetation that decreased soil erosion. However, the continual shift to lower $\delta^{15}N$ and $\delta^{13}C$ would suggest that the catchment has been relatively slow to recover from deforestation. A slow recovery from deforestation is expected considering it typically takes more than 50 years for a forest floor to reaccumulate the lost organic matter (Covington, 1981). While there is large uncertainty surrounding the chronology prior to the 20th century, it is likely that the 20th century declines in $\delta^{15}N$ and $\delta^{13}C_{org}$ values have occurred at least 150 years after deforestation. However, the pollen analysis by Oldfield *et al*. (2003) indicates that woodland recovery around Lake Gormire did not occur until around the 1950s, when an increase in *Betula* pollen is detectable. Therefore woodland recovery is unlikely to be the cause of the increase in algal biomass at the start of the 20th century.

The influence of the catchment on lake organic matter appears to be less important during the 20th century. Fisher *et al*. (2003) found a strong covariance between TOC and % pollen from trees and shrubs throughout the sedimentary record. For instance, while there is an increase from 25% to 78% in tree and shrub pollen in the post Romano period of forest regeneration (~600AD), TOC also increases from 8% to 24%. This relationship exists throughout the vast majority of the 3,500-year sampling period until the 20th century (Fisher *et al*., 2003). While pollen from trees and shrubs increased from ~40% to 47%, TOC doubles from ~7% to 14% in the most recent sediments (dated at ~1970). Therefore, it appears as though the covariance between tree pollen and TOC may be weaker in Lake Gormire since the start of the 20th century, likely reflecting a greater contribution of algae to the sedimentary OM pool. Fisher *et al*. (2003) also reported increasing algal biomass at Lake Gormire during the 20th century, with an increase in n-alkenoic and branched acids (derived from autochthonous algae). The increase of these lipids likely reflects enhanced aquatic productivity which has historically been attributed to deforestation events. However, there is no evidence of any further deforestation in the catchment prior to the 19th century, with the middle of the 20th century representing a period of woodland recovery. Therefore, whilst deforestation has likely stimulated algal productivity in the past, the 20th century increases likely relate to a different driver.

McGowan *et al*. (2018) found that across six arctic lakes, catchments with the greatest forest cover had higher sedimentary alloxanthin concentrations. This is likely driven by an enhanced supply of C sources to these lakes. Therefore forest regeneration could have contributed to the increased alloxanthin concentrations in Lake Gormire since the 1950s. Along with increases in cryptophytes there are concurrent increases in chlorophytes from the start of the 20th century. Unlike the second half of the 19th century there is also a concurrent increase in diatom biomass with little change in filamentous and colonial cyanobacteria. This may indicate a change in the source and/or type of N driving these increases in biomass. Donald *et al*. (2011) found that while NH_4^+ favoured colonial cyanobacteria, chlorophytes and cryptophytes, at the expense of diatoms, NO_3^- favoured diatoms, along with chlorophytes and cryptophytes. NO_3^- additions were shown to only stimulate some species of cyanobacteria. A switch in nutrient source, such as NH_4^+ to NO_3^-, between the 19th and 20th centuries may help to explain why total cyanobacterial biomass did not respond as strongly as during the 20th century. Additionally, the start of the 20th century also represents a period of increasing water clarity in the lake, in particular since the 1930s. This may have further reduced the competitive advantage of some of the shade tolerant cyanobacteria taxa.

In the Windermere catchment, all lakes but the most upland tarns experienced significant increases in lutein concentrations during the 20th century, which was attributed to extensive anthropogenic eutrophication (Moorhouse, 2016). The importance of nutrient availability to chlorophyte growth was highlighted by Elliott *et al*. (2006). They investigated the response of Bassenthwaite Lake, Cumbria, to increasing nutrients and temperature and found that chlorophyte (*Chlorella*) biomass was strongly linked to water nutrient loading. Chlorophyte biomass increased with nutrients even under conditions when temperatures declined, indicating the dominance of nutrient availability to chlorophyte productivity. While there is no evidence for anthropogenic eutrophication of Lake Gormire, it seems likely that the increasing algal biomass of the 20th century is also related to increasing nutrient availability.

While Lake Gormire has no point source entry for nutrients, it is possible that there have been increases in atmospheric N depositions during the 20th century. Even though there has been a decline in $\delta^{15}N$ during the 20th century, Holtgrieve *et al*. (2014) found the most pronounced changes across the Northern Hemisphere have occurred since ca.1950. The decline has been attributed to the expansion of industrial N fixation which has resulted in increased atmospheric N deposition to lake catchments. For lakes in the Windermere catchment, there were relatively rapid declines in

$\delta^{15}N$ values in the later part of the 20th century (Moorhouse, 2016). Stickle Tarn decreased from 2.3‰ in 1970 to 0.8‰ by 1986 and Easedale Tarn declined from ~2‰ in 1940 to 0.8‰ by 2006. While Lake Gormire shares some similarities, the timing and magnitude of change is different, with a remarkably consistent decline in $\delta^{15}N$ values since ~1926, several decades before the expansion of industrial N fixing processes. The consistent decline in $\delta^{15}N$ value differs greatly from all 25 lakes analysed by Holtgrieve *et al.* (2014). Most showed 'hockey stick' declines in $\delta^{15}N$ values, accelerating from the 1950s, which is consistent with the expectation of lakes impacted by atmospheric N deposition.

Additionally, $\delta^{15}N$ values start to decline ~25 years after $\delta^{13}C_{org}$ and are very strongly correlated for the rest of the 20th century. This would suggest that the cause of the change in $\delta^{13}C_{org}$ values is the same as that responsibly for declining $\delta^{15}N$ values during the 20th century. Therefore, it is unlikely that atmospheric N deposition is the dominant process impacting sedimentary $\delta^{15}N$ values in Lake Gormire. More likely, that the trends in $\delta^{15}N$ and $\delta^{13}C_{org}$ values reflect the changes in the algal biomass of the lake. Reuss *et al*. (2010) found that $\delta^{13}C_{org}$ was inversely correlated to algal abundance across 100 lakes in Sweden. Such a relationship suggests that the DIC pool is being adequately resupplied with ^{12}C, as algae will preferentially utilise ^{12}C resulting in high residual $\delta^{13}C_{org}$ values in the lake. Considering the morphology of Lake Gormire and its catchment, it would be expected to receive high quantities of catchment materials. Therefore, it seems likely that the lake has a constant supply of DIC.

The picocyanobacteria expansion during the 20th century has been experienced in many lakes across the western world, primarily regulated by an increase in nutrient concentrations (Dolman *et al.*, 2012; Taranu *et al.*, 2015). For eutrophic temperate lakes, a typical seasonal pattern of plankton succession is frequently observed with a spring diatom bloom followed by a summer cyanobacteria bloom (Shatwell and Köhler, 2019; Townsend *et al.*, 1992). Moorhouse (2016) reported that most lakes in the Windermere catchment had increasing concentrations of zeaxanthin from 1800 onwards, apart from the two most upland tarns. The change was greater for the lakes which had been historically impacted by anthropogenic eutrophication, highlighting the dominance of nutrient loading promoting cyanobacteria growth. In Lake Windermere, zeaxanthin concentrations increased concurrently with P detergent use in the catchment which entered the lake via treated wastewater, and also the modernisation of agriculture (Mcgowan *et al.*, 2012). While cyanobacteria are expected to dominate in nutrient rich waters their ability to migrate vertically and resist grazing mean they should also thrive in warmer waters (O'Neil *et al.*, 2012; Sommer *et al.*, 1986).

The period of increased algal biomass in Lake Gormire coincides with the end of the Little Ice Age. An increase in lake algal biomass with warmer weather was also detected for some lakes in the Windermere catchment. Moorhouse (2016) found a clear climate signal for two upland tarns, which have experienced limited impact by anthropogenic eutrophication. In Stickle Tarn and Easedale Tarn there were significant increases in chlorophyll-*a* which started from ~1900. Algal change at these two sites was best explained by the Central England Temperature index, accounting for around 23% of the variation (Moorhouse, 2016). For Lake Gormire, whilst there are large dating uncertainties around the start of the 20th century, the regression analysis presented in section 4.2.6 shows a significant relationship between temperature and algal pigments from 1901. Temperature explained 6-14% of the variation, depending on the particular pigment, which would suggest that warmer temperatures have contributed towards increasing algal biomass in the lake since at least the start of the 20th century.

Increasing water clarity may also be related to the increase in algae during the 20th century. Romero-Viana *et al*. (2010) reported that in Lake La Cruz, Spain, picocyanobacteria biomass had a positive relationship to reconstructed solar activity over the previous ~300 years. This suggested that underwater light conditions were particularly important to picocyanobacteria and any changes are likely to be a controlling factor on growth. For diatoms, light availability is equally as important as temperature in Lake Barleber, Germany (Kong *et al*., 2021). A combination of water sampling, monitoring and modelling indicated there was a complex interaction between light availability and water temperature. Therefore the broad increase in algae from the start of the 20th century likely reflects the combination of environmental changes following the end of the Little Ice Age, with increasing temperatures, reduced ice cover, improving water clarity and enhanced nutrient supply.

The increase in algal biomass from the start of the 20th century occurs around the same time as heavy metal concentrations increase (e.g. Cu, Cd, Zn) which is summarised by PCA axis 1 for the trace elements data (Fig. 4.10). Concurrent increases in heavy metals around this time is a common feature of UK lake sediments and is indicative of increased atmospheric pollution since the industrial revolution (ROTAP, 2012; Yang and Rose, 2005a). It is possible that the increases in heavy metals are derived from the increase in algae themselves. Fielding *et al*. (2020) reported that for Lake Windermere increased algal biomass occurred with an increase in sedimentary Zn and Cu concentrations during 1910-1920 in the North Basin. However, these concurrent changes occurred around 30 years later in the South Basin. The delayed response of the South Basin indicated that it was the enhanced algal biomass at the time that were increasing sedimentary concentrations, rather than it being derived from atmospheric sources. However the divergence between algal pigments and heavy metal concentrations later in the 20th century suggest that this is unlikely. Therefore, for

Lake Gormire they are likely to represent atmospheric deposition. While these elements can have a stimulative effect, Yang and Rose (2005b) reported that Lake Gormire has surface sediment concentration of Cu and Cd that exceeded threshold effect levels while Zn exceeded the probable effect level, the concentration at which adverse effects are expected to occur frequently. Therefore it is unlikely that the concentrations of heavy metals in Lake Gormire have had a net beneficial impact on algal biomass.

4.4.4 Zone 4 (1970 - 2018)

For Lake Gormire, the 1970s represents a period of acceleration for the increase in algal biomass which is summarised by the PCA axis 1 score for the pigment data (Fig. 4.12). There were clear increases in all algal taxa during this period, including all forms cyanobacteria, where echinenone and canthaxanthin concentrations had remained relatively stable during the first half of the 20th century. The concurrent increase in all algal taxa indicates a general expansion in population and increasing dominance of algae of Lake Gormire during the second half of the 20th century.

Increasing algal dominance during the second half of the 20th century was also recorded in Rostherne Mere where from the 1960s C/N values declined with average values since 1955 of 11.3 (anoxic sediments) and 12.9 (oxic sediments) compared to a mean of 10.3 for Lake Gormire. TOC also increased and in the early 1980s the decline in $\delta^{13}C_{org}$ values and C/N became more rapid indicating increasing proportions of autochthonous organic matter. Surface sediment $\delta^{13}C_{org}$ of −28.8‰ in Lake Gormire is comparable to the low and stable values of −29.4‰ in the highly eutrophic Rostherne Mere (Lacey *et al.*, 2018). The cause of the increase in algae in Rostherne Mere was likely a result of increased eutrophication from the sewage treatment works servicing a larger population (Carvalho *et al.*, 1995; Moss *et al.*, 2005). While Lake Gormire has no point source entry for anthropogenic pollution, it still appears that the lake has a similar magnitude of change compared to a highly eutrophic site.

Moorhouse *et al*. (2018) found decreases in $\delta^{13}C_{org}$ values, C/N and increased %C across seven lakes analysed within the Windermere catchment. The two most productive lakes (Blelham Tarn, Easedale Tarn) had the lowest $\delta^{13}C_{org}$ values, which until the 1990s were relatively stable at ~−29‰ before progressing to lower values (<−30‰) by the start of the 21st century. For most sites, the magnitude of change in $\delta^{13}C_{org}$ values is relatively small (almost all <2‰), which contrasts with the 4.4‰ in Lake Gormire since the start of the 20th century. Lower C/N values were also experienced around the start of the 20th century, with more greater declines from the 1960s and 1970s (Moorhouse, 2016). The change in C/N for Lake Gormire is ~3.5 from the start of the 19th century, which is similar to some of the greatest change experienced in the Windermere catchment, with Easedale Tarn reducing by 4 units (Moorhouse, 2016). In comparison to most lakes in the Windermere catchment, Lake Gormire has experienced substantially greater increases in algal biomass, again comparable to lakes subject to anthropogenic nutrient enrichment.

Due to their relatively high P concentrations, algal productivity in closed basin lakes can often be limited by N availability (James *et al*., 2003; McGowan *et al*., 1999). In a productive forested catchment, N mineralisation can be extensive (Quan *et al*., 2014) and further enhanced through warming (Gudasz *et al*., 2010). Therefore, some of the increase in algal biomass may be related to increased catchment productivity (Maberly *et al*., 2013). The increase in algal biomass during the second half of the 20th century may be related to the recovery of the surrounding woodland. However, the trends in Lake Gormire from the 1970s differ from those in the second half of the 19th century, and the findings of Stevenson *et al*. (2016), where cryptophytes were favoured. From the 1970s the magnitude of change in cryptophyte biomass is more similar to that of the other algal groups, most notably diatoms, which had a much more muted increase during the 1850s. This indicates that while it is possible that the documented recovery of the woodland has contributed towards stimulating algal growth, there are likely other drivers increasing the biomass of all algal taxa in Lake Gormire during this period. In Lake Windermere, there have been increased cryptophytes recorded through monitoring between 1943 and 2003, with an increase in temperature y delaying the peak of *Cryptomonas* spp. (Feuchtmayr *et al*., 2012). Increased temperatures also resulted in an increase in cryptophytes in the Qu'Appelle lakes, Canada during the second half of the 20th century. This was caused by a decrease in ice cover which prolonged the spring growing season along with anthropogenic nutrient enrichment (Patoine and Leavitt, 2006).

In Lake Muggelsee, Germany there was a correlation between the extent of winter ice cover and spring diatom biomass (Adrian *et al*., 1999). Warming between 1979 and 2003 resulted in shorter periods of ice cover and earlier ice break up. As a result, diatom biomass increased and peaked ~4.5 weeks earlier from 1988, compared with the preceding decade (Adrian *et al*., 2006). There were similar findings in Lake Erken, Sweden where diatom abundances were shown to be impacted by changes in the extent of ice cover during the second half of the 20th century, which typically breaks up in April (Weyhenmeyer *et al*., 1999). Diatom abundances ranged from 20-98% of the total algae spring community, with relatively low abundances during particularly cold years characterised by extensive ice covers. In the absence of ice cover, diatoms were found to outcompete other taxa (such as dinoflagellates) with the spring peak shifting ~30 days earlier over a 45-year period, reflecting 20th century warming. The reductions in ice cover extended the growing season for diatoms, along with providing more beneficial light conditions and turbulence. The concurrent increase of diatoms with cryptophytes, picocyanobacteria and chlorophytes during the 20th century may indicate that the change was driven by planktonic taxa. As with Lake Gormire, Pal *et al*. (2015) found greater increases in zeaxanthin than echinenone in Lac des Loups, Canada in the most recent 30 years. These trends were likely to represent both an increase in cyanobacteria but also a relative shift in the community composition towards more picocyanobacteria, which may contain more planktonic taxa. Shifts to a planktonic diatom assemblage during warmer climate periods were found by Dong *et al*. (2011) in Esthwaite Water. There was a replacement of the benthic *Aulacoseira* by planktonic *Cyclotella* taxa which has been widely observed across arctic, alpine and temperate lakes.

While N availability is likely to be a controlling factor in the amount of chlorophyte biomass, additional warming can lead to increased N uptake by chlorophytes (Oleksy *et al*., 2021). Oleksy *et al*. (2020) reported an increase in chlorophyte-derived pigments in the small mountainous lake of Sky Pond, USA during the second half of the 20th century. The rate of chlorophyte biomass increase accelerated from ~1950 representing the greater increases in air temperature from anthropogenic climate change, coupled with atmospheric N deposition. Modern concentrations of lutein in Sky Pond are three to four times higher than those in the early 20th century, which is the magnitude of change also observed in Lake Gormire. In general, these results of Oleksy *et al*. (2020) share a striking resemblance to those in Lake Gormire, with a gradual increase in chlorophyte biomass during the first half of the 20th century followed by a greater increase since the 1970s. There is also evidence of a slowdown in the increase in biomass from the start of the 21st century. The similarities between these data highlight how the combination of temperature and nutrient increases can help to explain the algal changes observed in Lake Gormire.

The influence of temperature on cyanobacteria growth was highlighted by the work of Jeppesen *et al*. (2009). Analysis of data collected from 250 Danish lakes indicated that higher temperatures resulted in the dominance of cyanobacteria biomass. This was accompanied by an increase in chlorophyll-*a*, indicating an overall increase in algal productivity, rather than a shift in community composition. Kosten *et al*. (2012) also found a similar relationship in 143 lakes across Europe and South America. The proportions of cyanobacteria in the algal communities increased with temperature but also TN. The data indicate a synergistic effect from both nutrients, climate and also light conditions that determined the proportion of cyanobacteria in the algal community. Increasing water temperature can also result in a positive feedback loop for cyanobacterial bloom biomass. In lakes that experience little fluvial or wind mixing, such as Lake Gormire, increases in water temperature can result in the lake water becoming stagnant and this leads to buoyant cyanobacteria floating up to the surface resulting in the formation of dense blooms (Paerl and Huisman, 2009).

Surface blooms have been shown to increase water temperatures through light absorption by photosynthetic and photoprotective pigments. In Lake Ijsselmeer, the Netherlands, surface water temperature within the bloom was 3°C higher than the surrounding waters (Ibelings *et al*., 2003). Therefore, the presence of cyanobacteria blooms can stimulate further algal production through this mechanism (Hense, 2007).

Similarly, while nutrient supply is typically attributed as the most important factor in predicting cyanobacteria biomass, Rigosi *et al*. (2014) found that nutrients and temperature were both important. However, this varied depending on the trophic state of the lake and the taxon. Nutrients were more important in oligotrophic lakes, whereas in mesotrophic lakes temperature was the dominant driver of changes in cyanobacterial communities. For some filamentous cyanobacteria taxa (e.g. *Aphanizomenon*) and picocyanobacteria (*Synechococcus*, *Coelosphaerium*), nutrient availability explained all the variation in lake biomass while for others, temperature was much more important (e.g. *Oscillatoria*). As Lake Gormire is mesotrophic, this would suggest that temperature is a relatively important driver of cyanobacteria biomass which is supported by the strong relationship between cyanobacterial pigment concentrations and summer temperatures during the 20th century.

Modelling of Bassenthwaite Lake showed that filamentous cyanobacteria (*Anabaena*) increased in biomass with increasing temperature and nutrients. *Anabaena* flourished in the warmer summer waters and became more dominant in the summer bloom (Elliott *et al*., 2006). These filamentous N-fixing cyanobacteria have been recorded in Lake Gormire during the 20th century (Scott, 1948). Increases in these potentially toxic taxa were also reported by Donald *et al*. (2011) in response to NO_3^- additions. There was little response by N_2-fixing cyanobacteria to additions of NO_3^-, however, it did result in a shift towards a greater abundance of potentially toxic cyanobacteria. The colonisation of large amounts of toxic cyanobacteria due to increased temperatures was reported by Callieri *et al*. (2014) in Lake Maggiore, Italy, with an increase in water temperature from 1980 to 2011 resulted in a high degree of WLF. While the degree of WLF at Lake Gormire has not been quantified, it is likely to be large and is quite apparent from site visits between winter and summer months. Lakes which experience large WLFs often experience extensive blooms forming in years of greater water loss. As more of the littoral zone dries, P mineralisation is enhanced supplying the lake with increased P availability when rewetted (Rigosi *et al*., 2014). In conjunction, the lowering of the water level will lead to the concentration of existing lake nutrients, enhance water temperature warming and increase light penetration (Bakker and Hilt, 2015). Therefore, the impact of temperature driven enhanced WLF is likely to be amplified in closed basin lakes such as Lake Gormire.

4.5 Summary

The algal community of Lake Gormire appears to have changed through time, from diatom domination in the early 18th century to greater proportions of chlorophytes following a period of catchment deforestation (Fig. 4.29). Chlorophytes become less dominant during the 19th century, replaced by cyanobacteria, likely reflecting more favourable light conditions. The 19th century was defined by high allochthonous inputs with periods of pollution and increased nutrient loading from the catchment, potentially enhanced by wetter weather. There was also a rapid increase in cryptophytes during the middle of the 19th century although this was relatively brief, possibly indicating catchment activity. The latter parts of the 19th century recorded a rapid decline in lake cryptophytes and diatoms, likely driven by adverse meteorological conditions, whilst cyanobacteria became more dominant before they declined into the start of the 20th century. In the first half of the 20th century, cyanobacteria continue to decline possibly reflecting a loss of competitive advantage as water clarity improved and a shift in nutrient source. Cryptophytes and diatoms became more dominant during the 20th century, which may reflect a more favourable climate for spring growth. From the second half of the 20th century, chlorophytes become more dominant in the lake at the expense of cryptophytes, cyanobacteria and diatoms. This likely represents the influence of increased summer temperatures and enhanced nutrient availability driving high chlorophyte growth rates. The combination of nutrient loading and climate change was also attributed to the observed increases in algal biomass and community level changes experienced in the Windermere catchment by Moorhouse (2016). However, unlike the Windermere catchment, the increase in nutrient supply for Lake Gormire is not likely to be due to be directly related to anthropogenic nutrient loading. Although it cannot be ruled out as some degree of atmospheric N deposition would have impacted the lake, the $\delta^{15}N$ data indicate that this is not a dominant influence. Therefore, the increase in nutrients to Lake Gormire are likely to be due to a combination of increased temperatures, precipitation changes and woodland recovery.

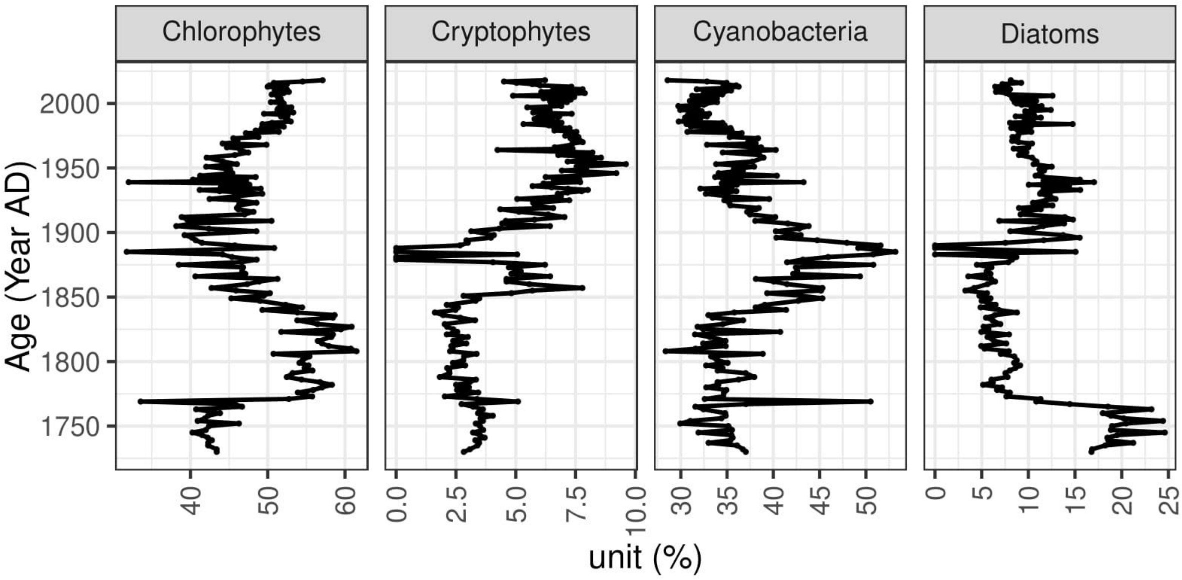

Fig. 4.29 Changes in the relative abundances of dominant algal groups in Lake Gormire.

The significant relationship between summer temperature and lake algal biomass indicates that Lake Gormire may be particularly sensitive to annual or sub-annual changes in weather conditions and as a result climate change. This supports the assessment that for mesotrophic lakes, temperature is often the dominant driver of changes in algal biomass (Rigosi *et al*., 2014). It also supports the findings of Moorhouse (2016) that lake algal community change is largely controlled by catchment characteristics, with lakes with relatively small catchments experiencing greater changes due to greater connectivity between the lake and catchment. The specific catchment and lake basin characteristics appear to have a profound impact on Lake Gormire. As Lake Gormire has a small catchment dominated by a steep sided slope it would be expected to respond quickly to changes in the catchment, including changes in land use practise and precipitation. Periods of turbidity are likely a regular phenomenon in Lake Gormire although the extent of these have clearly been compounded by anthropogenic catchment activities in the past. Along with the size and topography of the catchment, the closed basin of Lake Gormire likely acts to amplify the impacts of climate change through enhanced WLF. This combination of factors suggest that Lake Gormire is a system extremely sensitive to climate and environmental change and as a result the conditions can vary each year.

The environmental changes indicated by the organics data from Lake Gormire broadly align with those reported by Oldfield *et al*. (2003) and Fisher *et al*. (2003) but expands beyond their ~1970 endpoint with additional isotope and pigment analysis. C/N values are broadly in line with those reported by Fisher *et al*. (2003) with declines from ~14 to ~10 since around the start of the 18th century. Preceding this period of decline, C/N values had been increasing in Lake Gormire for ~500 years which probably reflects a period of woodland recovery, as recorded by the pollen analysis undertaken by Oldfield *et al*. (2003). Both $\delta^{13}C_{org}$ and C/N values have changed considerably through time suggesting that Lake Gormire may have had relatively more macrophytes than algae in the past.

Overall it is likely that Lake Gormire has progressed to a higher tropic state over time. Comparing the data presented in this chapter to the findings of Oldfield *et al* (2003) and Fisher *et al*. (2003), this indicates that the lake is currently more algal dominated than at any other point in at least the last 3,500 years. The progression towards increasing algal dominance has most likely been accelerated by anthropogenic activities such as deforestation, which increased nutrient loading to the lake. However, the increasing algal biomass of the 20th century is likely to also be enhanced by increasing temperatures, especially since the 1970s.

5. Blea Tarn

This chapter presents the results and interpretations for the data generated from the Blea Tarn sediment core. It will discuss a timeline of events and explore the causes for any such changes, along with an assessment as to the impact of 20th century climate warming.

Fig. 5.1 Photograph of Blea Tarn taken from the south bank, August 2018.

5.1 Background

5.1.1 Historical land cover and vegetation

Palynological records from Blea Tarn show multiple phases of elm decline from 6350 BP and 5850 BP probably as a result of human activities, climate change and disease (Grosvenor *et al.*, 2017). Temporary forest clearings of the surrounding catchment were coupled with changes in the sediment source and increases in the pollen of grasses (Pennington, 1991). After the elm decline there is no evidence in the sedimentary record of soil erosion or vegetational change until the 20th century (Pennington, 1964). Sheep density grew steadily from the late 19th century although grazing was predominantly at lower altitudes and downstream from the lake (Haworth, 1969). The increase in livestock is reflected by the proportion of rough grazing in the catchment which reached a maximum of 80% of the land cover in 1931 (Moorhouse, 2016). Deforestation of a portion of the existing woodland also occurred around 1940 (Hürrig, 1999) but Blea Tarn appears to have avoided the eutrophication experienced in many of the lowland lakes in the region (Haworth, 1969). In the second half of the 20th century the proportion of land used for rough grazing declined. Today there is minimal anthropogenic land use with a single farm and a small number of sheep (Moorhouse, 2016).

The most recent assessments have recorded catchment cover as comprising predominantly acid grassland (66.4% of the catchment area) with areas of rough grassland (11.2%) and heather (9.9%; Fig. 5.2). The lake catchment also has an area of woodland on the western edge of the tarn comprised of a mix of coniferous (6.2% of the catchment area) and broadleaf woodland (3.4%) (Morton *et al*., 2011). Most recently in 2019, the lake and catchment appeared undisturbed and similar in appearance to photographic documentation from 1992, the only notable difference being the larger conifer trees on the west side of the catchment (Ogden, 2019).

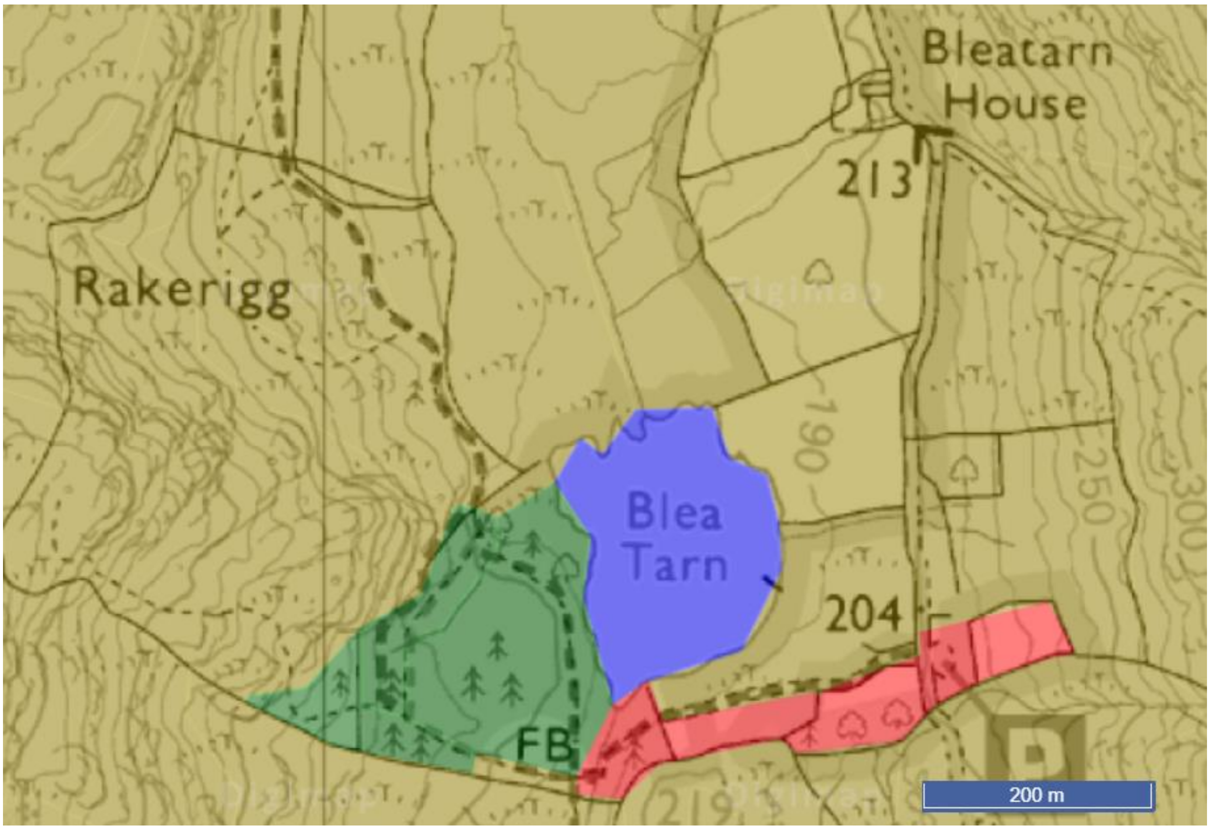

Fig. 5.2 Land cover map of Blea Tarn catchment showing areas of acid grassland (light brown), woodland (green) and heather grassland (pink).

Little work has been undertaken to document the submerged macrophyte community but it had previously been noted that the tarn supports a range of taxa with littoral grasses and sedges (Haworth *et al*., 2003). Blea Tarn is oligotrophic with an algal flora typical of base-poor acid *Sphagnum* bogs (Haworth, 1969). Blea Tarn was designated as Site of Special Scientific Interest (SSSI) in 1989 as it is a key site for palaeoenvironmental studies due to its long late glacial record. During the early Holocene period the rate of sedimentation was rapid enough to produce sufficient material to enable radiocarbon dating of changes in forest composition (Ogden, 2019).

5.1.2 Water quality and monitoring

Palaeolimnological research during the 1960s recorded a slight natural acidification from the early to mid-Holocene likely due to the evolution of catchment soils which were washed into the lake (Haworth, 1969). In the 1980s mean lake water pH was measured at 6.9 with a mean alkalinity of 78μeq L^{-1} (Sutcliffe and Carrick, 1988). In the summer months of 2000, the mean total dissolved N was measured at 0.39 mg L^{-1} (Jones *et al*., 2004). Environment Agency monitoring from 2005 to 2008 recorded the same mean pH as in the 1980s, with 0.22 mg L^{-1} of nitrate and 13 µg L^{-1} of soluble reaction phosphorus (SRP) (Environment Agency, 2008). SRP measured between 2012 and 2013 showed a reduction to ~7.5 µg L^{-1} in winter with a pronounced decline to <1 µg L^{-1} in the summer months (Moorhouse, 2016). An NTU of 1 suggests that the lake was of very low turbidity during the 21st century, with hardness ($CaCO_3$) of 9 mg L^{-1} and low conductivity of 35 µS cm^{-1}. There is some indication of oxygen depletion with 12.7 mg L^{-1} in winter and 9.8 mg L^{-1} in summer, likely due to higher respiration rates in summer months. The water temperature ranges from 4.5°C-17.6°C between winter and summer months (Environment Agency, 2008). Mean heavy metal concentrations from water samples were also recorded (Table 5.1).

Table 5.1 Mean heavy metal concentrations for Blea Tarn, 2005 – 2007 (Environment Agency, 2008).

Lead	1.2 ug L^{-1}
Cadmium	0.1 ug L^{-1}
Potassium	0.2 mg L^{-1}
Magnesium	0.7 mg L^{-1}
Chromium	0.5 ug L^{-1}
Aluminium	52 ug L^{-1}
Copper	0.75 ug L^{-1}
Zinc	5.1 ug L^{-1}
Nickel	5 ug L^{-1}

5.1.3 Weather and climate

Blea Tarn lies around 20 miles inland on the west coast of England and has a mild and wet climate. The surrounding mountains have a large impact on the climate of the Blea Tarn, driving orographic rainfall whilst reducing temperatures and sunlight through shading (George *et al.*, 2007a; Kenworthy, 2014). Winter air temperatures in the Windermere catchment can occasionally drop to below -10°C with the smaller tarns regularly freezing over in winter months (George *et al.*, 2007a).

Mean daily maximum temperatures at Newton Rigg (~20 miles NE from Blea Tarn) have increased from 12.3°C between 1960-1989 to 13.1°C between 1990-2018 (Met Office, 2021b). Consequently, the three highest annual temperatures have all occurred in the 21st century with the warmest in 2007 (14.0°C) and 2014 (14.0°C) followed by 2003 (13.7°C) (Fig. 5.3). The mean maximum daily summer temperatures have also increased from 18.1°C (1960-1989) to 18.7°C (1900-2018). However, the three highest maximum daily summer temperature are spread throughout the time series with the warmest in 1995 (21.1°C) followed by 1976 (20.9°C) and 2018 (20.5°C) (Fig. 5.4).

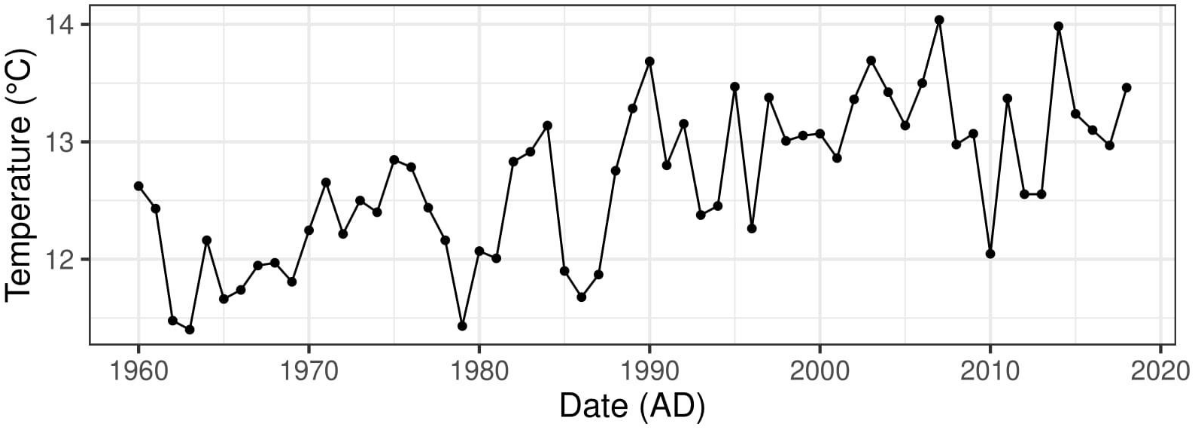

Fig. 5.3 Mean annual daily maximum temperature at Newton Rigg weather station (Met Office, 2021b).

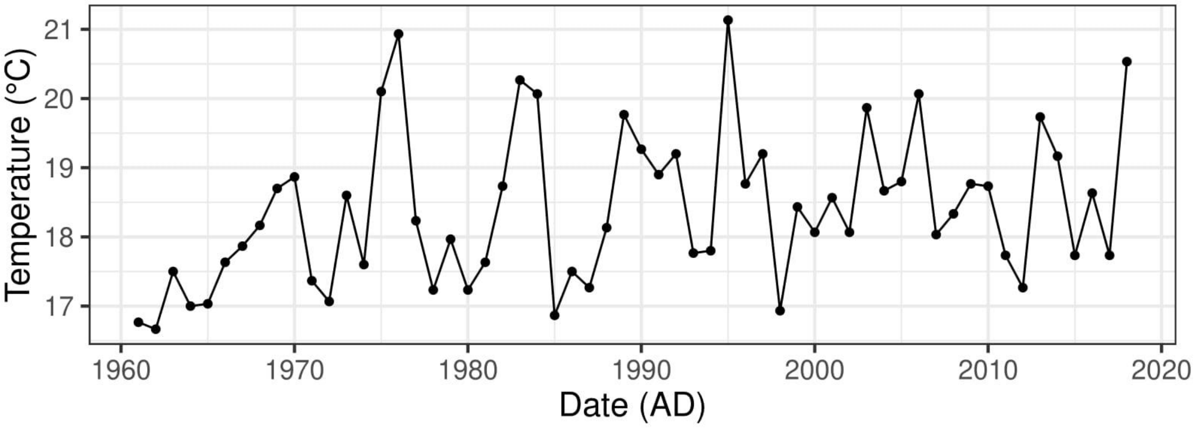

Fig. 5.4 Mean daily maximum summer temperature at Newton Rigg weather station (Met Office, 2021b).

Mean monthly precipitation has been 7% higher since the start of the 21st century (80.7mm) compared to the period of 1960-1989 (75.4mm) with winter rainfall increasing by 32% between the same time periods (Fig. 5.5, Met Office, 2021b). The two wettest winters have both occurred in the 2010s with the wettest in 2016 (196.5mm month^{-1}) followed by 2014 (188.9mm month^{-1}) and 1990 (180.2mm month^{-1}). For annual precipitation, the wettest years were 2015 (101.9 mm month^{-1}) followed by 1967 (100.3 mm month^{-1}) and 2000 (99.9 mm month^{-1}). A proportional increase in winter precipitation is consistent with the trends across much of the UK with enhanced winter rainfall becoming increasingly more intense between 1961 and 2009 (Barker *et al*., 2004; Burt and Ferranti, 2012). The intensification of winter precipitation appears to have been particularly prominent at higher elevations, enhanced by orographic effects (Malby *et al*., 2007).

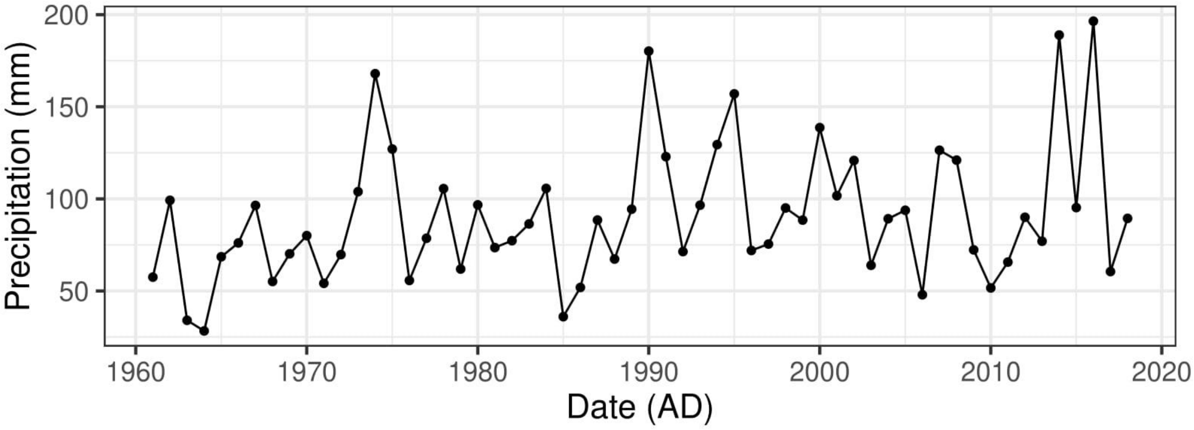

Fig. 5.5 Monthly mean winter rainfall at Newton Rigg weather station (Met Office, 2021b).

5.2 Results

5.2.1 Sediment chronology

Total ^{210}Pb activity reaches equilibrium with supported ^{210}Pb activity at a depth of around 26 cm from the top of the core (Fig. 5.6a). Unsupported ^{210}Pb activities, calculated by subtracting ^{226}Ra activity (as supported ^{210}Pb) from total ^{210}Pb activity, decline irregularly with depth (Fig. 5.6b). The maximum unsupported ^{210}Pb activity is under the surface sediments, which implies an increase in sedimentation rates in recent years. There are two sections of decline at 2.88 – 20.13 cm section and 21.88 – 24.88 cm section, with different decline gradients between them, suggesting differences in changes of sedimentation rates. The ^{137}Cs activity versus depth profile shows a peak at around 16.88 cm (Fig. 5.6c), which was derived from the fallout of atmospheric testing of nuclear weapons with a maximum level reached in 1963. A peak of ^{241}Am activities at 15.63 cm confirms that the ^{137}Cs peak around 16.88 cm was from atmospheric testing of nuclear weapons (Fig. 5.6c). Use of the constant initial concentration (CIC) model was precluded by the non-monotonic variations in unsupported ^{210}Pb activities. ^{210}Pb chronologies were therefore, calculated using the constant rate of ^{210}Pb supply (CRS) dating model (Appleby and Oldfield, 1978; Appleby, 2001). The CRS dating model places the 1963 depth between 15.63 and 16.88 cm, which agrees with the ^{137}Cs and ^{241}Am records of the core. Sedimentation rates calculated from ^{210}Pb activities show relatively constant accumulation before the 1920s, with a mean value at 0.006 g cm^{-2} yr^{-1}, followed by a gradual increase reaching 0.028 g cm^{-2} yr^{-1} in the most recent sediments (Fig. 5.7).

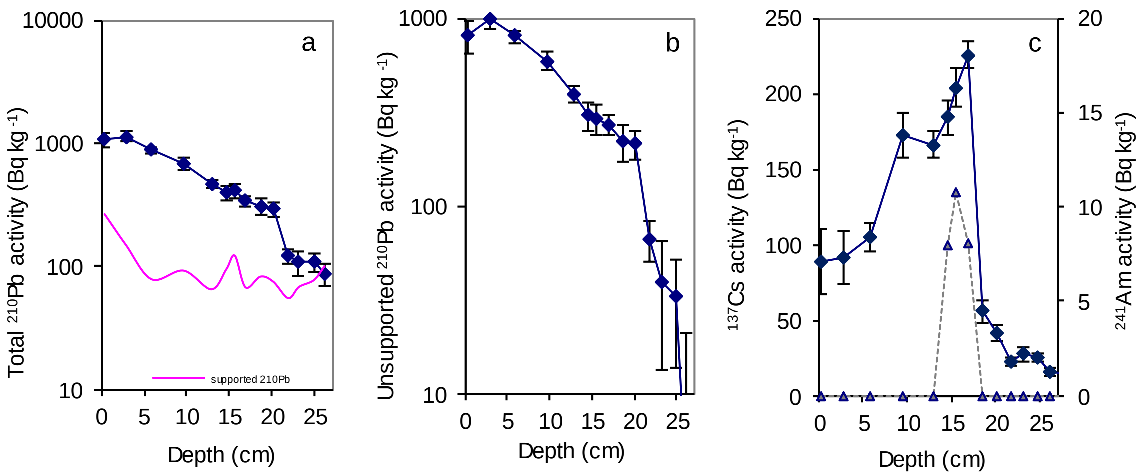

Fig. 5.6 Fallout radionuclide concentrations in core taken from Blea Tarn, showing (a) total ^{210}Pb (blue line) and supported ^{210}Pb (pink line), (b) unsupported ^{210}Pb, and (c) ^{137}Cs (solid line) and ^{241}Am (dashed line) concentrations against depth.

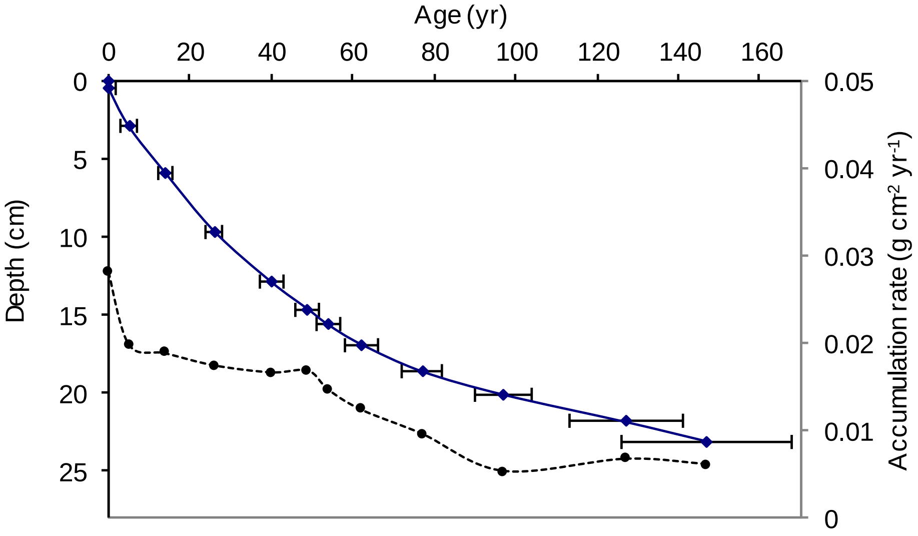

Fig. 5.7 Radiometric chronology of core taken from Blea Tarn, showing the CRS model ^{210}Pb dates and sedimentation rates. The solid line shows age and the dashed line indicates sedimentation rate.

While absolute ages are used in the following text, they represent the CRS model's estimated age with uncertainty increasing with depth. Dates prior to 1871 were estimated based on the sedimentation rate calculated from the deepest ^{210}Pb dating point (23.13 cm). Therefore uncertainty in the estimated ages of the sediments may be greater for samples deeper than 23.13 cm.

5.2.2 Sediment lithology

OM content gradually increases from 29.7% in 1631 to 33.9% in 1900 (Fig. 5.8a). The increase in organic matter content continues during the 20th century to 38.0% in 1952, 40.3% in 2002 and reaching a peak of 44.2% in 2016. Minerogenic content generally decreases over time from 59.4% in 1651 to 57.1% in 1900 (Fig. 5.8b). The decline in minerogenic content continues for much of the 20th century to 53.9% in 1993. Following a period of increase in the 2000s to 57.3% in 2009, minerogenic content declines to 51.7% in 2016. The carbonate content broadly increases between the 17th to 19th centuries from 7.5% in 1631 to 11.0% in 1888 (Fig. 5.8c). This is followed by a rapid decrease during the first half of the 20th century to 3.3% in 1931 and a subsequent gradual increase over time to 5.9% in 2014.

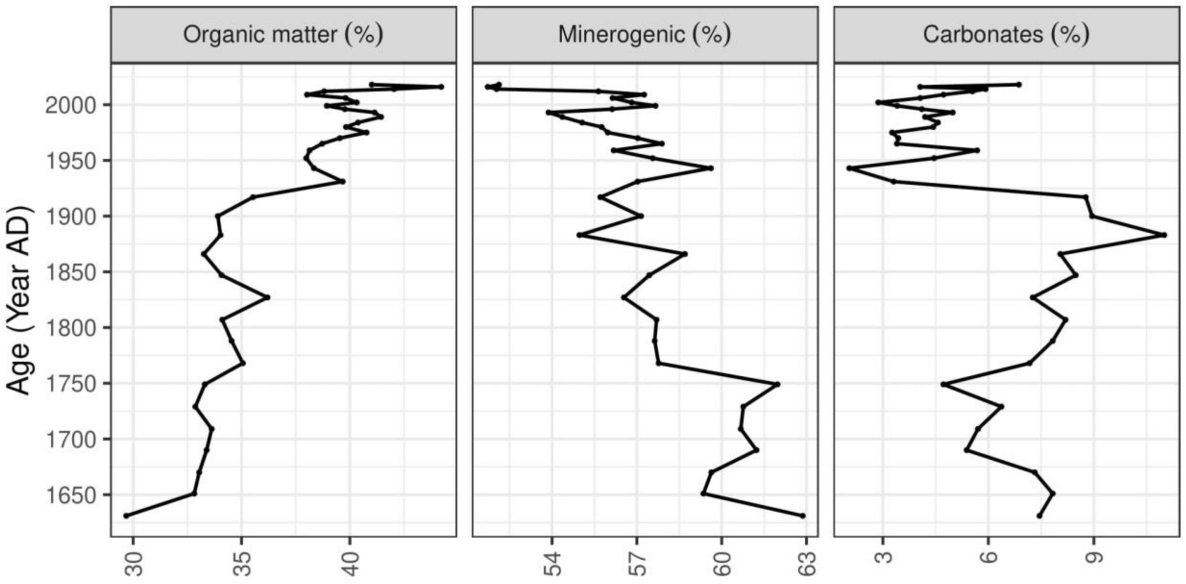

Fig. 5.8 Main sedimentary parameters from loss on ignition analysis: organic matter content (a), minerogenic content (b) and carbonate content (c) for Blea Tarn sediment core.

5.2.3 Sedimentary trace elements

Lithogenic elements (Li, Mg, K) all share similar trends of concurrent increase and decline during the 17th century, which is followed by increasing concentrations to the middle of the 19th century (Fig. 5.9). From ~1850 concentrations of these elements all start to decline to the 1950s after which they increase again. Aluminium differs from these trends with a gradual increase in concentrations during the 17th to 19th centuries from 18.0 mg g^{-1} sediment in 1636 to 36.1 mg g^{-1} in 1921. Aluminium concentrations reduce during the rest of the 20th and 21st centuries to 21.8 mg g^{-1} in 2017. This general trend is mirrored by Pb and many of the other heavy metals (Cd, Cu, Zn) although the timing of peak concentrations vary slightly with Cd peaking at 10.9 µg g^{-1} in 1945 and Zn at 702.6 µg g^{-1} in 1961. Copper concentrations broadly decline from 52.2 µg g^{-1} in 1904 except for a period of rapid increase when concentrations peak at 55.8 µg g^{-1} in 1997 before reducing to 38.9 µg g^{-1} in 2006. Fe concentrations increase during the 17th century to 33.5 mg g^{-1} in 1675 after which they remain relatively stable until the start of the 20th century. Concentrations of Fe increase to a peak of 49.2 mg g^{-1} in 1952 before reducing to 42.7 mg g^{-1} in 1967, after which concentrations remain relatively stable until the start of the 21st century when they reduce from 42.7 mg g^{-1} in 2003 to 33.2 mg g^{-1} in 2012. Cr concentrations closely follow the trends in Fe, peaking at 177.2 µg g^{-1} in 1954. Ni experiences fluctuating concentrations during the 17th century followed by a broadly stable trend with 14.4 µg g^{-1} in 1904. Ni concentrations increase to 24.5 µg g^{-1} in 1972 and is followed by a large single spike in concentration to 67.1 µg g^{-1} in 1977. Ni rapidly declines to 27.1 µg g^{-1} in 1981 after which there is a general decline to 9.1 µg g^{-1} by 2017.

Phosphorus concentrations broadly increase from the start of the 17th century from 1.2 mg g^{-1} in 1636 to 1.4 mg g^{-1} in 1753. Concentrations decline to 1.1 mg g^{-1} in 1812 which is followed by a period of increase into the 20th century. Concentrations peak at 1.4 mg g^{-1} in 1954 and then decline to 1.1 mg g^{-1} in 2000 before increasing slighty to 1.2 mg g^{-1} in 2016. Mn increases during the start of the 17th century from 0.9 mg g^{-1} in 1616 to 1.1 mg g^{-1} in 1655 and remains relatively stable through to the middle of the 20th century. Concentrations increase to a peak of 1.4 mg g^{-1} in 1977, and are followed by a relatively rapid decline to a low of 0.8 mg g^{-1} in 2012. Ba concentrations remain relatively stable during the 17th and 18th centuries before declining from 100.6 µg g^{-1} in 1871 to 85.0 µg g^{-1} in 1921. Ba concentrations increase during the rest of the 20th century to peaks of 105.0 µg g^{-1} in 1977 and 1997 before reducing to 86.4 µg g^{-1} in 2012. Ca concentrations remain relatively stable up until the 20th century when there is a spike in concentration from 2.4 mg g^{-1} in 1945 to 3.0 mg g^{-1} in 1954. After the spike in Ca, concentrations remain relatively stable until a rapid increase from the 1990s with 3.7 mg g^{-1} in 2000 reaching a peak of 4.1 mg g^{-1} in 2017. Na concentrations remain relatively stable up until the second half of the 20th century when they have two notable spikes in concentration to 344.3 µg g^{-1} in 1977 and 587.1 µg g^{-1} in 1997. Na concentrations rapidly decline to 253.6 µg g^{-1} in 2006 before increasing to 474.5 µg g^{-1} in 2016.

PCA axis 1 (39.6%) and PCA axis 2 (29.0%) scores account for 68.6% of the total variance in the trace element data (Fig. 5.10). There were positive strong correlations between Cu, Cd, Fe, Zn, Al with some divergence of Pb, P and Mn on the PCA 2 axis. Mg and Li are also partially explained by the PCA 2 axis but diverge from P and Mn with negative PCA axis 1 scores while K diverges from Mg and Li with negative PCA axis 2 scores.

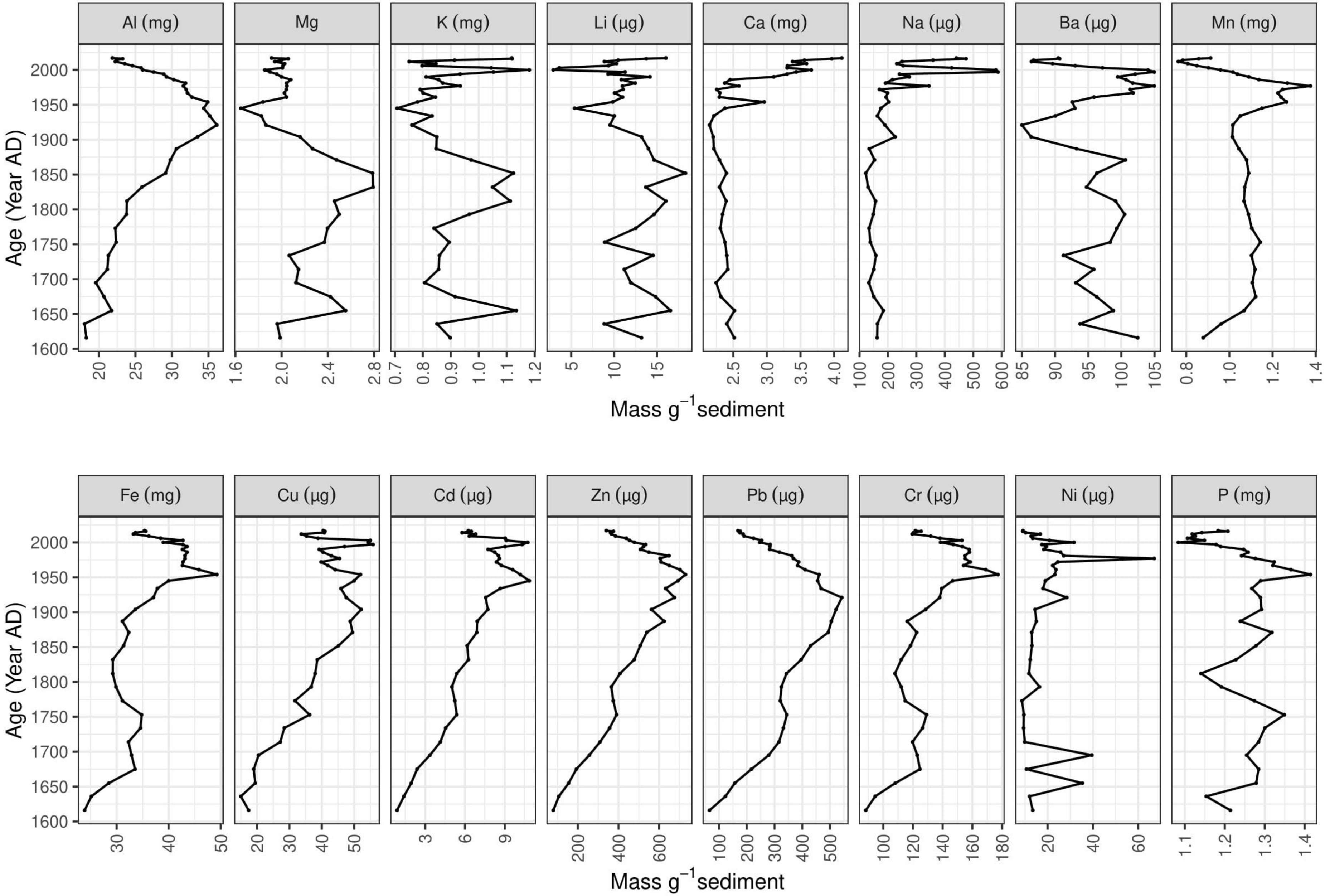

Fig. 5.9 Blea Tarn sedimentary trace elements.

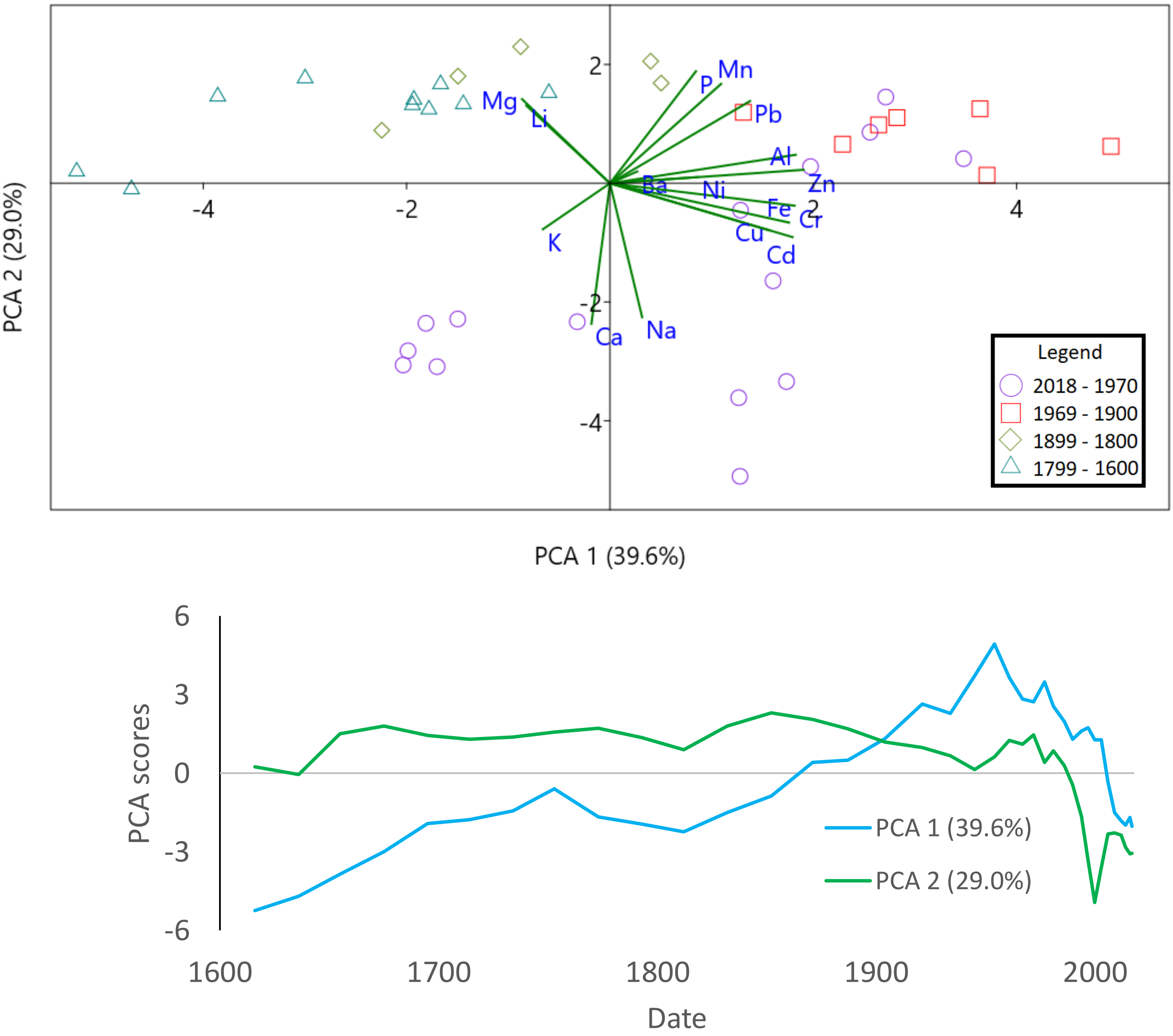

Fig. 5.10 Biplot of PCA scores and graph of change over time for sedimentary trace element concentrations in Blea Tarn.

5.2.4 Sediment C/N mass and stable isotopes ($\delta^{13}C$, $\delta^{15}N$)

%C and %N values both remain relatively stable during the 17th century. Trends start to diverge from the start of the 18th century with a slight increase in %C to 16.6% in 1739 while %N remains stable (Fig. 5.11a). From the middle of the 18th century both %C and %N remain stable until the second half of the 19th century when %C declines to 15.8% in 1928. %C and %N increase during the second half of the 20th century with %C of 19.4% in 1990 and %N of 1.46% in 1994. %C and %N continue to increase during the 21st century reaching concurrent peaks of 23.0% and 1.8%, respectively, in 2018. C/N values gradually increase during the 17th and first half of the 18th centuries from 12.5 in 1616 to 13.9 in 1749. C/N values remain relatively stable until the turn of the 20th century when they reduce to 12.7 in 1917. Following this, C/N increase to 13.6 in 1965 and decline to a low of 12.0 in 2016. $\delta^{13}C_{org}$ values increase slightly from the start of the 17th century from −28.5‰ in 1601 to −27.5‰ in 1921. Values remain relatively stable until the middle of the 20th century when they decrease to −28.0‰ in 1959. $\delta^{13}C_{org}$ values return to stable values until the 1980s when they decline to lows of −29.6‰ between 2012 and 2018. $\delta^{15}N$ values follow similar trends to $\delta^{13}C_{org}$, gradually increasing from the start of the 17th century with 2.3‰ in 1601 and 3.1‰ in 1871. This is followed by an increase to a peak of 4.3‰ in 1917. $\delta^{15}N$ values decline during the rest of the 20th century to 3.3‰ in 1979, followed by a more rapid decline from the 1980s to 0.9‰ in 1998 and reaching a low of −0.1‰ in 2014.

5.2.5 Sedimentary pigments

Chlorophyll-*a* concentrations gradually decline from the start of the 17th century with 149.9 nmole pigment g^{-1} OC (nmole) in 1611 to 77.3 nmole in 1788 (Fig. 5.11c). Following a period of greater variability during the 19th century, chlorophyll-*a* broadly increases during the 20th century, with the greatest increase from the 1970s to 389.1 nmole in 1981. Concentrations remain relatively stable during the rest of the 20th and 21st century before increasing in 2018, representing the top 0.25cm of sediment. Phaeophytin-*a* follows similar trends to chlorophyll-*a* except that there is a greater increase in concentrations during the first half of the 20th century. There is also a more consistent increase in phaeophytin-*a* from the 1970s, compared to chlorophyll-*a*, and as a result, preservation conditions vary during the 20th century. Chlorophyll-*b* concentrations broadly increase during the 17th and 18th centuries. Following a period of enhanced concentration during the first part of the 19th century, chlorophyll-*b* declines to a low of 2.8 nmole in 1861. Concentrations increase from the 1970s, with a brief period of decline at the start of the 21st century. Alloxanthin decreases during the 17th and 18th centuries and remains stable for the 19th century. Concentrations increase during the

1970s after which they remain stable and start to decline during the 2010s. Canthaxanthin exhibits large variability through time but almost entirely within the range of 11 and 25 nmole. Echinenone broadly increases from the start of the 17th century to the middle of the 19th century, with 12.6 nmole in 1866. Following a period of decline, echinenone increases from the 1970s in line with most other pigments. Following a decline during the first half of the 17th century, the UV index decreases gradually to the end of the 19th century, when it reaches minimum values (Fig. 5.11b). The gradual increase in UV index over the 20th century is followed rapid increase during the 21st century. Diatoxanthin concentrations remain relatively stable during the 17th century, followed by a period of decline around the middle of the 18th century. From the start of the 19th century concentrations increase to the end of the century when they peak at 149.3 nmole in 1887. Concentrations rapidly decline at the end of the 19th century to 63.3 nmole and the remain relatively stable until the 21st centuiry when concentrations start to decline. PCA axis 1 (53.8%) and PCA axis 2 (21.2%) scores account for 75% of the total variance in the pigment dataset (Fig. 5.12). The PCA biplot shows that chlorophyll-*a*, lutein, zeaxanthin, alloxanthin and echinenone are well correlated on PCA axis 1. There is a divergent trend for diatoxanthin and canthaxanthin on PCA axis 2 which do not increase in concentration from the 1970s as with the other pigments.

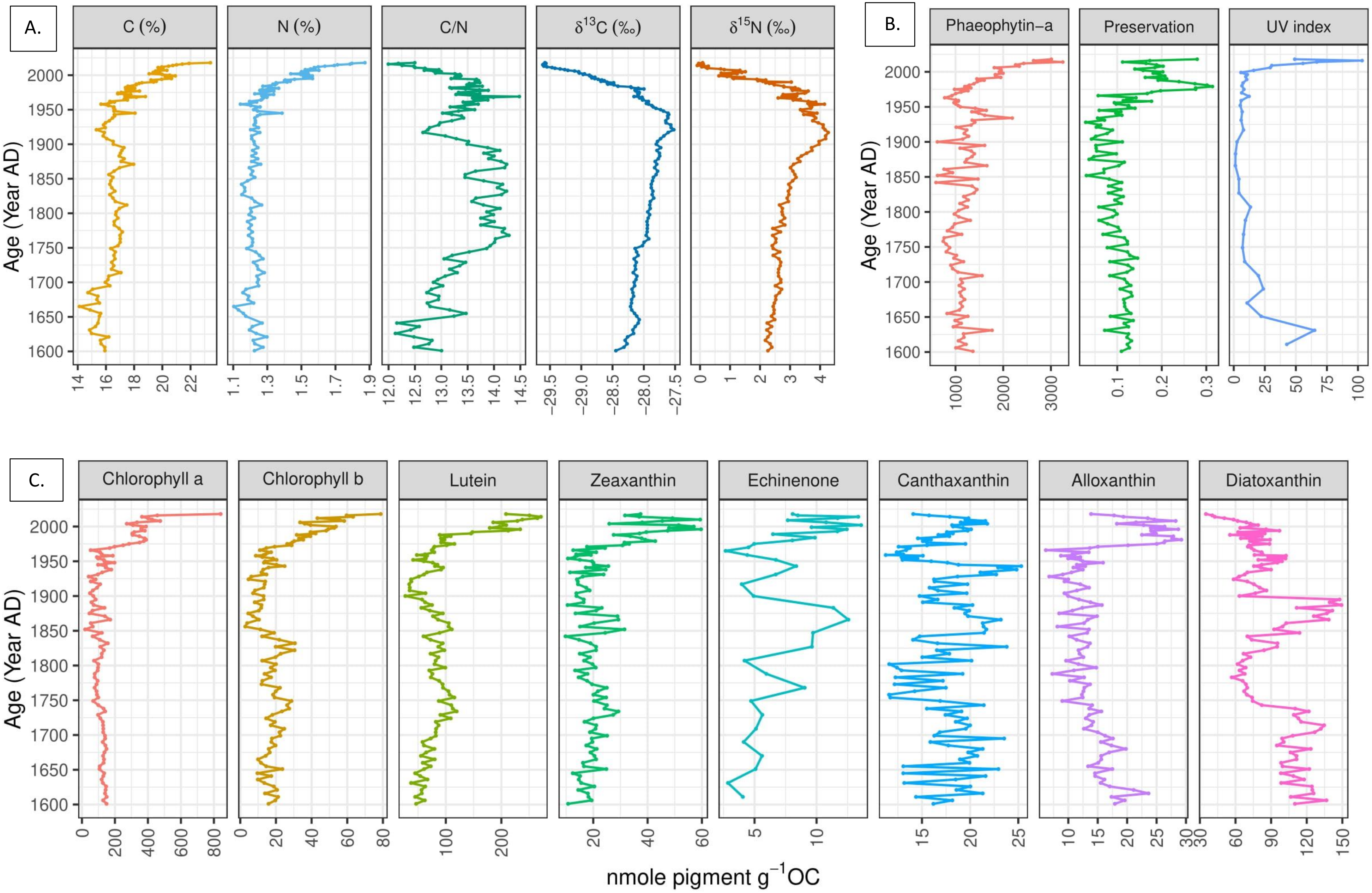

Fig. 5.11 Changes in Blea Tarn bulk organic C, N and their isotopes (A), preservation condition and UV index (B), sedimentary chlorophylls and carotenoids (C).

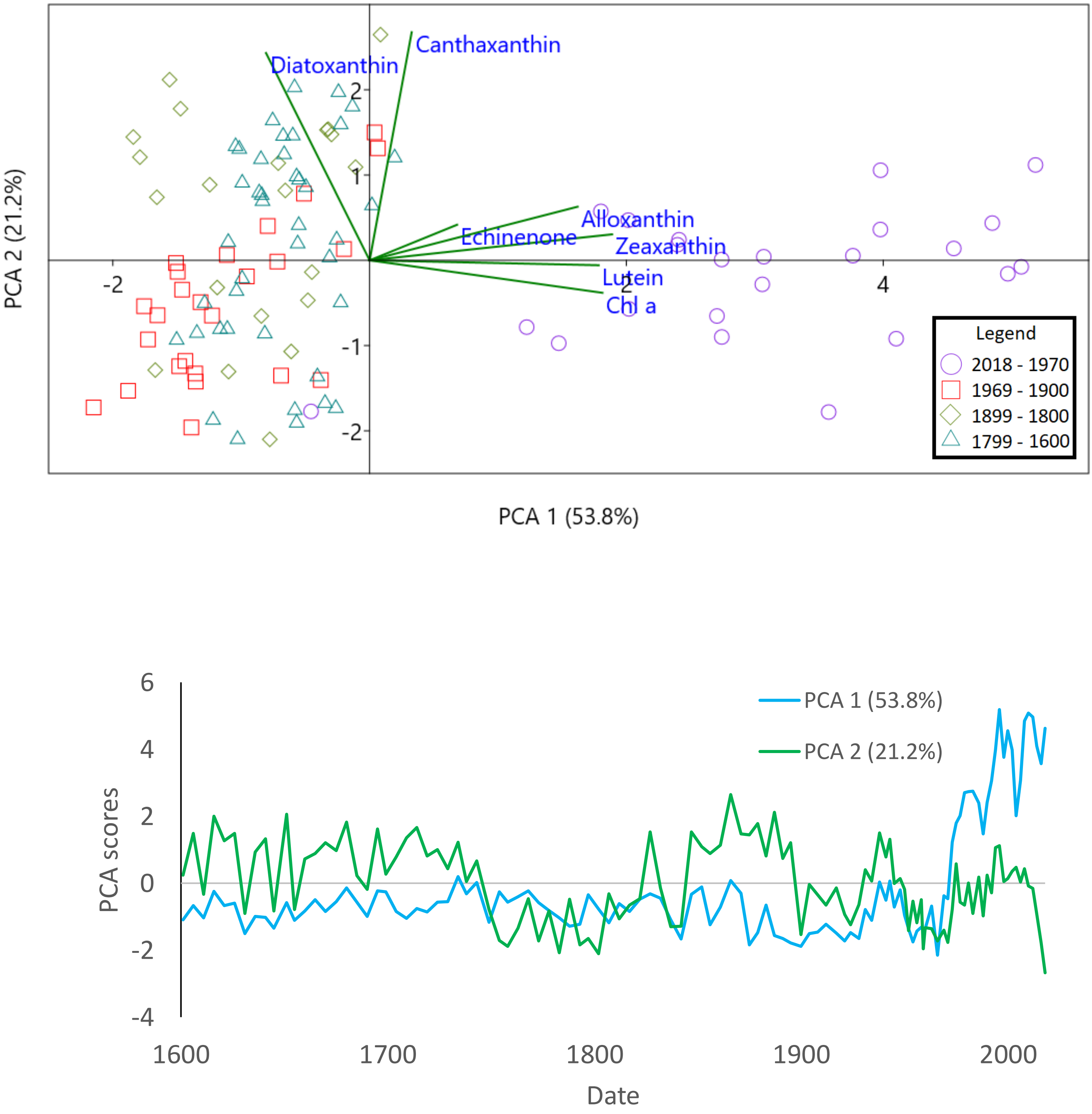

Fig. 5.12 Biplot of PCA scores and graph of change over time for sedimentary pigment concentrations in Blea Tarn.

5.2.6 Regression analysis of meteorological data and sedimentary pigment concentrations

The mean daily maximum summer temperatures had no significant impact ($p>0.05$, $n=28$) on any of the sedimentary pigment concentrations. However, the mean daily maximum annual temperatures had a significant positive impact ($p<0.05$) on lutein, canthaxanthin and chlorophyll-*a* concentrations (Fig. 5.13). There was a significant ($p<0.05$) negative relationship between annual temperatures and diatoxanthin concentrations. Both annual and seasonal temperature trends had no impact on sedimentary alloxanthin and zeaxanthin concentrations. The residuals for each of the linear regression models were randomly distributed indicating that the errors were independent, validating the assumptions of the models (Fig. 5.14).

Annual precipitation had no significant impact on any of the pigment concentrations (Table 5.2). The mean monthly winter precipitation did have a significant impact on lutein concentrations ($r^2=0.19$, $p<0.05$), but not for any other pigments. Multiple linear regression was performed on lutein concentrations for annual temperature and winter precipitaiton, accounting for ~30% of the variation in sedimentary concentrations ($r^2=0.30$, $p=0.014$). While canthaxanthin was better explained by annual precipiation, there were marginally non significant trends annual temperature and precipitation on sedimentary concentrations ($r^2=0.21$, $p=0.063$).

Table 5.2 Regression analysis statistics (r^2, p value) of sedimentary pigment concentrations at Blea Tarn with meteorological data from Newton Rigg (n=28).

Pigment	*Temperature*	*Precipitation*	*Temperature and precipitation*
Diatoxanthin	**0.18 (p=0.027)***	0.001 (p=0.87)	0.21 (p=0.06)
Lutein	**0.28 (p=0.0045)**	0.13 (p=0.071)	**0.30 (p=0.014)**
Zeaxanthin	0.030 (p=0.39)	0.046 (p=0.28)	0.055 (p=0.51)
Alloxanthin	0.0051 (p=0.72)	0.018 (p=0.51)	0.018 (p=0.81)
Canthaxanthin	**0.15 (p=0.043)**	0.14 (p=0.056)	0.21 (p=0.063)
Chlorophyll-*a*	**0.15 (p=0.045)**	0.018 (p=0.51)	0.15 (p=0.14)

Significant relationships ($p<0.05$) are in bold,*indicates a negative relationship

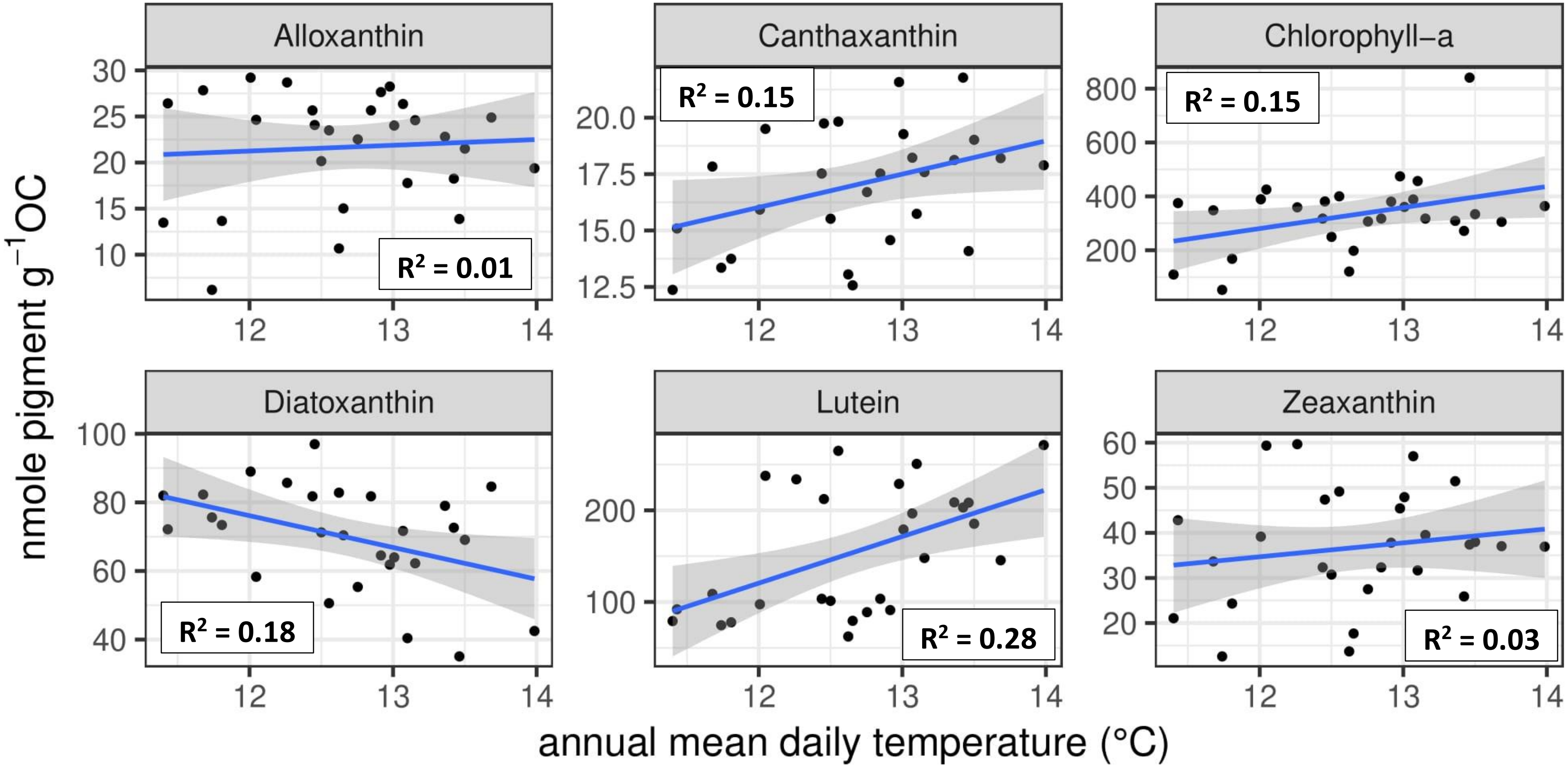

Fig. 5.13 Regression analysis of dated sedimentary pigment concentrations and temperature recorded at Newton Rigg weather station.

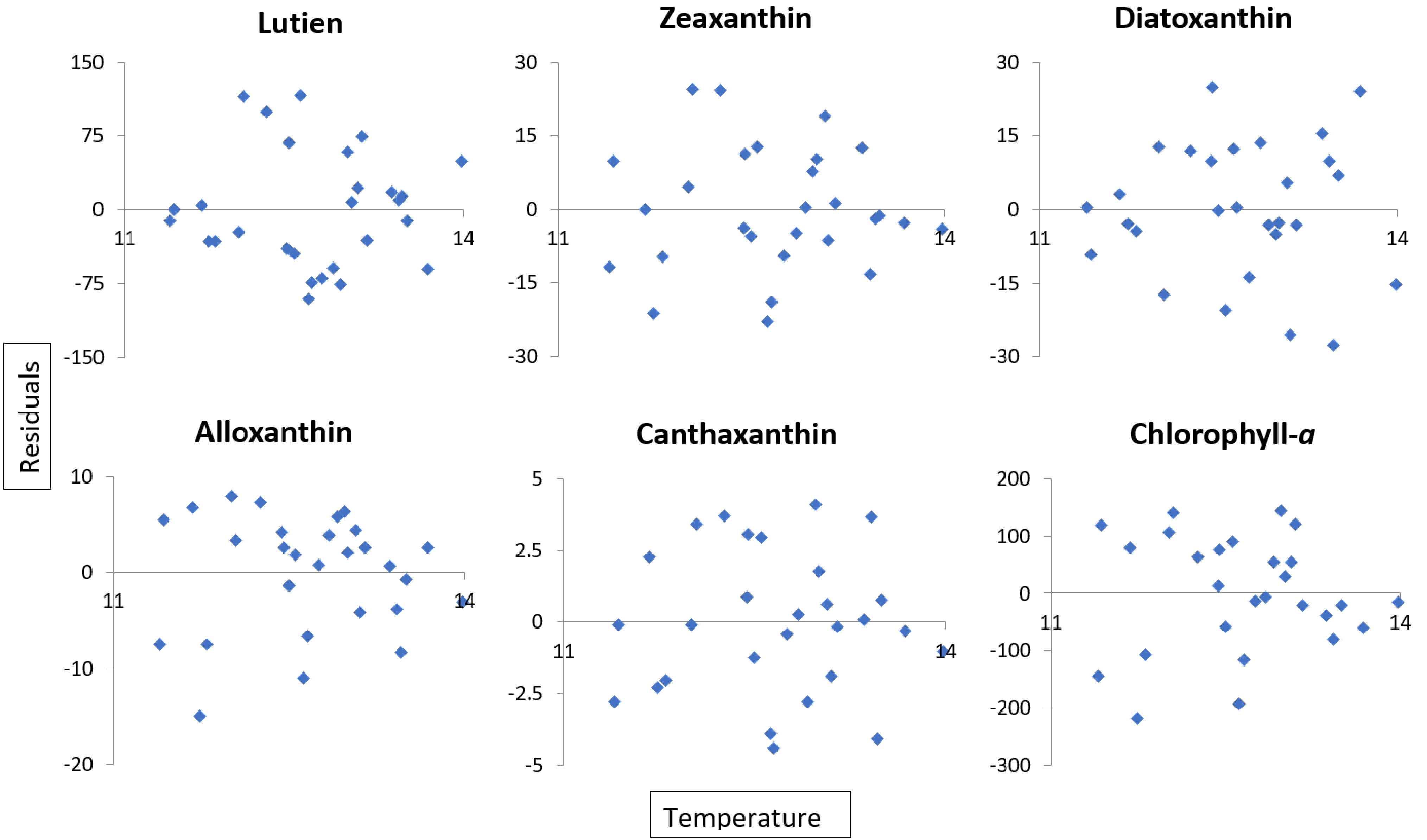

Fig. 5.14 Residuals of regression analysis between mean annual daily maximum temperatures at Newton Rigg weather station and sedimentary pigment concentrations in Blea Tarn.

To corroborate the results from the Newton Rigg weather monitoring station, changes in sedimentary pigment data was also analysed with annual temperatures derived from the HadUK-Grid climate dataset for the 5 x 5 km grid covering the Blea Tarn catchment. The relationship between sedimentary pigment concentrations and temperature from 1960 is similar to that of the Newton Rigg dataset (Table 5.3).

Table 5.3 Regression analysis statistics (r^2, p value) of sedimentary pigment concentrations with annual daily maximum temperature for the Blea Tarn 5km^2 grid from the HadUK-Grid climate dataset (n=54).

	Temperature (from 1960)
Diatoxanthin	0.05 (0.10)*
Lutein	**0.33 (<0.0001)**
Zeaxanthin	0.05 (0.11)
Alloxanthin	0.00 (0.63)
Canthaxanthin	**0.12 (0.01)**
Chlorophyll-*a*	**0.09 (0.03)**

Significant relationships ($p<0.05$) are in bold,*indicates a negative relationship

As with the Newton Rigg dataset there is a strong and high significant relationship between daily maximum temperature and lutein concentrations. In addition there is also a significant positive relationship to temperature for canthaxanthin and chlorophyll-*a.* However, the negative relationship between temperature and diatoxanthin is insignificant ($p>0.05$) when using the HadUK-Grid climate dataset for Blea Tarn. In general, the similar results for both of these datasets would indicate that the temperature changes recorded at the Newton Rigg weather station is likely to represent changes experienced at Blea Tarn.

5.3 Interpretation

5.3.1 $\delta^{13}C_{org}$ indicating different C sources

The $\delta^{13}C_{org}$ values and C/N of the sediments in Blea Tarn indicates that OM is to be a mix of algal and terrestrial material, with a potential contribution from macrophytes (Fig. 5.15). While C/N values stay relatively stable throughout much of the core there are several points of notable change. From the start of the 17th century, $\delta^{13}C_{org}$ stays relatively constant and there is a gradual shift towards higher C/N values, which indicates that while the sources of OM remain the same, the proportions of

OM derived from individual sources changed. The decline in water clarity during the 17th century suggests that this may have been a period of greater allochthonous inputs. Increased terrestrial or stream derived OM could have increased turbidity and supressed productivity of some algal groups. Historical information indicates that water was extracted from Blea Tarn in 1630 to supply a stamp mill in the area (Rollinson, 1967). Therefore it is possible that the divergence of the water to the mill may have increased catchment disturbance during that time. Alternatively, an increase in floating macrophyte abundance could also produce such an effect, shading the lower water column and restricting available habitats for some algae.

The increase in C/N values continues to the end of the 19th century, along with minor increases in $\delta^{13}C_{org}$ (0.7‰) and %C (1%). The increase in $\delta^{13}C_{org}$ and C/N values would suggest a relatively minor reduction in algal biomass during this period, which is supported by a decline in chlorophyll-*a* concentrations. However, it is likely that there have also been increases in allochthonous inputs during the same period, supported by the gradual increase in lithogenic elements (Al, Mg, K, Li). Greater quantities of catchment OM would likely have contributed towards the declining water clarity and algal biomass, resulting in higher sedimentary C/N. While there is an increase, the trend in %C is more variable, largely ranging between 14-18% during this time period. The relatively small fluctuations during this period are likely driven predominantly by changes in terrestrial organic matter inputs (Hu *et al*., 2014). It is possible that this general increase in catchment inputs represents some level of human activity in the catchment, such as minor amounts of woodland clearance that would have reduced catchment productivity and decreased the delivery of low $\delta^{13}C$ DIC to the lake. However if there were any anthropogenic pressures during these centuries, they have not had a major ecological impact on the lake. The magnitude of change is relatively small and indicates that the lake has remained relatively stable, with only minor and gradual change over relatively long time periods. As the catchment of Blea Tarn is relatively large compared to the lake surface area, there could be a wide range of allochthonous material delivered to the lake. Therefore, due to its relatively large size, the Blea catchment will have a strong influence on the ecological community of the lake (Moorhouse, 2016).

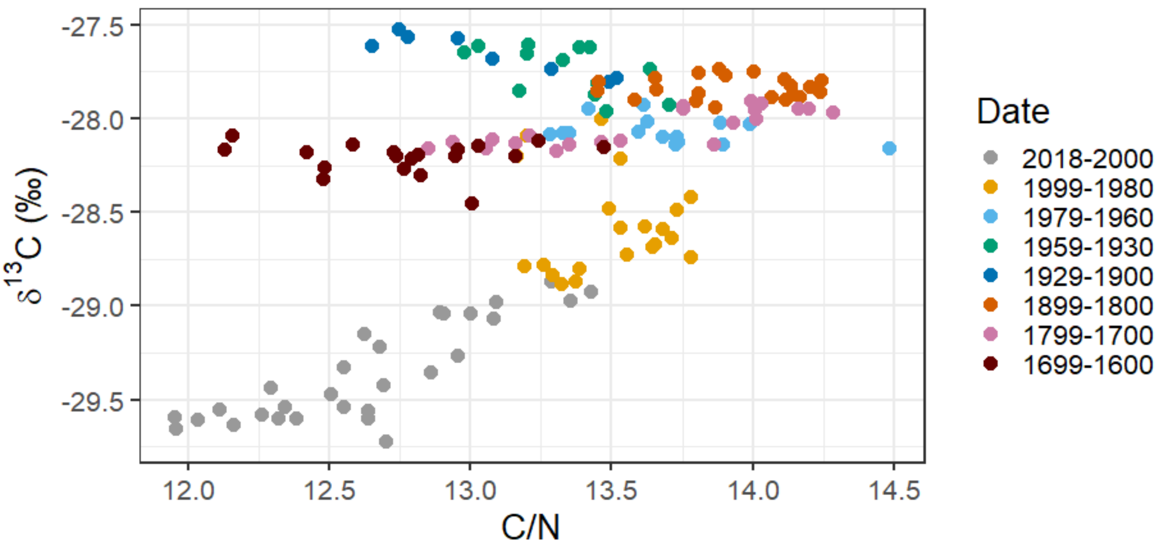

Fig. 5.15 $\delta^{13}C_{org}$ and C/N values for Blea Tarn sediment core.

There is a more notable period of change at the start of the 20th century, as indicated by a more rapid increase in $\delta^{13}C_{org}$ with a concurrent decline in C/N and %C. This period of change may represent increased catchment disturbance that could have resulted in the delivery of low C/N organic material to the lake, such as degraded soils (Paul, 2016). There is evidence that the early 1900s was a period of catchment disturbance as a result of tree felling prior to 1939 (Hürrig, 1999). Deforestation in the early 20th century would have reduced the forest cover in parts of the catchment, however the woodland closest to the lake still remains present today. Increased deforestation can enhance erosion delivering increased minerogenic material along with increased forms of catchment derived organic matter (Fisher *et al*., 2003). However, the impact of deforestation appears to be relatively minor, with a slight increase in $\delta^{13}C_{org}$ from the start of the 20th century of <0.2‰ which occurs along with a reduction in C/N of ~0.8. While woodland loss will have inevitably impacted the lake, a large majority of the catchment is grassland comprising over 90% of the catchment today, which is comparable to the late 19th century (Moorhouse, 2016). Therefore, the loss of a proportion of the woodland in the early 20th century may have had a relatively minor impact when the large size of the Blea Tarn catchment is considered.

Lake productivity appears to have remained relatively stable for most of the time series, based on the small amount of variation in the $\delta^{13}C_{org}$ and %C record (Fig. 5.16). This apparent stability in lake productivity persists until the middle of the 1980s when there is a clear shift towards a concurrent reduction in C/N with $\delta^{13}C_{org}$, along with increases in %C and most algal pigments. This is indicative of enhanced algal productivity, which compared to the previous ~350 years, progresses relatively quickly. Therefore it is likely that these data indicate the first major period of ecological change in the tarn since at least the start of the 17th century. Although C/N values have declined since the start of the 20th century, the lowest values during the 2010s are within a very similar range to those experienced in the early 17th century. This highlights that while there is evidence for increased algal biomass since the 1980s, the proportion of algal material in the lake sediments may be similar to that of almost 400 years ago. Therefore, while overall productivity in the tarn may be increasing, the ecological community themselves may have remained of a similar composition.

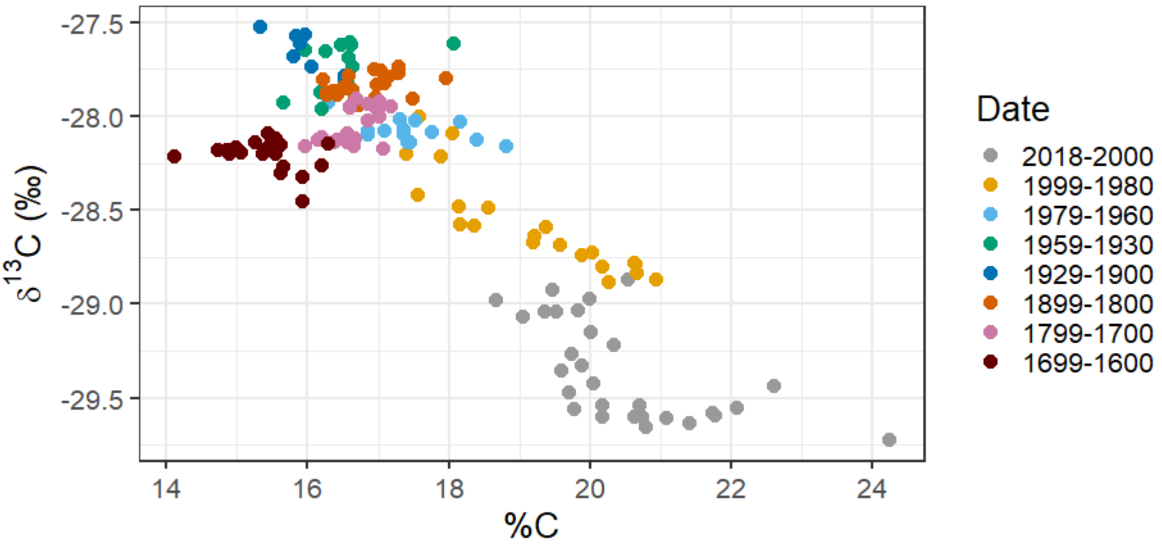

Fig. 5.16 $\delta^{13}C_{org}$ and %C for Blea Tarn sediment core.

In general, %C follows similar trends to that of $\delta^{13}C_{org}$ indicating relatively similar levels of productivity through time, until an increase from the middle of the 1980s. Typically, higher algal biomass leads to increased sedimentary $\delta^{13}C_{org}$ values as algae will preferentially utilise ^{12}C in the lake water and increase the relative proportion of ^{13}C in the DIC pool (Meyers and Teranes, 2001). However, for Blea Tarn it is likely that there is sufficient resupply of DIC that the increases in algal productivity do not deplete the ^{12}C in the lake water substantially. The relatively high catchment to lake surface area of Blea Tarn, coupled with high annual precipitation in the Lake District, would be a considerable source of organic and inorganic C to the lake. Therefore in lakes where algal material dominate the sedimentary OM, $\delta^{13}C_{org}$ is most likely to reflect the changes in algal productivity directly (Reuss *et al*., 2010). Considering the concurrent increase in %C and pigments with a decline in C/N, reduced $\delta^{13}C_{org}$ is most likely reflective of increased algal biomass in Blea Tarn.

Although the decline in $\delta^{13}C_{org}$ from the 1980s has been relatively rapid, the absolute change is still relatively small, with a decrease of ~1‰. Considering the initial decline in $\delta^{13}C_{org}$ from the 1950s is not accompanied by a concurrent decline in C/N, this may represent a change in the source of terrestrial C or reflect a shift in algal community composition (O'Beirne *et al.*, 2017). There is also an indication that $\delta^{13}C_{org}$ values may have stopped decreasing during the 2010s although there are relatively few data points to draw a firm conclusion. Despite the lack of increase in $\delta^{13}C_{org}$, %C continues to increase and C/N declines which indicates that algal biomass may still be increasing during this period. It is possible that the sediments at Blea Tarn are already reaching a natural limit of $\delta^{13}C_{org}$ change from increased algal production. The $\delta^{13}C_{org}$ values have not been corrected for the Suess effect (Verburg, 2007). Therefore, it is possible that the Suess effect has had an impact on reducing $\delta^{13}C_{org}$ values after the 1950s. However, the change in $\delta^{13}C_{org}$ is relatively small overall and there is a concurrent decline in C/N and increased pigments. Therefore, it is more likely that decreasing $\delta^{13}C_{org}$ values during the 20th century are reflecting increased algal productivity.

5.3.2 $\delta^{15}N$ indicating different sources of N

Changes in $\delta^{15}N$ are very similar to that of $\delta^{13}C_{org}$ (Fig. 5.17) with values starting to decline from the middle of the 1980s. The strong correlation between $\delta^{15}N$ and $\delta^{13}C_{org}$ ($r^2=0.90$, $p<0.05$) indicate how they are both likely to be responding to the same shifts in organic matter source through time. While both $\delta^{15}N$ and $\delta^{13}C_{org}$ share very similar trends there is some indication that there is a greater increase in $\delta^{15}N$ during the second half of the 19th century. $\delta^{15}N$ values increase by ~1‰ from 1861 to 1908, indicating a moderate shift in the source of N to the lake. This may represent an increase in agricultural activity in the catchment and potentially more of the catchment being used for livestock grazing. Therefore, it is possible that the late 19th and early 20th centuries were a period of increased nutrient loading to the lake. However as previously mentioned, this is likely to be of relatively low intensity, with the majority of the grazing occurring downstream of the tarn. There is also no indication of an increase in algal productivity during this period, where C/N declines from ~1871 to 1917, $\delta^{13}C_{org}$ values increase, while %C plus the majority of algal pigments (including chlorophyll-*a*) decline from ~1871 to 1917. Therefore it seems unlikely that the late 19th century increase in $\delta^{15}N$ values represents an increase in nutrient loading.

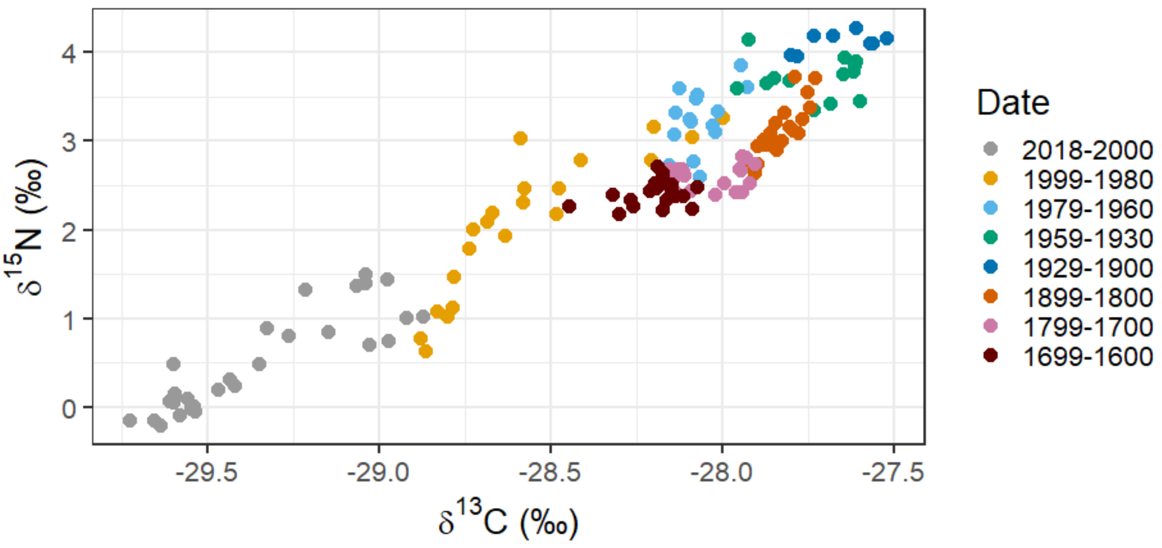

Fig. 5.17 δ^{15}N and $\delta^{13}C_{org}$ for Blea Tarn sediment core.

Considering the lack of stimulation of algal productivity in Blea Tarn, it is likely that the increase in δ^{15}N is more reflective of a relative increase in catchment-derived material entering the lake, which has higher δ^{15}N. Increased allochthonous inputs can result from an increase in anthropogenic activity. There have been documented increases in woodland clearing and some agricultural activity within the catchment during the early 20th century. Although such land use changes can have a dramatic impact on a lake environment they do not appear to have impacted Blea Tarn during this period. Due to the relatively large catchment area, there is likely to be a greater uptake of nutrients by catchment vegetation, which would reduce additional nutrients entering the lake (Schindler, 1998). Climate regulated terrestrial DOM and catchment productivity ultimately controls the quantity and type of organic matter that enters a lake. Therefore any change in the catchment (whether it be anthropogenic or natural) can have an impact on δ^{15}N, and potentially be the most dominant influence (Moorhouse, 2016).

There is a decline in δ^{15}N from the 1950s to the present, in line with the changes in $\delta^{13}C_{org}$ declining by ~3.7‰. However, comparing this to δ^{15}N values at the start of the 17th century (representing pre-industrial conditions) the decline in δ^{15}N is ~2.3‰. The timing of change is somewhat consistent with atmospheric N deposition, which typically shows greater impacts from the 1950s. However, there is also a concurrent decline with $\delta^{13}C_{org}$ and no clear increases in algal pigments until the 1970s, 10-20 years later. The lack of stimulation of algae until at least the 1970s suggests increased atmospheric N deposition may not be the controlling factor in reducing δ^{15}N at this time. This is supported by the lack of the typical ‘hockey stick’ profile in δ^{15}N change, which is common in most lakes directly impacted by atmospheric N deposition (Holtgrieve *et al.*, 2011). The concurrent decline with $\delta^{13}C_{org}$ indicates that there has been an increase in organic productivity, potentially relating to the catchment derived OM. Therefore, the decline in $\delta^{15}N$ from the 1950s may represent an increase in catchment productivity, or a change in the source of allochthonous OM inputs.

Considering the consistent decline in sedimentary P concentrations since the 1950s, any impact on the lake from increases in rough grazing from the 1970s appears negligible. There is a relatively brief period during the 1970s when $\delta^{15}N$ values increase by ~0.8‰. This relatively minor shift in $\delta^{15}N$ values ends quickly and returns to declining values from the end of the decade. Therefore, any impact of eutrophication from increased livestock during this period appears to be either minimal and/or quickly overwhelmed by other sources of N with lower $\delta^{15}N$

While $\delta^{15}N$ values broadly decrease during the 20th century they do not start decreasing beyond the historical baseline until the 1980s (Fig. 5.18). There is also considerable variability in $\delta^{15}N$ from the 1930s to 1970s with periods of relatively brief decline followed by increases. It is possible that there was a confounding effect from the dual inputs of N-enriched and N-depleted sources to the lake during this period (Leavitt *et al.*, 2006). The declining $\delta^{15}N$ along with $\delta^{13}C_{org}$, C/N and increases in pigments from the 1980s likely represents an increase in algal derived material, as algae preferentially uptake ^{14}N over ^{15}N when N availability is sufficient (Sachs *et al.*, 1999).

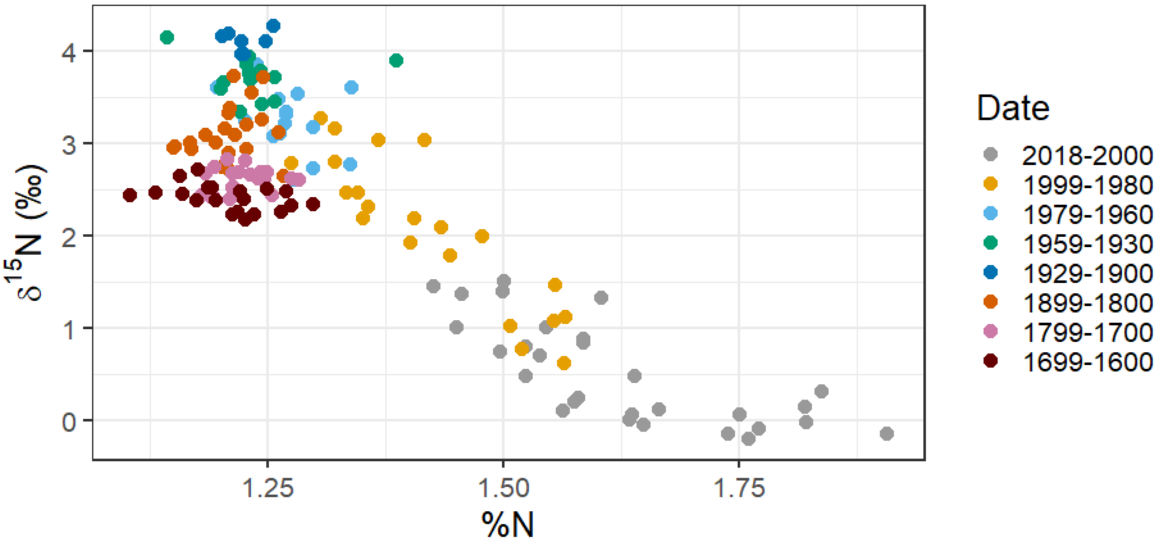

Fig. 5.18 $\delta^{15}N$ and %N for Blea Tarn sediment core.

Declining $\delta^{15}N$ values can also be driven by diagenesis which results from microbes preferentially utilising ^{14}N over ^{15}N (Brahney *et al.*, 2014). Declining $\delta^{15}N$, C/N and an increase in %N can indicate diagenesis is impacting $\delta^{15}N$ values in the second half of the 20th century. However, considering this was a period of increasing algal productivity this makes the impact of diagenesis on the $\delta^{15}N$ signal less clear. Diagenesis has been reported to increase $\delta^{15}N$ by 1-2‰ within the first 50 years after burial (Brahney *et al.*, 2014). Blea Tarn sediments on the other hand increased by ~3.5‰ within the first 50 years. Therefore, while diagenesis may be playing a role in the observed changes in $\delta^{15}N$ it is unlikely to be a dominant driver. This theory is also supported by the concurrent changes in the $\delta^{13}C_{org}$ data which are not impacted by diagenetic effects in the same way as $\delta^{15}N$ (Hodell and Schelske, 1998; Meyers and Lallier-Verges, 1999).

5.3.3 Total algae (chlorophyll-*a*, phaeophytin-*a*)

Chlorophyll-*a* at Blea Tarn remained essentially stable between the 17th and 19th centuries with 95.4 nmole in 1793 (Fig. 5.19). These relatively low concentrations indicate that the OM of the sediments was mostly of allochthonous origin (Moorhouse, 2016). There is a period of increased chlorophyll-*a*, and more notably, phaeophytin-*a* concentrations during the 1930s to 2311.7 nmole in 1937 (Fig. 5.20). This occurs after what is likely to be a signal of deforestation in the catchment, inferred by the $\delta^{13}C_{org}$ and C/N record. Therefore, deforestation of parts of the catchment may have resulted in greater nutrient loadings to Blea Tarn, at least temporarily, enhancing algal biomass. Sedimentary P concentrations peak in the 1950s, and may be related to the deforestation in the catchment during the first half of the 20th century. The peak in P during the 1950s is 10-20 years after catchment deforestation initially stimulated algal growth and would indicate prolonged high in-lake P concentrations. Following enhanced external P loading, internal P loading can remain high for decades after external inputs decline (McCrackin *et al.*, 2017). The decline in algal biomass while P concentrations were high would indicate that it is not likely the limiting factor on algal growth.

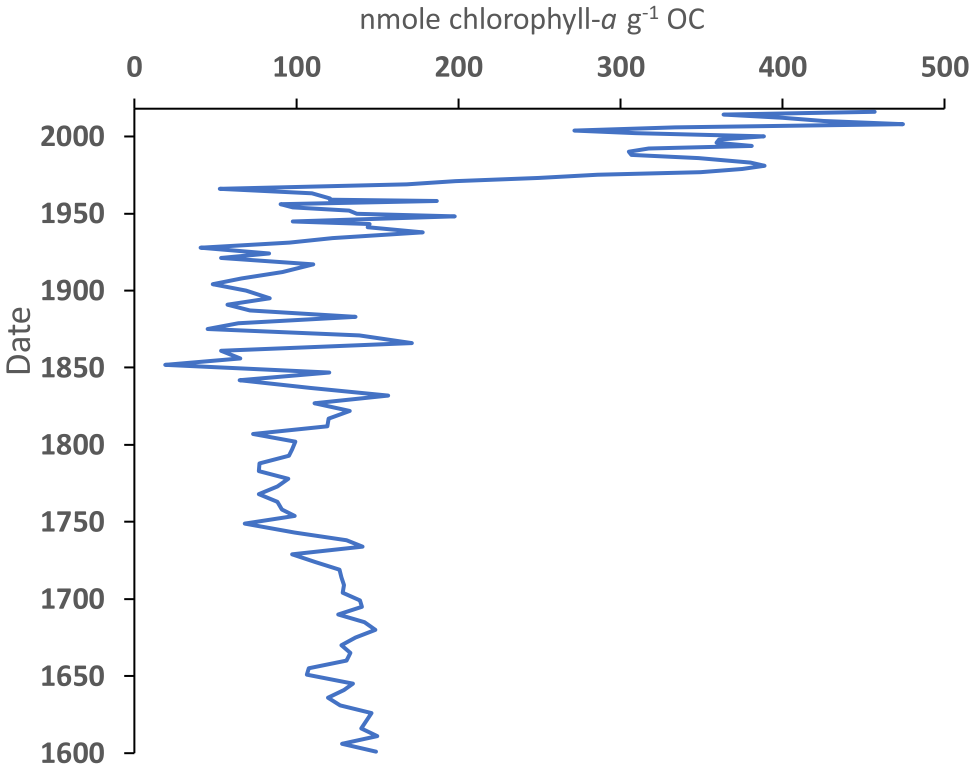

Fig. 5.19 Concentrations of chlorophyll-*a* from Blea Tarn sediment core.

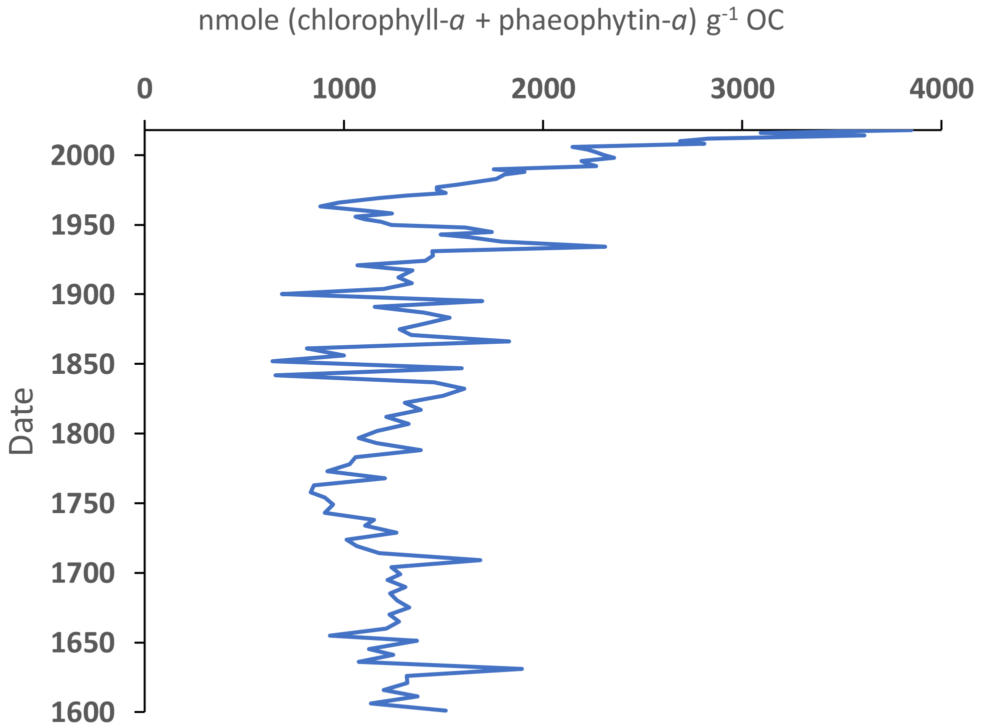

Fig. 5.20 Concentrations of chlorophyll-*a* and phaeophytin-*a* from Blea Tarn sediment core.

There is a clear increase in total algal biomass during the 20th century, in particular from the 1970s indicated by an increase in chlorophyll-*a* and phaeophytin-*a* to 2356.9 nmole in 1998 (Fig 5.19, Fig. 5.20). It is notable that after the rapid increase in concentrations during the 1970s, chlorophyll-*a* concentrations effectively stabilise from the 1980s until the start of the 21st century with 388.5 nmole in 2000. Whilst this may indicate that lake algae had maintained similar annual biomass during this period, it is unlikely to be the case due to the increase in phaeophytin-*a* (Fig 5.12b). Further declines in $\delta^{13}C_{org}$, C/N and increases in %C are all indicative of further increases in autochthonous OM production during this period. Considering chlorophyll-*a* can be relatively labile under certain environmental conditions, it is likely that sedimentary chlorophyll-*a* concentrations in Blea Tarn were being impacted somewhat by changes in their preservation. This impact is reflected by the preservation conditions (Fig. 5.11b), where the increase during the 1970s is likely to reflect the increased chlorophyll-*a* supplied to the sediment (Buchaca and Catalan, 2007). The reversal and relatively rapid decline in chlorophyll-*a* to phaeophytin-*a* ratios indicates a period of enhanced chlorophyll-*a* degradation. The time when preservation conditions start reversing (1980) occurs along with a decline in C/N and a more rapid decline in $\delta^{13}C_{org}$. This would suggest that this was a period of enhanced algal productivity and so concurrent increases in chlorophyll-*a* would also be expected.

Changes in preservation conditions indicate that chlorophyll-*a* preservation was likely impacted during this period. However, concentrations of the more labile pigments (e.g. fucoxanthin) do not appear to have been impacted during this period (Fig. 5.11c). Therefore, the variations in preservation conditions are unlikely to reflect changes in the post depositional environment, such as through bottom water O_2 availability. The suggestion that O_2 availability has not changed substantively is supported by the consistent presence and relatively high abundances of oxygenated derivatives of chlorophyll-*a* (e.g. hydroxyphaeophytin-*a*, purpurin-18-phytyl ester) found during this period. Therefore the change in preservation condition is likely to represent a change in how much chlorophyll-*a* is degraded pre-sedimentation, such as after cell death as it sinks down to the sediments. The degree of pigment degradation is controlled by a range of factors, one of the most important being distance/time of travel to the sediments (Buchaca and Catalan, 2007). Therefore the lack of concurrent increase in chlorophyll-*a* with phaeophytin-*a* (and other pigments and proxies) may represent a shift in community structure to a greater proportion of pelagic phytoplankton. A shift in the algal community from the 1980s is supported by the increase in typically pelagic taxa (e.g. cryptophytes) while the typically benthic diatoms experience little change. Therefore the increase in chlorophyll-*a* production may have been offset by enhanced degradation rates during this period due to a higher proportion of chlorophyll-*a* produced by pelagic taxa.

A shift towards more planktonic phytoplankton is often symptomatic of an increase in nutrient loading (e.g. Scheffer and van Nes, 2007; Vadeboncoeur *et al*., 2003). There is a highly significant correlation between $\delta^{15}N$ and chlorophyll-*a* ($r^2=0.65$, $p<0.0001$) since the start of the 20th century. Increases in chlorophyll-*a* coupled with decreases in $\delta^{15}N$ can suggest that N fertilisation from atmospheric deposition has increased primary production (Wolfe *et al*., 2003). While there is a strong relationship between $\delta^{15}N$ and chlorophyll-*a* concentrations, they appear to be offset, possibly by ~10 years. The greater increases in chlorophyll-*a* start during the 1970s with $\delta^{15}N$ in the 1980s, mirroring the trends in $\delta^{13}C_{org}$. Therefore the decline in $\delta^{15}N$ may be more reflective of the increase in productivity rather than be the cause of it. Increased algal growth can lower $\delta^{15}N$ values through enhanced fractionation and may be driving some of the reductions in the second half of the 20th century (Woodward *et al*., 2012). Therefore, although it is possible that atmospheric N deposition has directly stimulated lake algal biomass, it is unlikely to be the dominant driver.

It is notable that sedimentary P concentrations have consistently declined from the 1950s to the start of the 21st century. Declines in sedimentary P typically indicate a reduction in external P loading (Søndergaard *et al*., 2003). A decline in P loading is supported by the concurrent decline in sedimentary Mn. P is often strongly adsorbed to Mn along with Fe (Davidson, 1993) which also declines although less consistently than P and Mn. P is often immobilised in the water column by iron-based compounds, which become deposited in the sediment, reducing in lake P concentrations (Wang *et al*., 2021). While there is a concurrent peak in P with Fe in 1954 the relationship between these elements is generally poor since the start of the 17th century ($r^2=0.019$, $p=0.4$). This would indicate that Fe has not typically driven P concentrations and although they share a peak and decline during the middle of the 20th century, the second half of the 20th century was a period when many concentrations of anthropogenic derived heavy metals peaked and declined (e.g. Cu, Cd, Cr, Zn). Therefore the concurrent peaks in P and Fe during the 1950s may just represent a peak in anthropogenic emission during this period. As a result it seems unlikely that the reduction in P represents a reduction in P immobilisation, which would effectively result in increased concentrations in the water column. While a reduction in sedimentary P may also be related to greater utilisation of P by algae, with greater proportions being flushed out, the decline starts around 20 years before the initial increase in algal biomass.

There does not appear to be any detectable impact of a reduction in P loading, with total algal biomass increasing from the 1970s. Increasing algal biomass during a period of declining P loading would suggest that this nutrient is not a limiting factor. Algae are often P limited, however most terrestrial ecosystems on temperate soils are thought to be N-limited (Du *et al*., 2020). Considering the relatively large catchment to surface area ratio of Blea Tarn, the lake will be strongly regulated by the wider catchment. Therefore it seems likely that Blea Tarn is N limited, which would suggest that the increases in total algal biomass from the 1970s are caused by increased N supply. While there is unlikely to be a direct impact from atmospheric N deposition on the tarn, it may have had a stimulating effect on the catchment vegetation. An increase in both nutrients and temperature from the second half of the 20th century may have worked synergistically to increase the productivity across the catchment. It is also notable that sedimentary pigment concentrations do not increase until at least the 1970s, some 20 years after start of the decline in sedimentary P and $\delta^{13}C_{org}$. This could represent a longer-term response from the catchment vegetation, which would uptake more of the P that would typically be delivered to the lake. Increased productivity in the catchment would result in DIC with lower $\delta^{13}C$ being supplied the lake (Maberly *et al.*, 2013). Therefore the reductions in $\delta^{13}C_{org}$ and P may reflect the start of the period of enhanced catchment productivity, with a delayed impact in stimulating lake algae.

Regression analysis indicates that temperature has had a significant impact on total algal biomass since the 1960s, explaining ~15% of the variation. Therefore, while there are clear impacts from increasing temperatures during the second half of the 20th century, it may not be the dominant driver. Changes in temperature and precipitation will affect the timing of freshwater and nutrient input. In shallow non-stratified lakes, such as Blea Tarn, P release can be stimulated by higher temperatures where enhanced precipitation may increase nutrient concentrations (Jeppesen *et al.*, 2009). Nutrients derived through allochthonous sources can stimulate algal growth and lead to a shift in algal community composition (Heisler *et al.*, 2008). While it might be expected that increased precipitation would stimulate algal growth through enhanced nutrient delivery this does not appear evident through the analysis with the meteorological record. Higher precipitation may not necessarily lead to higher lake nutrient concentrations as it will also increase dilution (Jeppesen *et al.*, 2009). Therefore, the impact of precipitation on algal biomass may be variable, depending largely on-site specific characteristics including catchment size, slope and dominant vegetation.

5.3.4 Diatoms (diatoxanthin)

Diatoxanthin concentrations are relatively high during the 17th century but experience slight declines from 125.7 nmole in 1616 to 99.3 nmole in 1695. The high concentrations of diatoxanthin during this period suggest that diatoms were dominant in the lake at that time. While the decline in diatoxanthin concentration is relatively small and gradual, it may indicate a change in lake conditions that restricted their growth. There is a notable decline in the UV index during the 17th century which may help to explain the decline in diatoms during this period (Fig. 5.21). The decline in water clarity during the 17th century may be driven by enhanced catchment inputs. There are increases in lithogenic derived elements (K, Mg, Li) during the first half of the 17th century, reaching a peak between the 1650s and 1670s, which is in line with the rapid decline in UV index during this period. Changes in catchment inputs may also help to explain the subsequent increase in diatoxanthin concentrations at the end of the 17th century. There was a concurrent increase in UV index around this time along with declining K, Mg and Li concentrations. The relatively rapid decline in diatoxanthin concentrations to 66.0 nmole in 1778 may also be related to water clarity, considering the concurrent increase in lithogenic elements along with a decline in diatoxanthin and maintenance of a low UV index.

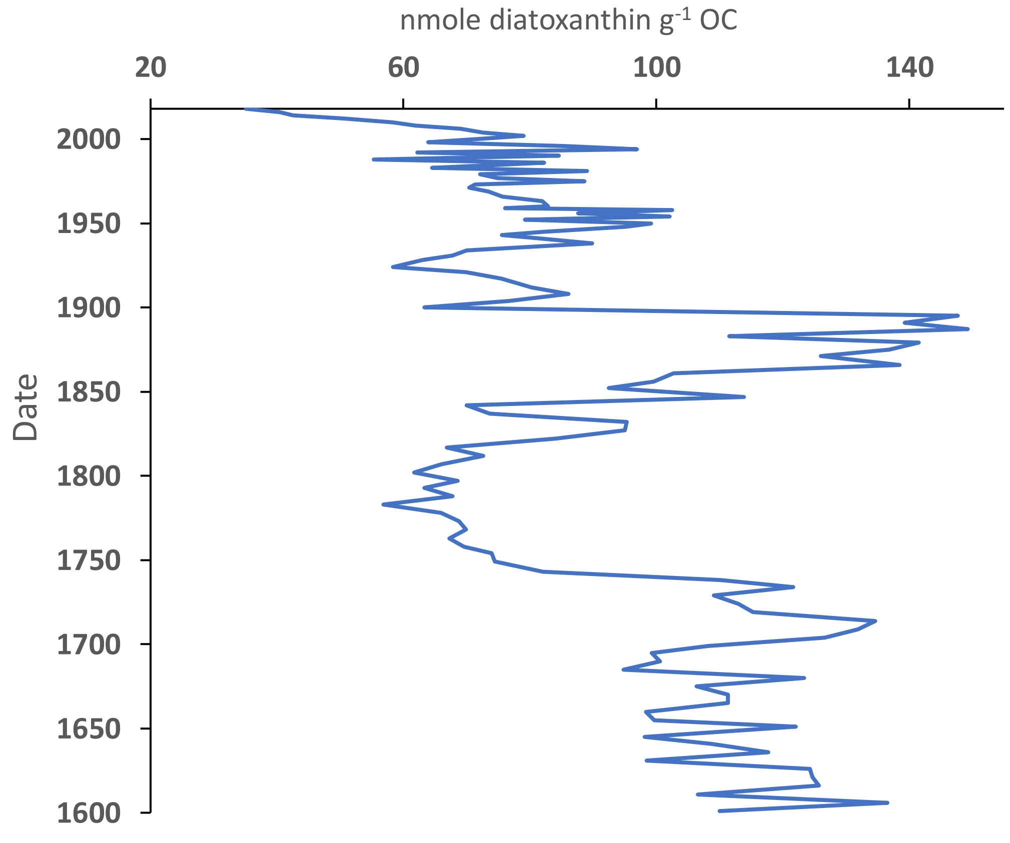

Fig. 5.21 Concentrations of diatoxanthin from Blea Tarn sediment core.

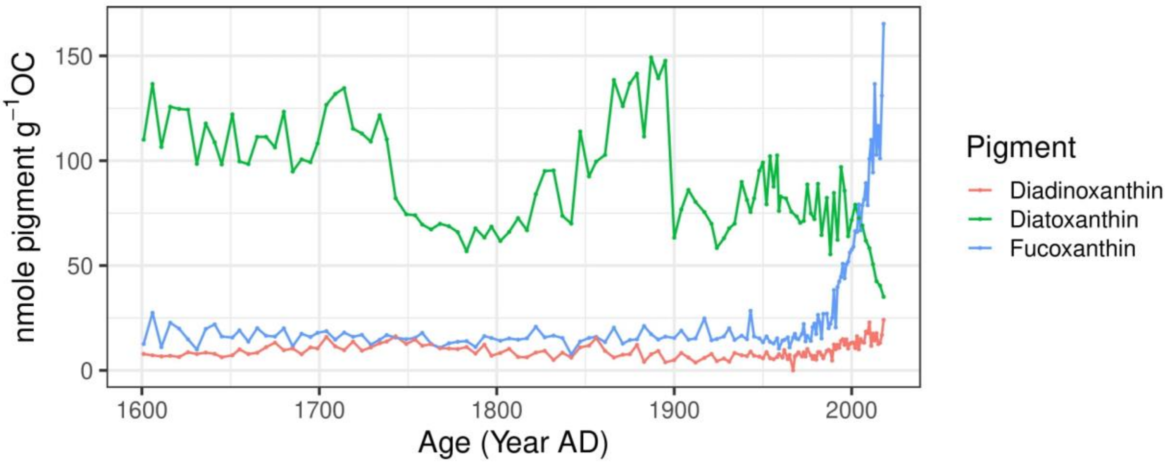

Fig. 5.22 Concentrations of diatom derived pigments from Blea Tarn sediment core.

Generally, Al derives from erosion of catchment material, however it can also be sourced from atmospheric deposition (Liu *et al*., 2020). The near consistent rise in Al from the start of the 17th to the 20th century may suggest an overall increasing in catchment inputs during this period. However, the increase in Al also coincides with a period of intensification of industrial activity in the UK, peaking in concentrations during the 1920s. In addition, there is a very strong correlation between Al and Pb at the start of the 18th century and in the 1920s (r^2=0.95, p<0.0001), suggesting that they are most likely derived from the same source. Since the industrial revolution Pb would typically be delivered to lakes through atmospheric deposition. Additionally there is no correlation between Al and the other elements having a characteristically terrigenous origin such as K, Mg or Li (p>0.7) which is reflected in the PCA biplot (Fig. 5.10). Al and K are major constituents of common silicate minerals and can originate from the weathering of bedrock (Wilcke *et al*., 1998). The lack of correlation between these two suggests that there are additional sources driving the trends in Al (Ma *et al*., 2016). Therefore it seems likely that Al trends have been impacted by anthropogenic sources, and as a result they are unlikely to best reflect trends in catchment derived inputs for Blea Tarn.

The trend of increased lithogenic elements (K, Mg, Li), declining UV index and diatoxanthin concentrations follow broadly concurrent trends until the start of the 19th century. From the start of the 19th century diatoxanthin concentration starts to increase concurrent with an increase in lithogenic elements and a slight decline in the UV index. The relationship between these proxies changes again in the second half of the 19th century as there is a continued increase in diatoxanthin to 149.3 nmole in 1887. There is also a decline in K, Mg and Li concentrations while the UV index remains relatively low and even slightly reduces. This indicates that the catchment inputs are not controlling water clarity during this period and that that low concentrations of UV protective compounds are related to other factors. Considering the second half of the 19th century represents the end of the Little Ice Age, which resulted in cold winters (Parker *et al*., 1992), it may reflect periods of extensive ice cover that would have reduced light penetration to the sediment surface. However, this was a period in which diatoms increased in biomass, indicating that they were stimulated throughout most of the 19th century.

The 19th century was a period of intense industrialisation in the Lake District, with an intensification in the mining of heavy metals (e.g. Cu, Pb, Zn, Fe) during the second half of the century (Miller *et al*., 2014). Greenburn Copper Mine is approximately 1.5 miles south of Blea Tarn and was the largest mine copper mine in the Windermere catchment, processing large quantities of copper pyrites and copper oxides (Postlethwaite, 1975; Fig. 5.23). While the mine was first used towards the end of the 17th century, it rapidly expanded in size and was operated intensively from 1845 to 1861 before closing in 1885 (Oswald *et al*., 2001). The site around the mine was also used to process the ore and included a crushing mill and smithy. Whilst there were further extractions reported to have occurred between 1906 and 1917, the processing machinery were likely made inoperable shortly after 1885. It is notable that the timings of the intensification of mining activity, and subsequent closure, occur during the period of enhanced diatoxanthin concentrations.

Fig. 5.23 Greenburn Copper Mine in relation to Blea Tarn (OpenStreetMap, 2020).

The impact of Cu mining activity is likely reflected in the sedimentary record of Blea Tarn. There is an increase in sedimentary Cu concentrations from the start of the 18th century, which increase until the start of the 20th century with 52.2 µg g^{-1} sediment recorded in 1904. There is also widespread evidence that the mining activity was accompanied by the quarrying of stone and slate overlooking the processing area (Oswald *et al*., 2001). In addition, it is likely that some of the nearby rocks were blasted open to test for the presence of further ore veins. These activities would have produced large quantities of dust and particulate matter that could have deposited in the lake and catchment. This may help to explain the low UV index during this period, with minimum values between the 1850s and the start of the 20th century.

It is also possible that these industrial activities resulted in the delivery of Si to the lake. Dust from slate milling operations can contain between 5-20% silica which could have deposited in the catchment (Taylor, 1985). Si is a major nutrient for diatoms and has been attributed to enhanced spring diatom growth with its limitation often terminating a diatom bloom (Billen *et al*., 2001; Kong *et al*., 2021). Stimulation though enhanced Si inputs may also explain the sudden decline from elevated diatoxanthin concentrations at the end of the 19th century, which coincides with the cessation of mining activities. An increased delivery of Si would also explain why it was only diatoms that were stimulated during this period. While it is possible that mining and processing activities resulted in increased diatom biomass in Blea Tarn, it is likely that only pelagic taxa and/or those that can tolerate low light conditions were stimulated considering the reduction in water clarity in the lake during this period.

While diatoxanthin concentrations stay broadly stable during the 20th century, they increase slightly during the first half of the century to 102.5 nmole in 1958 followed by decline to 79.0 nmole in 2002. Considering the significant negative correlation between diatoxanthin concentrations and temperature since the 1960s, it appears that the decline from the second half of the 20th century is partially driven by warming. As with chlorophyll-*a*, it is possible that this decline relates more to a habitat shift in diatoms. Increased planktonic biomass may have been offset by a reduction in benthic environments. As warming occurs benthic habitats may become more habitable for a wider range of taxa. In such conditions, diatoms may be outcompeted by faster growing taxa. Therefore, as water temperature and lake nutrients increase, planktonic diatoms also increase but overall diatom abundance declines. Precipitation was shown to be a marginally insignificant driver of change (r^2=0.21, p=0.06) of diatoxanthin concentrations. Precipitation may be expected to have an impact on diatom biomass, considering Si is often delivered to lakes through the erosion and transport of terrigenous material (Officer and Ryther, 1980). Therefore it is also possible that this decline in diatoms is due to increased Si limitation.

5.3.5 Cryptophytes (alloxanthin)

There is a broad and steady decline in alloxanthin concentrations during the 17th century to 12.4 nmole in 1754 (Fig. 5.24). The decline in alloxanthin coincides with a decline in water clarity during this period, likely driven by enhanced catchment inputs. Typically, cryptophytes thrive in low light conditions as their mixotrophy enables them to switch between photosynthesis and consuming OC for energy (Findlay *et al*., 2001). However, during this period, they were one of the few algal taxa to decline, along with diatoms to an extent, although the timing and magnitude of the decline differs. Considering both diatoms and cryptophytes are spring blooming taxa this may indicate a seasonal driver. Colder temperatures during the Little Ice Age may have contributed towards their decline as the 17th century was particularly cold in winter months (Lamb, 1965). This cold period would have resulted in extensive winter ice cover which would have considerable impacts on primary production during spring months, through a reduction in the length of the growing season (Reuss *et al*., 2010). Considering the concurrent decline in diatoxanthin with alloxanthin during 17th century, it appears that these spring blooming taxa are equally impacted. There is also indication that this was a period of enhanced catchment erosion, which would have contributed towards the reduction in water clarity and potentially changing nutrient regimes. It is notable how this is also a period when $\delta^{15}N$ values increase and sedimentary P values broadly declined, indicating a reduction in nutrient loading.

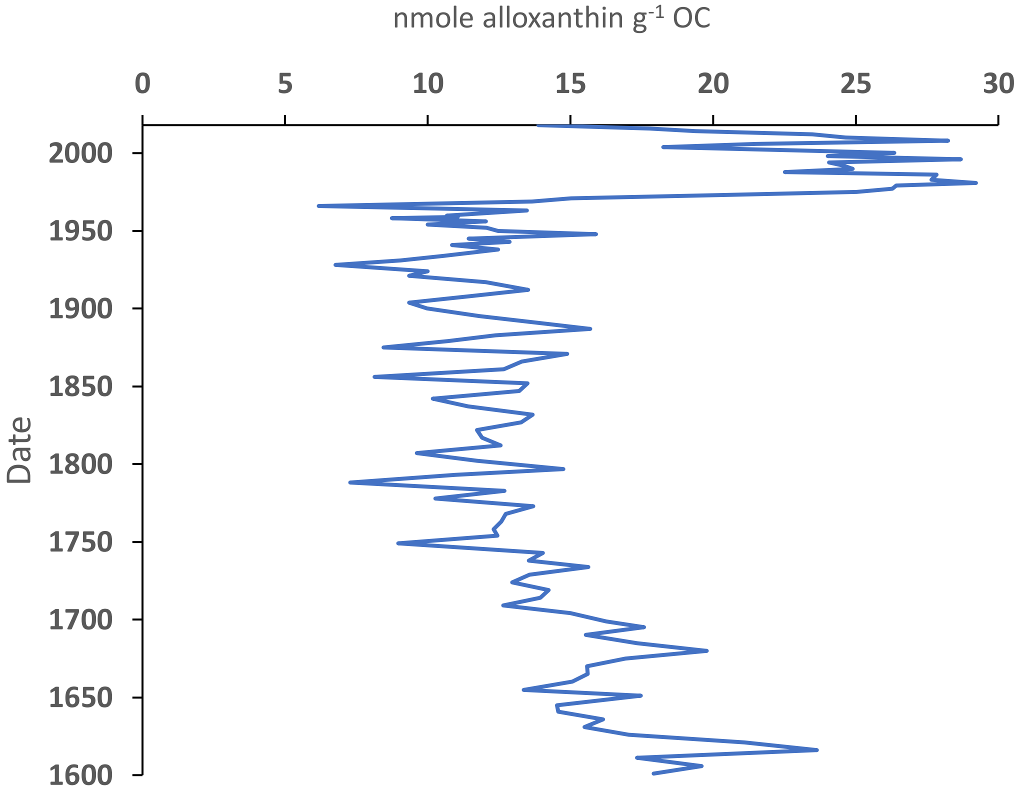

Fig. 5.24 Concentrations of alloxanthin from Blea Tarn sediment core.

Alloxanthin concentrations remain relatively stable from the middle of the 18th century through to the second half of the 20th century. This contrasts to diatom biomass which exhibits greater variability over time. Considering both of these are spring blooming taxa, the greater stability of cryptophytes may indicate that they have been more resilient to change in the past. The adaptations of cryptophytes may enable them to use their motility and mixotrophy to better respond to changes in environmental conditions. Overall, whilst there is a decline in cryptophyte biomass during the 17th century, they maintain relative stability in Blea Tarn for much of the time series.

There is an increase in alloxanthin concentrations from the start of the 1970s to 27.7 nmole in 1983, in line with the increase in other algal taxa (e.g. cyanobacteria, chlorophytes) and along with chlorophyll-*a*. These concurrent increases indicate how the start of the 1970s was a period of enhanced productivity that broadly stimulated the algal community, except for diatoms, likely reflecting an increase in primarily planktonic taxa. After the rapid increase in alloxanthin concentrations during the 1970s, concentrations stabilise from the 1980s and start to decline. The decline is only marginal at first but becomes more rapid to 23.5 in 2012, which occurs concurrently with a rapid increase in the UV index during the 21st century. Elevated water clarity, inferred from sedimentary pigments, is consistent with the monitoring data from the Environment Agency between 2005 and 2008 (Environment Agency, 2008), which recorded an NTU of 1. This indicates low turbidity equivalent to the ideal drinking water standard set out by the World Health Organisation (WHO, 2017). For an open basin lake, an increase in water clarity can often be associated with a decrease in DOC concentrations (Jones, 1992). The control of precipitation on DOC concentrations is a particular feature of upland lakes which typically experience lower DOC concentrations than lowland lakes (Sobek *et al*., 2007; Toming *et al*., 2020). A reduction in DOC during the 21st century, resulting in increased water clarity, could also help to explain the subsequent decline in cryptophyte biomass. As cryptophytes are mixotrophic, they have a competitive advantage in their ability to utilise OC as an energy source.

An increase in water clarity may also be driven by enhanced water loss in summer months, as a reduction in water depth would increase underwater light penetration. The impact of this may be particularly prominent for shallow, non-stratifying lakes with increases in WRT (Bakker and Hilt, 2015). Therefore, the trends in cryptophytes and water clarity may be explained by increased seasonality. Enhanced winter-spring rainfall would have a dilution impact on DOC and nutrient concentrations for spring blooming taxa. On the other hand, enhanced water loss in summer months would increase UV radiation to the sediment surface, which results in greater proportions of cyanobacteria producing UV screening compounds in lakes where they are present. Despite these points, regression analysis showed that there was no significant impact of temperature or precipitation on alloxanthin concentrations. DOC levels are generally low in the Lake District compared to elsewhere in the UK (Tipping *et al*., 2000). Due to this, even a relatively small change in DOC can be enough to impact cryptophyte populations. Therefore, any impact of temperature and precipitation on cryptophyte biomass, as a result of changes in DOC concentrations, may be largely obscured or confounded by other factors.

5.3.6 Chlorophytes (lutein, chlorophyll-*b*)

Lutein concentrations broadly increase during the 17th century to 119.6 nmole in 1734 (Fig. 5.25). This period of increase occurs when spring blooming taxa (diatoms, cryptophytes) decline. Therefore the increase in chlorophytes may represent an increased supply of nutrients available to summer blooming taxa due to a reduced utilisation by diatoms and cryptophytes (McGowan *et al*., 2012). It may also be related to an increase in catchment inputs during the 17th century, which would deliver more nutrients to the lake. The potential cause of a decline in spring blooming taxa has been discussed in previous sections but likely reflects less favourable spring conditions during this period. Considering that chlorophytes have high nutrient demands, any increase in their abundance is typically indicative of an increase in nutrient availability (Bogard *et al*., 2020).

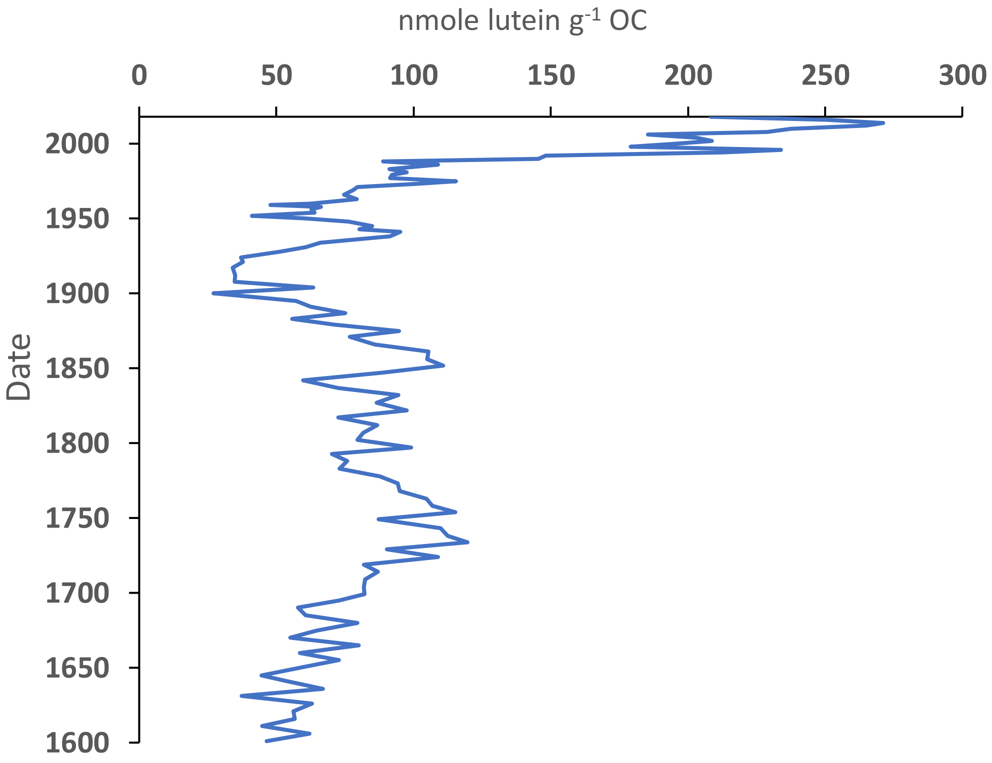

Fig. 5.25 Concentrations of lutein from Blea Tarn sediment core.

Declines in lutein concentrations during the second half of the 18th century to 94.4 nmole in 1832 indicate a slight reduction in chlorophyte biomass. This period of reduced lutein and chlorophyll-*b* concentrations occurs along with the period of reduced diatoms and likely indicates generally low productivity in the lake at the time. This period most likely reflects high catchment inputs and low water clarity at the time, that would have supressed algal productivity. After a period of increasing chlorophyte pigment concentrations during the 1840s there is a clear and consistent decline around the start of the 1850s to 27.1 nmole in 1900. Considering this was the period of intensification of the nearby mining activity, it may have negatively impacted chlorophytes. Chlorophyte pigments decline to relatively low concentrations during this period, with minimum values of both lutein and chlorophyll-*b* recorded during the second half of the 19th century. This highlights how mining activity has likely contributed to a restructuring of algal communities, with some taxa stimulated and others supressed.

It is also possible that the decline in chlorophytes is related to changes in catchment inputs. There is commonality between changes in lutein concentrations and lithogenic elements during this period (e.g. Mg, K). Both Mg and K peak during the 1850s and then follow a relatively rapid decline through to the start of the 20th century. This likely represents a decrease in catchment inputs, which could have resulted in a decline in nutrients delivered to the lake. Considering chlorophytes have particularly high nutrient demands any decline would likely restrict their growth. The decline may also be impacted by temperature, as this period was defined by particularly cold conditions at the end of the Little Ice Age. Chlorophytes are thought to be sensitive to climatic variations and they are often the predominant algal taxa during warm periods (Elmslie *et al*., 2020; Florian *et al*., 2015).

Chlorophyte biomass remains relatively low during the start of the 20th century which is a period when heavy metal concentrations continue to increase and catchment inputs continue to decline. There is a notable increase in lutein concentrations towards the end of the 1930s which peaks with 95.1 nmole in 1941. This occurs during the period of documented deforestation in the catchment. The period of increase is present across many algal groups and likely represents enhanced nutrient loading to the lake. Chlorophytes appear to have responded particularly strongly during the period of deforestation. While most other algal groups show increases, the increase in lutein is particularly high with concentrations increasing by 44% from 1934 and 1941. Picocyanobacteria increase by a comparable amount during this period (51%), while diatoms increase by 16%, cryptophytes by 18% and total algae by 18%. The strong response of chlorophytes could reflect their higher efficiency in nutrient uptake compared to other algae (e.g. diatoms) (Litchman *et al*., 2007) along with their more rapid reproduction, for example compared to heterocystous cyanobacteria (Finlay *et al*., 2010). While chlorophytes tend to have a greater affinity towards ammonium over nitrate, they can efficiently utilise a variety of N sources (Donald *et al*., 2011). Therefore, chlorophytes are typically fast growing under conditions of high nutrient loading (Fernandez and Galvan, 2007).

After the period of enhanced chlorophyte biomass, lutein and chlorophyll-*b* concentrations decline until around the 1970s. While there is an increase in lutein concentrations during the 1970s, this is relatively muted compared to the trends in chlorophyll-*a* with 208.7 nmole in 2004. However, the trend in chlorophyll-*b* is more consistent with the increases in other algal pigments at the time. Considering chlorophyll-*b* is produced almost exclusively by chlorophytes (Lami *et al*., 2000) along with the increases in chlorophyll-*a* since the 1970s it seems likely that chlorophytes have increased in biomass since the 1970s in line with the most other algal taxa.

There has likely also been some warming impact on chlorophytes in Blea Tarn, indicated by the significant relationship between annual temperatures and lutein concentrations. However, with temperature accounting for 28% of the variation in lutein concentrations it is not the dominant driver of change. High N deposition, and the aforementioned impacts elevated N transfer would have on the catchment, could have resulted in an enhanced nutrient supply to the lake. Preferential warming in shallow zones may benefit algae with higher thermal optima, such as chlorophytes (Raven and Geider, 1988; Trochine *et al*., 2011). Therefore, the increase in chlorophytes with the concurrent decline in diatoms may reflect an increase in habitat availability for chlorophytes and their superior competitiveness. For example, both cryptophytes and chlorophytes can replace non-motile diatoms during periods of thermal stratification due to their motility (Hickman, 1974; Reynolds, 2006). Therefore diatoms may be expected to decline under conditions of strengthened thermal stratification. Whilst the stratification regime of Blea Tarn is unknown (or whether it stratifies at all), it remains possible that enhanced stratification could be driving some of the trends in chlorophyte biomass.

There is some indication that the increase in chlorophyte biomass may have slowed down or even stabilised during the 21st century. This may reflect chlorophytes in the lake reaching some limiting factor, potentially nutrient availability or habitat availability for benthic chlorophytes. Sedimentary P concentrations have declined consistently since the 1950s and are probably still declining. It may be that P availability has started to restrict growth. While increased temperatures are likely to have stimulated chlorophyte growth, they would have further enhanced the already high nutrient demands of chlorophytes (Thrane *et al*., 2017). Therefore, P limitation may have started to restrict chlorophyte growth during the 21st century, indicated by a period of relatively little change in chlorophyte biomass compared to the 1970s – 1990s.

5.3.7 Cyanobacteria (echinenone, zeaxanthin, canthaxanthin)

Canthaxanthin concentrations fluctuate over time but largely stay within relatively well-defined boundaries of between 10 and 25 nmole (Fig. 5.28). Conversely, zeaxanthin concentrations follow similar trends to that of lutein (r^2=0.66, p<0.0001) over time (Fig. 5.27). The concurrent increase in zeaxanthin and lutein indicates that both chlorophytes and picocyanobacteria are likely responding to environmental changes in a similar way. However, as previously discussed (section 4.3.7)**,** there may be some zeaxanthin produced by chlorophyte taxa. Echinenone also follows similar trends to that of lutein, increasing in concentration during the 17th century to 9.0 nmole in 1768 (Fig. 5.26). Chlorophytes and non-heterocystous cyanobacteria can often respond strongly to increased nutrient availability due to their high efficiency in utilising N sources (Finlay *et al*., 2010; Herrero *et al*., 2004). The 17th and 18th centuries experienced a decline in diatom biomass which may suggest a competitive dynamic with cyanobacteria during this period. Cyanobacteria are known to respond quickly to environmental changes which can often lead them to outcompeting other algal taxa (Kosten *et al*., 2012).

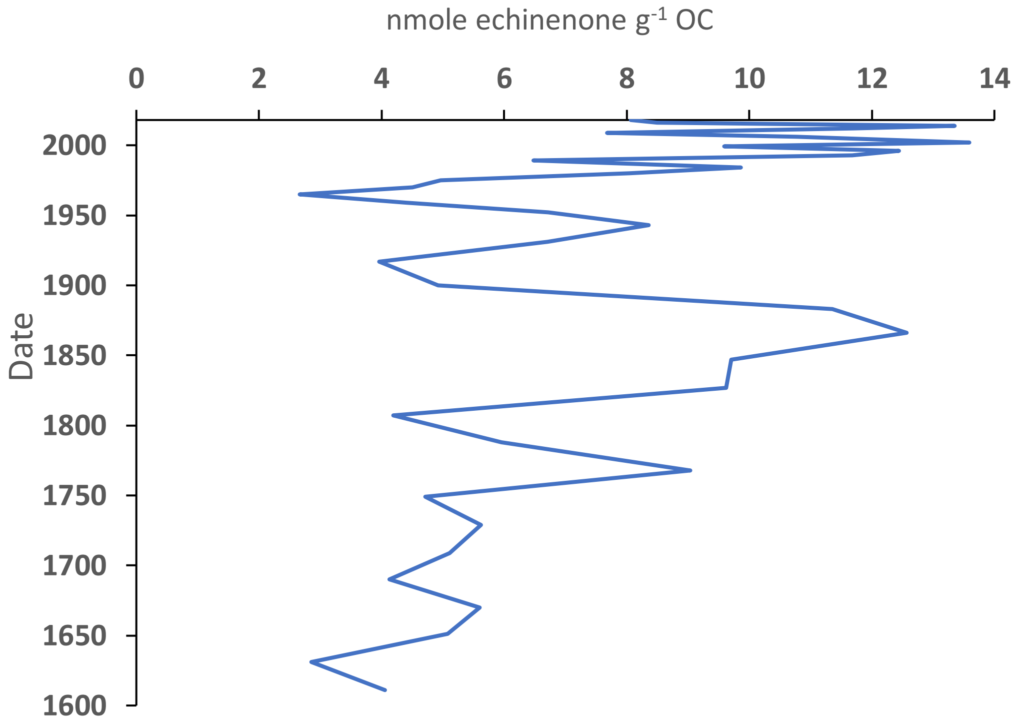

Fig. 5.26 Concentrations of echinenone from Blea Tarn sediment core.

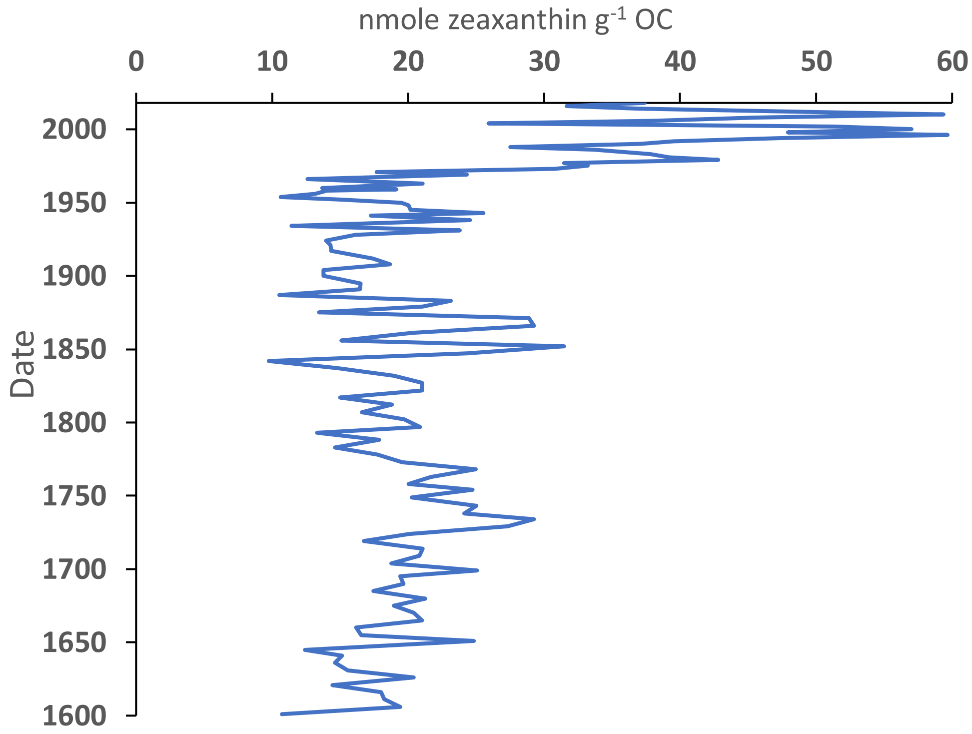

Fig. 5.27 Concentrations of zeaxanthin from Blea Tarn sediment core.

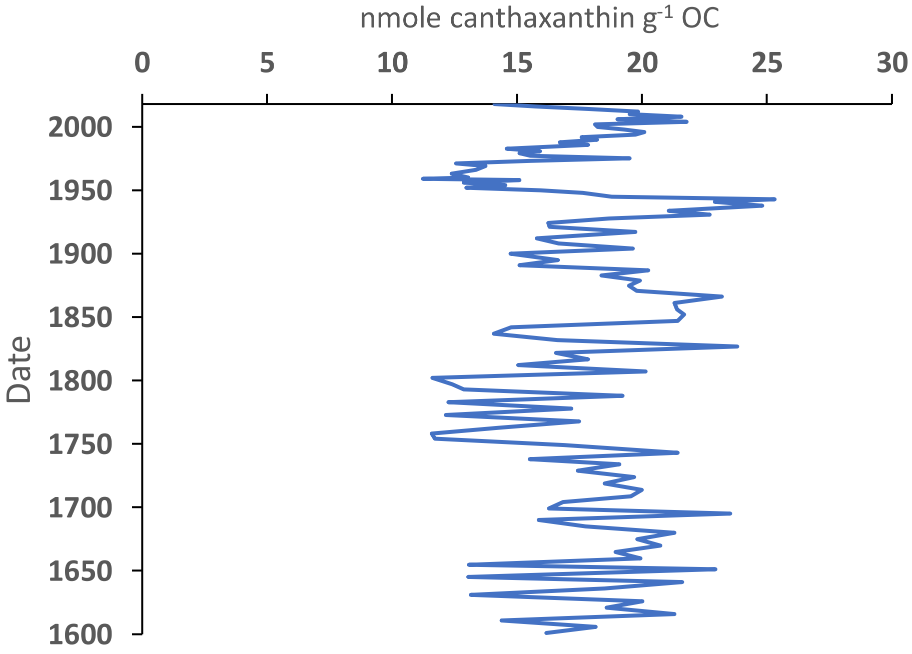

Fig. 5.28 Concentrations of canthaxanthin from Blea Tarn sediment core.

The general increase in cyanobacteria biomass occurs with increasing lithogenic elements. While cyanobacteria biomass may be controlled in part by diatom abundance, they are also likely to be regulated with nutrient loading from the catchment. The 17th and 18th centuries were also a period of declining water clarity, which cyanobacteria are known to be well adapted for as they can switch to utilising higher wavelengths of light that are associated with lower energy (Gisriel *et al.*, 2020). This allows cyanobacteria to photosynthesise even under conditions where visible light has been severely absorbed or scattered by high concentrations of UV absorbing compounds, such as DOC (Gan and Bryant, 2015). In lakes which experience a decline in water quality, cyanobacteria may dominate due to a competitive advantage in low light conditions. Therefore, catchment inputs may stimulate cyanobacteria in multiple ways, by supressing diatom growth through reduced water clarity whilst increasing nutrient supply. However, other taxa are also known to be well adapted to low light conditions (e.g. some species of chlorophytes) and as a result cyanobacteria may not dominate in all lakes with low water clarity (Huisman *et al.*, 1999). While cyanobacteria increase during this period of more favourable conditions, they do not appear to have become dominant. This is likely due to the species of chlorophytes present in the lake also responding positively to the changes in environmental conditions at the time.

While concentrations of echinenone broadly increase from the start of the 17th century to the middle of the 19th century, there is a period of decline during the second half of the 18th century to 4.2 nmole in 1807. Considering this was a period when chlorophytes and cryptophytes also declined and diatoms increased, this may suggest a competitive dynamic between these taxa. The increase in diatoms with a decline in cryptophytes may represent a greater increase in benthic production and a decrease in planktonic biomass. The decline in total cyanobacteria corresponds with a notable decline in sedimentary P concentrations during the second half of the 18th century, which may suggest a reduction in nutrient availability. In general, the trend in echinenone largely follows sedimentary P concentrations which may suggest a strong control of P on cyanobacteria biomass. There is no indication of a reduction in catchment inputs during this period that could result in a reduction in external P loading. On the contrary, this was a period of increasing lithogenic elements suggesting an increase in catchment derived inputs from the 1750s to the 1850s. The decline in P with increased lithogenic elements suggests that P supply may not be primarily driven by change in terrigenous inputs during this period, such as through catchment erosion. Therefore, the reduction in P may represent changes in catchment vegetation type or overall productivity. Considering the P supply to Blea Tarn is predominately SRP, changes in the quantities of P delivered from degraded catchment vegetation would have a large impact on overall P availability (Huser *et al.*, 2018). A reduction in P availability is also supported by the decline in canthaxanthin concentrations during the second half of the 18th century. In general, trends in canthaxanthin follow sedimentary P relatively well.

It is also possible that some of the trends in cyanobacteria during this period relate to the intensification of mining. The period of elevated cyanobacterial biomass ends before the start of the 20th century with echinenone concentrations more than halving from the 1880s to 4.9 nmole in 1900. This coincides with the cessation of mining activity and contrasts with some other algal taxa (e.g. chlorophytes) which decline at the start of the mining activity. Considering this was a period of minimum water clarity it is possible that cyanobacteria populations were expanding but chlorophyte productivity started to become limited by light availability. It is also notable how this was a period when cyanobacteria and diatom biomass concurrently increased. The parallel increase is absent from most of the time series which indicates that there was less competition for nutrients between these taxa. While this may indicate an increased nutrient supply it may also represent less competition in spring and summer months from other algal taxa which declined during this period. Therefore, the impact of mining activity may have resulted in the increase in cyanobacteria biomass but largely indirectly through supressing other taxa.

One of the more notable phases of higher canthaxanthin concentrations is from the 1930s increasing to 25.3 nmole in 1943, which likely represents the impact of deforestation. Whilst Blea Tarn has relatively little woodland cover, a deforestation event would be expected to increase cyanobacteria biomass through enhanced nutrient loading. Echinenone concentrations also increase in 1943 to 8.4 nmole, in line with many other pigments during this period. The increase is of a similar magnitude to that of chlorophytes, with concentrations more than doubling in under 20 years. During this period it is likely that there was an increase in nutrients that stimulated in-lake productivity in Blea Tarn uniformly across algal taxa.

Echinenone concentrations start to increase again from the 1970s to 12.4 in 1996 after which concentrations appear to have stabilised at concentrations similar to those experienced in the second half of the 19th century. The increase in echinenone and canthaxanthin is relatively muted compared to the increase in chlorophyll-*a*. Conversely the increase in zeaxanthin is more rapid than that of echinenone and canthaxanthin. Therefore, while total cyanobacteria have likely only experienced relatively moderate increases in biomass during the 20th century, there has also likely been a shift towards picocyanobacteria.

Whilst there is indication that P has been declining since the middle of the 20th century, at present Blea Tarn is still likely to have a relatively high P supply. A relatively high P supply is indicated by the high TP and SRP concentrations in the surface waters (Moorhouse, 2016). Considering the concurrent increase in non-heterocystous cyanobacteria and other planktonic taxa from the 1970s, the lake likely also has a sufficient supply of N that prevents N_2-fixing cyanobacteria from dominating. When there is high N availability non-heterocystous cyanobacteria and chlorophytes dominate over N_2-fixing cyanobacteria due to the lower energy efficiency of utilising atmospheric N_2 (Finlay *et al.*, 2010; Herrero *et al.*, 2004). Therefore, N_2 fixing cyanobacteria may be supressed by these faster growing taxa (Finlay *et al.*, 2010).

While the trends between zeaxanthin and lutein pigments are similar, zeaxanthin has a relatively greater increase in concentration during the 1970s to 42.8 nmole in 1979 (Fig. 5.27). The greater increase in zeaxanthin may indicate that picocyanobacteria during this period have become more dominant over chlorophytes, which have a more muted increase in comparison. Considering chlorophytes have relatively high nutrient demands, they require high and sustained inputs to compete with cyanobacteria (Bogard *et al.*, 2020). Therefore, the increase in picocyanobacteria during this period probably reflects a moderate increase in nutrient availability, with cyanobacteria having a competitive advantage over chlorophytes during the 1970s.

Zeaxanthin concentrations stop increasing from the end of the 1970s and decline slightly to 33.7 nmole in 1986. This decline is also present in alloxanthin concentrations indicating that the 1980s may have been a time when some phytoplankton biomass stopped increasing. The decline in these taxa could represent a period when nutrient availability in Blea Tarn declined. The middle of the 1980s were notably cool and dry at Newton Rigg, compared to the rest of the meteorological record. The third driest winter and third coolest summer on record occurred in 1985, with cool and dry conditions persisting until 1989. Cool and dry conditions would have reduced nutrient loading from the catchment, as vegetation productivity declined and nutrient leaching reduced. However, as discussed in section 5.3.3, the 1980s are also likely to represent a period of community shift towards greater planktonic production which may have been impacting pigment preservation. While it seems likely that algal biomass as a whole expanded during this period it also remains possible that meteorological conditions contributed to the decline in some particular taxa. Considering echinenone and canthaxanthin concentrations continued to increase from the 1970s to 1980s, it appears that picocyanobacteria may have been the primary cyanobacteria taxa impacted during this period.

From the end of the 1980s zeaxanthin concentrations increase again, more than doubling between 1988 and 1996 to 59.7 nmole. Given that there is a comparable increase in chlorophytes during this same time period, this would suggest that nutrient loading to Blea Tarn had progressed, enabling chlorophytes to compete with cyanobacteria. While zeaxanthin concentrations remained high during the 1990s, they decline again at the start of the 21st century to 49.2 nmole in 2012, a trend recorded in the other pigments (e.g. lutein, chlorophyll-*a*). As in the 1980s, the decline in zeaxanthin is of greater magnitude that the other pigments. This may indicate a competitive relationship between the algal taxa in Blea Tarn, with periods of less favourable conditions resulting in picocyanobacteria being outcompeted by chlorophytes. While cyanobacteria have been shown to outcompete chlorophytes in lower trophic states, when nutrient availability is sufficient chlorophytes can outcompete cyanobacteria (Bogard et al., 2020).

Regression analysis presented in section 5.2.6 indicates that filamentous cyanobacteria biomass has been stimulated by increases in temperature since the 1960s. However temperature only accounts for 15% of the variation in canthaxanthin, indicating there to be more dominant drivers of change. Canthaxanthin concentrations in the 21st century are comparable to the higher levels recorded in all previous decades and exceeded by those in the 1930s and 1940s. The relatively muted increase during the second half of the 20th century supports the interpretation that temperature is not the dominant driver of change in filamentous cyanobacteria abundance in Blea Tarn. Additionally, temperature had little stimulatory impact on picocyanobacteria, likely indicating the predominance of nutrient supply on the growth of these taxa. As Blea Tarn is currently classed as an oligotrophic lake, variations in nutrient concentrations are likely to be the predominant driver of algal change over temperature (Rigosi *et al.*, 2014). However, higher temperatures will increase nutrient supply and availability, enhancing degradation rates in the catchment and internal P loading in the lake (Jeppesen *et al.*, 2005; Liu *et al.*, 2018). Therefore temperature may represent an indirect driver of cyanobacteria biomass change. As noted in section 5.3.3, the impact of elevated nutrients and temperature would likely have a stimulatory impact on the lake catchment vegetation. Elevated catchment productivity, along with increased mineralisation rates, would have provided the lake with enhanced N supply, stimulating growth. The response of the catchment vegetation to changes in N deposition and temperature are likely to be relatively slow (Liao *et al.*, 2020). Therefore, for a lake in which the algae are highly controlled by catchment vegetation, the impact of temperature will likely be offset from the trends in meteorological conditions. Changes to the hydrological cycle can further enhance cyanobacterial growth as more enhanced precipitation will increase nutrient loading from the catchment.

Whilst there was no detectable relationship with precipitation, compared to the Newton Rigg meteorological record, it is possible that precipitation is still having some impact. As Newton Rigg is outside of the Lake District, it is possible that the particular hydrological conditions of the Windermere catchment are not well represented by the Newton Rigg dataset. Despite no longer term records, metrological data for the nearby village of Ambleside showed that average winter rainfall increased from 5.7 mm day^{-1} between 1940 and 1970 to 7.1 mm day^{-1} between 1970 and 2000 (George *et al*., 2007). This change represents an increase in precipitation of 24.6%, compared to the regional increase for the north-west of England of 7.5% over the same time period, recorded from the England and Wales precipitation index (Wigley *et al*., 1984). Therefore the full impact of precipitation change may be different or largely obscured.

Hydrological flushing is typically one of the dominant controls of cyanobacteria populations in lakes (Davis *et al*., 2003). In years when there is high hydrological flushing, colonies can be broken up which limits bloom development (Mur *et al*., 1999). Given the exposed nature of Blea Tarn, in an upland catchment predominantly of grasslands, it would be expected that the lake will also experience an impact from winds and storm events. Such conditions can result in intense water turbulence, which cyanobacterial bloom development can be particularly sensitive to (Mur *et al*., 1999). Therefore, while there is some indication that the WRT at Blea Tarn may be relatively high, the highly exposed environment of the lake may limit cyanobacteria blooms development and prevent them from dominating.

5.4 Discussion

5.4.1 Zone 1 (1600 - 1799)

The broad ecological stability of the tarn during this period conforms with the findings of Haworth (1969). The study found that the post glacial history of Blea Tarn's diatom community was devoid of any major changes over time. There was a general trend towards more acid preferring species, driven by the natural acidification of the tarn from the inwash of catchment material over thousands of years. However this trend was gradual indicating a lake largely resilient to change.

While overall algal abundance remained largely stable there is indication of community level shifts in algal taxa. A decline in diatom biomass at the start of the 17th century is likely to be related to the declining water clarity at the time. Light availability can have a large control on diatom growth, showing a stimulatory effect on diatoms (and cryptophytes) but no effect on filamentous cyanobacteria and picocyanobacteria (Vinebrooke and Leavitt, 1999). This is likely reflected by the trends in relative abundances of these taxa between the start of the 17th and middle of the 18th century. The concurrent declines in diatoms and cryptophytes, while chlorophytes and cyanobacteria increase likely indicates a shift to greater proportions of summer blooming taxa.

Under conditions where nutrient supply is limited, diatoms can often decline. Barker *et al*. (2005) found a decline in diatom abundance between 1945 – 1965 in Grasmere, with a shift towards less *Asterionella formosa* and more *Cyclotella comensis*. A rise in the oligotrophic *Cyclotella* taxa indicated a reduction in nutrient availability which was attributed to exceptionally wet and cold conditions, with periods of extended ice cover (Barker *et al*., 2004; George *et al*., 2004). However, chlorophytes are typically associated with higher nutrient waters and in such conditions will outcompete diatoms due to their superior growth rates, nutrient uptake kinetics and growth rates (Bogard *et al*., 2020; Donald *et al*., 2011).

In addition, heterocystous cyanobacteria (canthaxanthin) remain relatively stable through the 17th and 18th centuries. As many of these taxa can create their own N-based compounds they typically have a competitive advantage when N is limited (Mur *et al*., 1999). Under such conditions, this often results in greater proportions of N fixing cyanobacteria which can lead to them dominating the lake algal community (Hayes *et al*., 2015). Therefore, it is likely that there has been a consistent N availability in Blea Tarn during this period maintaining broadly stable heterocystous cyanobacteria abundances while sustaining chlorophyte growth.

Overall there appears to be an inverse relationship between the relative abundance of chlorophytes and diatoms, with diatoms declining as chlorophytes increase. This inverse relationship indicates competition between these taxa for resources, with variations depending on the environmental conditions at the time. A competitive dynamic between cyanobacteria and diatoms has been experienced in Lake Windermere, with larger spring diatoms blooms corresponding to lower abundances of cyanobacteria (McGowan *et al*., 2012). This would have resulted in diatoms exploiting lake water nutrients to a greater extent, which would then have reduced lake water nutrient concentrations for summer phytoplankton. Therefore, chlorophyte populations may be partly controlled by diatom abundances in conditions where nutrients are limited. In Blea Tarn, a suppression of diatom growth due to the reduction in water clarity would result in relatively more nutrients available for summer blooming taxa, including chlorophytes.

5.4.2 Zone 2 (1800 - 1899)

In Blea Tarn, the increase in sedimentary $\delta^{15}N$ towards the end of the 19th century likely represents enhanced agricultural nutrient inputs. An increase in nutrient supply to Blelham Tarn during the 19th and 20th centuries also resulted in an increase in sedimentary $\delta^{15}N$ (Moorhouse *et al*., 2014). The $\delta^{15}N$ of sediments increased steadily over time from ~3.4‰ in ~1850 to 4.7‰ in the 1970s after which values stabilise. These trends are likely driven by an increase in livestock density in the catchment since 1866, which increased animal excrement being washed into the lake. The increased $\delta^{15}N$ corresponded with declines in C/N values and increases in %C and sedimentary algal pigments, indicating that nutrient loading enhanced algal biomass. A similar impact of eutrophication was observed in Lough Neagh, Northern Ireland. Bunting *et al*. (2007) found that the $\delta^{15}N$ of sediments increased ~2‰ from 1964 to the mid-1970s and $\delta^{13}C_{org}$ declined nearly 1‰ after 1980. The increase in $\delta^{15}N$ also occurred with an increase in cyanobacteria (canthaxanthin) and cryptophyte (alloxanthin) pigments. The increase in pigment concentrations and lower $\delta^{13}C_{org}$ indicates increasing algal biomass in response to nutrient loading. Algal biomass was found to be strongly correlated to agricultural inputs of N to farms within the catchment, but weakly correlated to P inputs. This highlights how diffuse inputs of N based fertilisers can impact lake $\delta^{15}N$. For Blea Tarn, the increase in $\delta^{15}N$ at the end of the 19th century did not occur with any detectable increase in algal biomass. Therefore, any change in nutrient source had minimal impact on algal biomass at the time.

The second half of the 19th century is dominated by the impacts of the intensification of nearby mining activities. The Cu concentrations in Blea Tarn are currently comparable to those in Lake Windermere, which is downstream of the Greenburn Copper Mine (Miller *et al*., 2014). However, the increase in sedimentary Cu concentrations during the second half of the 19th century is not recorded in Lake Windermere. Miller *et al*. (2014) reported that for Lake Windermere, sedimentary Cu concentrations started to increase from around the 1960s to ~70 $\mu g\ g^{-1}$ sediment by the start of the 1980s. This was replicated in the Pb and Zn profiles which for Blea Tarn peak in 1921 and 1954, respectively, while for Lake Windermere, concentrations were still increasing during the 1980s. The differences between the impact of mining activity on these lakes reflect that Blea Tarn has been more impacted than a lake which directly received water from mining activity. For Lake Windermere, the lack of increase in sedimentary Cu during the time of highest metal outputs was attributed to upstream lakes acting as efficient sediment traps (Miller *et al*., 2014). Upstream lakes would have limited the amount of heavy metals being transported downstream. As a result, the sediments of upstream lakes such as Elterwater show a distinct period of Cu contamination from the time of the mining activities (Pickering, 2001).

The stream waters immediately downstream of Greenburn Copper Mine have elevated levels of copper, lead and zinc, exceeding 100, 200 and 500ppm, respectively (Miller *et al*., 2014). Blea Tarn is upstream of this mining activity, with many of these elements at comparable concentrations. This indicates that Blea Tarn has likely been impacted by atmospheric pollution from mining and other industrial activities at the time of operation. The continued elevated Cu concentrations may represent a high store of metals in the catchment from atmospheric deposition that is transported to the lake when catchment erosion is high (Yang, 2010). It is notable that the secondary peak in Cu at the start of the 20th century coincides with a spike in K concentrations, typically a signal of catchment erosion. For Lake Windermere, the increases in Cu from the 1960s covaried with Pb and Zn which suggested flood induced metal inwash or the weathering of catchment material (Miller *et al*., 2014).

Diatoms have been shown to be responsive to pollution derived from the Greenburn Copper Mine. During the 20th century there was a corresponding peak in sedimentary Cu concentrations with the copper resistant diatom taxa *Brachysira vitrea* (Grunow) present in Little Langdale Tarn (Oswald *et al*., 2001). In addition, in Lake Windermere, the nearby quarrying for slate increased loads of fine rockflour entering the lake (Pickering, 2001). The increase in rockflour to the lake would be expected to decrease water transparency, which along with other particulate matter associated with the industrial activity at the time, reduced water clarity. The sudden decline in diatoxanthin concentrations following the end of nearby mining activity was also likely recorded by Moorhouse (2016) who found a clear decline in diatoxanthin. However, the timing of this decline is uncertain due to the lack of radiometric dating.

Heavy metal pollution is a potential cause for the decrease in chlorophyte biomass during the second half of the 19th century, as this was a period of increasing sedimentary heavy metal concentrations (e.g. Cd, Cu, Pb) reflected by the increasing PCA axis 1 scores for the trace element data (Fig. 5.10). Increased concentrations of these elements have been shown to have a toxic effect on chlorophytes. Visviki and Rachlin (1994) found that two species of chlorophytes (*Dunaliella salina* and *Chlamydomonas bullosa*) were both sensitive to elevated Cu and Cd concentrations, which reduced growth rates. Sedimentary concentrations of Cd during the second half of the 19th century (6.6 $\mu g\ g^{-1}$ sediment), Zn (556.6 $\mu g\ g^{-1}$), Pb (476.4 $\mu g\ g^{-1}$) all far exceed the Probable Effect Level (PEL) while Cu (47.8 $\mu g\ g^{-1}$) exceeds the threshold effect level (TEL) (Table 5.4). The PEL and TEL represent sedimentary concentration limits at which adverse effects frequently occur (PEL) or which adverse effects occasionally occur (TEL) to aquatic organisms (MacDonald *et al*., 2000). Therefore, the high concentrations of heavy metals in Blea Tarn during the second half of the 19th century could have been impacting algal growth, although for some of these elements they have exceeded the PEL from the start of the 17th (Pb) and 18th century (Zn, Cd). These boundaries are generalisations and the concentrations at which they start to have notable impacts on algal growth are likely to vary considerably between species and lakes. However, the exceedance of PEL for many heavy metals highlights how concentrations in Blea Tarn were likely high enough to have an impact on algal growth, with that likelihood increasing during the 19th century.

Table 5.4 Threshold Effect Level (TEL) and Probable Effect Level (PEL) of trace metals for freshwater sediments. Units are µg g^{-1} sediment (MacDonald *et al*., 2000).

	Ni	Cu	Zn	Cd	Pb
TEL	18	35	123	0.60	35
PEL	36	197	315	3.54	91.3

5.4.3 Zone 3 (1900 - 1969)

There are detectable impacts of catchment deforestation on algal biomass between the 1930s and 1940s**.** These changes are more prominently shown by the increases in lutein and canthaxanthin concentrations, which may indicate that some faster growing taxa were benefited to a greater extent. Cyanobacteria often respond strongly to nutrient loading and as such are often used as indicators of water quality degradation. This has been demonstrated in Lough Neagh, Northern Ireland, where a peak of canthaxanthin concentrations during the 1990s represented a period of maximum nutrient inputs (Bunting *et al*., 2007). Deforestation can result in increased nitrification which then can be leached more efficiently to receiving waters, although these impacts can often be short lived (e.g. <10 years) (Feller, 2009). Given that the period of enhanced chlorophyte biomass appears to last less than a decade, this would be consistent with a deforestation derived increase in nutrient loading. A broad increase in nutrients (N and N + P) has been shown to stimulate cyanobacteria, in addition to chlorophytes, cryptophytes and planktonic diatoms (Donald *et al*., 2011; Nydick *et al*., 2004).

The deforestation event is likely to have resulted in a broad increase in all lake algal groups, although the overall change is relatively minor. Enhanced algal production after land disturbance was also detected in the sediments of Lake Windermere by McGowan *et al*. (2012). This was attributed to enhanced terrestrial organic matter being delivered to the lake which would have increased nutrient supply. Stevenson *et al*. (2016) found that for lakes with relatively low forest cover in the catchment (<20%), the impact of forestry activity was relatively muted compared to lakes with higher woodland cover. There were largely inconsistent trends in C/N values following tree planting, with minor increases in $\delta^{13}C_{org}$ values for all lakes. Therefore, for lake catchments with relatively little forest cover, the impact of forestry activity may be minor or even undetectable. Considering the catchment of Blea Tarn currently is <10% woodland the relatively muted impact of deforestation is not surprising, especially considering the relatively large size of the catchment. The catchment likely mitigates for such activities, resulting in their impacts being relatively minor and short lived.

Therefore, the ecological stability of the lake over extended periods of time may be largely a result of catchment characteristics.

Increased algal productivity has been experienced in most lakes within the Windermere catchment during the 20th century (Moorhouse *et al*., 2018; McGowan *et al*., 2012) and other lakes in England (e.g. Lacey *et al*., 2018). Within the Windermere catchment, Moorhouse (2016) found that $\delta^{13}C_{org}$ of the upland tarns (>100 m.a.s.l.), were significantly higher (−27 to −29‰), than the lowlands lakes (−26 to −32‰). Blea Tarn has a mean $\delta^{13}C_{org}$ of −28.3‰, which places it in the overlap between the upland and lowland lakes in the catchment, reflecting its moderate altitude. The difference between the upland and lowland lakes likely represents their land use history, with anthropogenic activities being a dominant driver of change in lowland lakes (Moorhouse *et al*., 2018). In Lake Windermere, algal biomass started to increase in 1890 and accelerated after 1920, probably as a result of P enrichment (McGowan *et al*., 2012). The smaller Windermere South Basin was shown to the have a greater increase in algal biomass than the North Basin, probably because the smaller lake volume made it more susceptible to nutrient enrichment (McGowan *et al*., 2012; Pickering, 2001).

Diatoms have increased across the lowland lakes of the Windermere catchment during the 20th century (Moorhouse, 2016). This increase was attributed to high nutrient loading from sewage and agricultural activity. For the upland lakes, diatom biomass has declined over the same time period (Moorhouse, 2016). The decline in diatoms at these sites may reflect their naturally low major ion content in the waters due to the Borrowdale Volcanic Group bedrock (Moorhouse, 2016). Additionally, these sites have minimal anthropogenic land use and so Si delivery from the catchments will be low (Officer and Ryther, 1980). Therefore, relatively low anthropogenic activity in the catchment following the period of deforestation in the early 20th century may have maintained low Si delivery to Blea Tarn. The maintenance of relatively low Mg (and to some extent K and Li) concentrations during the 20th century would support this as a period of relatively lower catchment inputs. Therefore the relatively low diatom biomass during the 20th century may reflect low anthropogenic land use.

Whilst the $\delta^{13}C_{org}$ values in Blea Tarn during the 20th century are reflective of the tarn's mid altitude, mean $\delta^{15}N$ values (2.4‰) are typical of upland tarns in the Windermere catchment which have $\delta^{15}N$=<3‰ (Moorhouse, 2016). The low $\delta^{15}N$ values for Blea Tarn likely reflect a lower productive catchment compared to more lowland sites. Upland tarns typically have moorland catchments with minimal agricultural use and as a result are less productive (Moorhouse, 2016). Catchment productivity is largely controlled by climate, with Bunting *et al*. (2010) finding it to be the main variable affecting sedimentary $\delta^{15}N$ in sub alpine lakes. The $\delta^{15}N$ values in the most recent sediments is consistent with those recorded in Blea Tarn by Jones *et al*. (2004), with a $\delta^{15}N$ of 1.0‰ recorded in 2000. The values for lake macrophytes and benthic algae were 1.4‰ and 0.54‰ respectively.

Conversely, C/N values in Blea Tarn are within the range more typically associated with lowland productive lakes, than the upland tarns in the catchment. Blea Tarn sediments have a mean C/N of ~13.3 whereas the average for other upland tarns analysed in this catchment (e.g. Stickle Tarn, Easedale Tarn) have C/N = >15 (Moorhouse, 2016). The high C/N ratios of the upland tarns were attributed to the lower algal production compared to the lowland lakes. This indicates how Blea Tarn appears to have experienced relatively high autochthonous production, even during the first half of the 20th century. The C/N values decreased to a greater extent in upland tarns compared to lowland lakes with Stickle Tarn and Easedale Tarn declining by 7 and 4 units respectively from 1900 (Moorhouse, 2016). During the 20th century C/N values in Blea Tarn decreased by ~2 units, more similar to changes experienced in the larger, lowland lakes subject to eutrophication. The changes in C/N for the oligotrophic Stickle Tarn and Easedale Tarn are greater, but they are still likely to represent sites of lower algal productivity (Gorham *et al*., 1974).

In Blea Tarn, Moorhouse (2016) recorded sedimentary OM content of between 30 and 40% which was the second highest in the Windermere catchment. While the high OM and low C/N of the Blea Tarn sediments may be controlled by allochthonous inputs it may also reflect relatively high productivity in the lake. Considering its large catchment size, relatively small lake area and moderate altitude there is likely to be a large allochthonous supply from a more productive catchment than the lakes of higher altitude. The theory that Blea Tarn is naturally more productive than other upland tarns is supported by the contemporary water analysis undertaken by Moorhouse (2016). During 2012 and 2013, Blea Tarn was found to have the highest algal production (inferred by chlorophyll-*a* concentrations in the water) of the upland lakes with the highest winter SRP concentrations (7.5 $\mu g\ l^{-1}$) and third highest total P (TP) concentrations. SRP concentrations are particularly high in Blea Tarn, constituting >55% of the TP with Loughrigg Tarn, Stickle Tarn and Little Langdale Tarn recording 29%, 23% and 26% respectively. The only other upland tarn with notably high SRP to TP ratios was Easedale Tarn (43%) which was also the tarn with the second highest measured productivity. This may indicate that the productivity of these tarns is largely controlled by the proportion of delivered SRP, which are forms of P bioavailable to algae (Reynolds, 2006). The elevated SRP in these lakes likely reflects the delivery of diffuse P not found in the other upland lakes (Moorhouse, 2016).

The peak in sedimentary P may relate to the period of deforestation in the catchment during the first half of the 20th century. Shatwell and Köhler (2019) found that following a reduction in nutrient loading, the decline in sedimentary TP concentrations was delayed by around 20 years. This delay was due to the remobilisation of P from the sediments which can maintain high lake water P concentrations. High internal P loading can lead to the stimulation of lake algae for many years after external nutrient loading declines (Lacey *et al*., 2018). Considering elevated algal biomass declined before the peak in sedimentary P, it seems likely that P would not have been the limiting factor during this period, potentially indicating N limitation.

The consistent decline in sedimentary P from the 1950s would suggest that P loading has declined over time, potentially continuing to the present. While there is an increase in sedimentary P in the surface sediment, this likely reflects the naturally enhanced P pool which gets re-released to the water column. Typically, P concentrations in deeper sediments constitute around 30-40% of that in the surface sediments (Søndergaard, 2007). In comparison, the lowest P concentrations recorded in the Blea Tarn sediment core were ~80% of what occurs in the surface sediments. SRP concentrations go from the highest of those analysed in the catchment by Moorhouse (2016) in winter months to one of the lowest by the winter (<1 µg L^{-1}), indicating high utilisation. Therefore it is possible that greater algal utilisation is driving some of the declining trends in sedimentary P. However considering P concentrations declined from the 1950s, around 20 years before algal biomass started to increase, it is unlikely to be the dominant driver.

The decline in P from the 1950s occurs with a decline in $\delta^{13}C_{org}$ and $\delta^{15}N$. Maberly *et al*. (2013) showed that across 20 lakes in the English Lake District, lake water $\delta^{13}C$ was inversely proportional to catchment productivity. The more productive catchments deliver greater loads of allochthonous material, which can stimulate algal growth. In addition, they deliver DIC with lower $\delta^{13}C$ to lakes which can be assimilated by algae. Considering the concurrent decline in $\delta^{13}C_{org}$ at least two decades before the increase in algal pigments, the declines in sedimentary $\delta^{13}C_{org}$ (and $\delta^{15}N$) may be related to an increase in catchment productivity, potentially enhanced by N deposition in the catchment. However, shifts to lower $\delta^{13}C_{org}$ and $\delta^{15}N$ with increasing catchment productivity may not happen in all lakes, with $\delta^{13}C_{org}$ in Esthwaite Water remaining relatively stable while catchment land use for rough grazing increased from ~5% to 50% during the early 20th century (Moorhouse *et al*., 2016). Therefore, catchment productivity may only have a negligible impact on $\delta^{13}C_{org}$ for some lakes.

An increase in catchment productivity would also explain the concurrent declines in sedimentary P from the 1950s. Across 81 boreal lakes in Sweden, Huser *et al*. (2018) found that over 50% experienced a significant decline in lake water TP from 1988 – 2013. The decline in TP was attributed to warmer conditions resulting in greater P uptake by terrestrial vegetation. Deforestation can also lead to declines in P loading to lakes, through the loss of organic matter and uptake by catchment vegetation. Akselsson *et al*. (2008) found that tree harvesting resulted in the net losses of P in large parts of Sweden while Crossman *et al*. (2016) found that recovery from deforestation resulted in reduced P export to lakes, as the establishment of new vegetation increases P uptake. While Blea Tarn was subject to some deforestation during the 20th century it was a relatively small area of the catchment. However, a catchment wide increase in terrestrial productivity from the 1950s would likely have had a more profound impacts and may have contributed towards the initial decline in $\delta^{13}C_{org}$ and P.

An increase in catchment productivity from the 1950s may be partially explained by atmospheric N deposition. Atmospheric N deposition has been high in the northwest of England, especially since the 1950s from increases in synthetic fertiliser application (Jones *et al*., 2004; Pitcairn and Fowler, 1995). For the Windermere catchment, the concentration of wet deposition of NO_3 was one of the highest in the UK in 2008 (>5.7 kg N ha^{-1} yr^{-1}), along with total N deposition of >21 kg N ha^{-1} yr^{-1} (RoTAP, 2012). However there are no clear impacts on algal biomass from atmospheric N deposition, with a large proportion of the decline in $\delta^{15}N$ occurring prior to the increases in algal biomass. These trends differ from what was experienced in Sky Pond, USA, where a decline in $\delta^{15}N$ occurred concurrently with a decrease in C/N, increases in algal pigments and the documented increase in atmospheric N deposition (Oleksy *et al*., 2020).

Moorhouse (2016) found that the upland tarns in the Windermere catchment (Stickle Tarn and Easedale Tarn) shared near identical trends, with $\delta^{15}N$ values significantly declining after 1950 to values not previously recorded at these sites. A reduction in $\delta^{15}N$ was also experienced in many of the lowland lakes from ~1950 (e.g. Esthwaite Water, Blelham Tarn). The decline was less than the upland tarns and was preceded by a gradual increase in $\delta^{15}N$, which has also been experienced in Blea Tarn. However the impact on algal biomass has been largely variable. For Stickle Tarn, chlorophyll-*a* concentrations closely followed the trends in $\delta^{15}N$, with marked increases after 1950. In comparison, Easedale did not replicate the post 1950 increase in chlorophyll-*a*. In general, there has been consistent declines in sedimentary $\delta^{15}N$ values across the Windermere catchment, likely reflecting a regional increase in low $\delta^{15}N$ sources most likely associated with agricultural fertilisers (McGowan *et al*., 2012). Similarly in Ireland, $\delta^{15}N$ declined in five of the six lakes analysed by Stevenson *et al*. (2016) during the 20th century, with the decline in $\delta^{15}N$ attributed to atmospheric N deposition and/or precipitation driven changes in DOM influx.

While the trend in declining $\delta^{15}N$ values during the 20th century has been recorded across Europe, North America (Holtgrieve *et al*., 2011) and locally across the Windermere catchment (Moorhouse *et al*., 2018), these trends are not always uniform and can vary both between and within regions. Hu *et al*. (2014) showed that two alpine lakes in SE Tibet responded differently to similar atmospheric N deposition rates. Shade Co lake showed stable $\delta^{15}N$ during the 20th century while Moon Lake experienced a steady decline in $\delta^{15}N$. The lack of response in Shade Co lake likely reflects differences in catchment characteristics with a relatively larger catchment and more abundant vegetation cover. The $\delta^{15}N$ signal at Shade Co lake is therefore likely to be highly controlled by the surrounding catchment with greater potential for N storage and transformation in soils and vegetation. As a result, while lake catchments may be equally impacted by atmospheric N deposition the effect this has on $\delta^{15}N$ can vary depending on lake and catchment characteristics. Therefore, the relatively large catchment of Blea Tarn and its moderate altitude may allow for greater proportions of deposited N to be taken up by catchment vegetation, limiting the impact on the lake itself.

Considering the timing and magnitude of change in Blea Tarn, coupled with the coherence across the Windermere catchment, it could be determined that the $\delta^{15}N$ of Blea Tarn sediments is also affected by atmospheric N deposition. However, Jones *et al*. (2004) estimated that for the three Cumbrian lakes they sampled (which included Blea Tarn) atmospheric N deposition accounted for 11-55% of the total N loads, not enough to control $\delta^{15}N$ values in these lakes. This was supported by the considerable variability in sedimentary $\delta^{15}N$ between the 30 small upland lakes they sampled in Cumbria, Wales, Scotland and Northern Ireland ($\delta^{15}N$ range −3.06 to 7.31). Sedimentary $\delta^{15}N$ values showed a strong negative dependence on the availability of DIN, indicating reduced discrimination against the utilisation of ^{15}N when N availability is low (Jones *et al*., 2004). They concluded that sedimentary $\delta^{15}N$ is likely to be more reflective of the degree of N limitation in lakes where there is not a dominant source with a characteristic $\delta^{15}N$ signature. Therefore, whilst it is possible that $\delta^{15}N$ has been impacted by atmospheric N deposition from the 1950s, it may more accurately reflect greater N availability and utilisation by catchment vegetation.

5.4.4 Zone 4 (1970 - 2018)

Algal biomass increases for most pigments from the 1970s which is reflected by the increase in PCA axis 1 scores for the pigment data (Fig. 5.12). Increasing algal abundances in the most recent sediments of Blea Tarn was also found by Moorhouse (2016). However, the increase only occurs in the top 3cm of their sediment core compared to the ~13cm depth presented in this thesis, that is dated to the mid-1970s. As the core presented in Moorhouse (2016) was not dated it makes it difficult to ascertain the exact reason for this discrepancy, but it remains possible that the core collected by Moorhouse (2016) did not retain the upper most sediments. In general, the findings presented in this thesis support those by Moorhouse (2016) whilst providing key timings and additional geochemical data to support the interpretation of the potential drivers of change.

Whilst Blea Tarn in the past has $\delta^{13}C_{org}$ values in between those of lowland and upland lakes in the catchment, by the 21st century it has developed into a lake more similar to the eutrophic lowlands with a mean $\delta^{13}C_{org}$ of −29.6‰. A relatively small reduction in $\delta^{13}C_{org}$ was experienced in all lakes analysed by Moorhouse (2016) within the Windermere catchment. Almost all lakes declined in $\delta^{13}C_{org}$ by <2‰ from 1800 to the present although these changes occurred at different points in time between the lakes. In the lowland Blelham Tarn, $\delta^{13}C_{org}$ decreased by ~2‰ from 1990 to 2011 with Esthwaite Water decreased by ~1‰ from the late 1970s. These lakes represent the most productive and eutrophic sites in the catchment. For the upland tarns, such as Easedale Tarn, $\delta^{13}C_{org}$ decreasing by ~1.2‰ from ~1940 to 2006 with the most upland tarns (Stickle Tarn, Codale Tarn) showing more gradual and long-term declines in $\delta^{13}C_{org}$. For Blea Tarn, the decline in $\delta^{13}C_{org}$ has been ~1.5‰ since the 1980s, which highlights how $\delta^{13}C_{org}$ in Blea Tarn may be more similar to the productive lowland lakes in the catchment.

Whilst the changes in Blea Tarn may appear to suggest anthropogenic eutrophication as the driver of this change, these values are remarkably similar to those recorded in the mid-Holocene. Grosvenor *et al*. (2017) recorded $\delta^{13}C_{org}$ values of bulk organics in Blea Tarn sediments ranging from −28.8 to −29.7‰ between 5,810 and 6,232 BP. Therefore algal productivity in Blea Tarn during the 21st century, inferred from $\delta^{13}C_{org}$ values, may be comparable to that experienced long before modern human expansion. Grosvenor *et al*. (2017) also found that $\delta^{13}C_{org}$ values were not below −30.1‰ for the entire 1,500 year time series. Considering the rate of decline in $\delta^{13}C_{org}$ may have started to reduce in the 21st century, this may indicate that Blea Tarn is reaching a natural limit of $\delta^{13}C_{org}$ change from increased algal production. The consistent and relatively stable $\delta^{13}C_{org}$ values may also reflect the assessment made by Haworth (1969), that the tarn has been relatively ecologically stable up to the mid-20th century.

The main driving force behind increasing algal biomass in the lowland lakes analysed by Moorhouse (2016) was found to be overwhelmingly due to anthropogenic nutrient inputs, such as from agriculture and wastewater effluent. These sources of nutrients will stimulate algal production and result in lower C/N ratios, as was the case in Lake Windermere (McGowan *et al*., 2012). However, there are no known sources of direct anthropogenic pollution to Blea Tarn, and due to its altitude it is upstream of settlements and most agricultural activities. The percentage of land used for rough grazing in the Blea Tarn catchment has increased since the 1980s. However, it remains at a similar level to the rest of the 20th century with most of the grazing occurring downstream towards Little Langdale Tarn (Hayworth, 1969; Moorhouse 2016). As discussed in section 5.4.3, Little Langdale Tarn does not share similarly high SRP concentrations as Blea Tarn and has lower productivity. Therefore, the higher SRP concentrations in Blea Tarn are unlikely to be related to increased livestock grazing.

This may be driven by differences in catchment characteristics, such as vegetation or morphology, as these features have been shown to control nutrient availability (Maberly *et al*., 2003).

In the Windermere catchment, algal biomass increased in the latter part of the 20th century for both lowland and uplands lakes suggesting a regional scale driver (Moorhouse, 2016). For the upper most tarns, it was suggested that climate change and atmospheric N deposition has synergistically promoted phytoplankton growth. During the latter half of the 20th century temperature was found to be the main variable for increased primary production at these sites. The central England temperature index explained 20-30% of the algal biomass in the latter part of the 20th century for Stickle, Codale and Easedale tarns (Moorhouse *et al*., 2018). In comparison, for the lowland sites in the Windermere catchment wastewater treatment was found to be the most dominant driver of algal growth. However, even for some of the most polluted sites the impact of climate was still detectable. Annual air temperature variations accounted for 5.6% of the variability in algal biomass at Blelham Tarn (Moorhouse, 2016). For Blea Tarn, annual air temperatures explained ~15% of the variation in total algal biomass. However, it is possible that the full impact may be partially obscured due to an indirect effect from increased temperatures stimulating catchment productivity. The variations in the timing and magnitude of change between lakes in the Windermere catchment may also reflect differences in catchment characteristics, such as catchment size, vegetation cover and land use (Hu *et al*., 2014). The catchment of Blea Tarn may have largely acted as a buffer until some threshold in the 1970s, when changes in allochthonous inputs, coupled with warmer temperatures, started to stimulate lake algal growth. A lake such as Blea Tarn may be largely resilient to events that may highly impact smaller catchments (e.g. deforestation; *see Lake Gormire,* chapter 4.), but an increase in productivity of the entire catchment could have had a profound impact on lake algal biomass.

A consequence of concurrent increases in temperature and nutrient loading has been a shift from benthic to planktonic dominated diatom assemblages. This shift has been a common occurrence in temperate lakes in the northern hemisphere during the second half of the 20th century (e.g. Oleksy *et al*., 2021; Wolfe *et al*., 2003). In the South Basin of Lake Windermere there was a significant increase in abundance of the planktonic diatom *Asterionella formosa* (Maberly *et al*., 1994). This was attributed to longer ice-free periods leading to the advancement of the spring diatom bloom. Conversely, Talling and Heaney (1988) found that the diatom *Tabellaria flocculosa*, which inhabits both planktonic and benthic environments, used to be abundant in Lake Windermere between 1945 and 1968 but declined to low abundances since then. Whilst they attributed the decline to an increase in P loading, the large increase in cyanobacteria (e.g. *Anabaena flosaquae, Oscillatoria bourrellyi*) indicated that climatic factors and competitive exclusion may also have contributed to their decline. Cyanobacteria blooms can be further enhanced when elevated winter rainfall is followed by more intense summer drought (Paerl and Huisman, 2009). This has led to cases where summers with the highest temperature have not resulted in the highest algal bloom biomass due to the relatively drier winters than some other years. This situation occurred in 2003 when the European heatwave resulted in a significantly higher bloom biomass compared to the more extreme temperatures of 2006 (Huber *et al*., 2011).

Whilst a shift from benthic to planktonic taxa has often been linked to N deposition (e.g. Wolfe *et al*., 2001), this shift has also been experienced in lakes with notable decreases in nutrient concentrations. Sivarajah *et al*. (2016) found that in George Lake, Ontario an increase in *A. Formosa* from the mid-1980s to the present occurred during the warmest period in the meteorological record. The increase in *A. Formosa* was attributed to longer growing seasons which provided this taxon with a competitive advantage as its buoyancy means it can exploit internal nutrients near the thermocline or during spring turnover. These findings were also mirrored by Hadley *et al*. (2013), who surveyed a range of lakes in the south-central Ontario region between 1992 and 2008. They found a regional increase in planktonic diatoms in absence of increases in N availability which they attributed to climate warming.

The lack of relationship between precipitation and diatom biomass in Blea Tarn contrasts with the findings in other lakes in the Windermere catchment. McGowan *et al*., (2012) reported a decrease in diatom derived pigments (fucoxanthin and diatoxanthin) in years with wetter winters in Lake Windermere during the 20th century. This observation has also been recorded in Blelham Tarn, with winter precipitation significantly reducing the biomass of spring blooming diatoms (Moorhouse *et al*., 2014). The impact of winter precipitation is particularly pronounced in Blelham Tarn due to its very short water retention time. High winter precipitation was likely diluting diatom *inocula*, limiting spring blooms (Reynolds and Irish, 2000). This may indicate that Blea Tarn has a relatively long WRT, considering there does not appear to be any discernible impact of winter precipitation on diatom biomass.

The suggestion that Blea Tarn may have a particularly long WRT is highlighted by Moorhouse (2016). They showed that WRT was a key influence in controlling algal biomass and community composition in the Windermere catchment. Lakes with high WRTs had significantly lower C/N ratios than those with lower WRTs, likely because they are relatively more impacted by nutrient loading, maintaining favourable conditions for large algal blooms to develop (Moorhouse, 2016). At Blelham Tarn, increased summer temperatures and lower rainfall in 1974 led to longer WRTs. Longer WRTs caused the spring bloom to start earlier and prolong the summer-autumn growing season. A prolonged growing season resulted in the dominance of cyanobacteria with blooms persisting longer into the year (Jones and Elliott, 2007). These impacts were also reported by Moorhouse *et al*. (2014), who recorded concurrent increases in cyanobacterial pigments (zeaxanthin, canthaxanthin) between 1960-80 with a decline in annual precipitation. Conversely, declines in cyanobacteria after 1996 occurred along with increased precipitation, which would have decreased WRT and increased nutrient flushing (Moorhouse *et al*., 2014). The control of WRT and hydrological flushing has also been observed to control cyanobacteria biomass in the nearby lake of Elterwater (Goldsmith *et al*., 2003). The variations in cyanobacteria across the Windermere catchment may be controlled by changes in WRT, with periods of enhanced WRT resulting in larger blooms forming. Therefore, it is possible that Blea Tarn has a relatively high WRT that could be contributing towards the particularly low C/N ratios experienced in the lake. High WRTs could also help explain why SRP concentrations are relatively high as limited flushing would prevent a large proportion of nutrients leaving the lake (Jeppesen *et al*., 2005).

Increased cryptophyte biomass (*Cryptomonas spp*.) has been observed in several lakes in the Windermere catchment (Lake Windermere, Esthwaite Water and Blelham Tarn) between 1945-59 and 1990-2003 (Feuchtmayr *et al*., 2012). The relatively rapid increase in cryptophyte biomass in Blea Tarn during recent decades mirrors the profile recorded by Moorhouse (2016). Alloxanthin concentrations have increased consistently across the Windermere catchment in recent decades, except for the three highest upland tarns. The lack of increase in the upland tarns was suggested to reflect a recovery from acidification (Moorhouse, 2016). Recovery from acidification should increase lake water DOC concentration which would reduce light availability for deeper blooming taxa (Monteith *et al*., 2007). Although there is there is little direct evidence, it has often been assumed that DOC levels have increased in the Lake District, particularly in the uplands, as lakes recover from acidification (Evans and Monteith, 2001; Tipping *et al*., 2002). However, despite no direct assessment of changes in lake water DOC concentrations, the increased water clarity, very low NTU units and increasing algal biomass in Blea Tarn would indicate a reduction in lake water DOC. Spatial surveys from Sweden showed that algal abundance was inversely correlated to lake water DOC, which suggests that primary production was partially governed by the effect of terrestrial organic matter on light availability (Reuss *et al*., 2010). However, a decreasing trend in DOC concentrations would be inconsistent with the general trend in UK lakes. There is evidence from around the UK of an increase in DOC concentrations in the majority (77%) of streams and lakes during the second half of the 20th century, with no sites showing a significant decrease (Worral *et al*., 2004).

While changes in environmental conditions impact DOC concentrations, the precise impacts vary lake to lake. Increased precipitation often leads to an increase in DOC exports from the catchment

(Monteith *et al*., 2007) and could also result in a decrease in DOC concentrations due to increased dilution (McDonough *et al*., 2020). Therefore, it is possible that an increase in precipitation around Blea Tarn may have reduced DOC concentrations, despite the recovery from acidification increasing the solubility of DOC (de Wit *et al*., 2007). Increasing temperatures can also impact lake DOC concentrations as this will increase organic matter mineralisation rates (Laudon *et al*., 2012). Additionally, temperature driven increases in mineralisation rates can increase to a greater extent than that of vegetation productivity, especially in catchments with readily decomposable litter (Hobbie *et al*., 2000). Therefore, increased temperatures can also result in a reduction in lake water DOC, both from a reduction in DOC transport and greater in-lake decomposition rates. In general, while the increase in water clarity at Blea Tarn is likely to reflect a decrease in DOC concentrations, the cause of this change is unclear.

An increase in water clarity would impact cryptophyte populations directly as demonstrated in the Canadian shield lakes. Increased water transparency led to habitat shifts for cryptophytes, as taxa used their motility to avoid UV radiation (Vinebrooke *et al*., 2002). There is typically an optimal range of water clarity for algal growth. Although light is needed for photosynthesis, too much exposure of UV will start having detrimental effects (McGowan *et al*., 2018). Therefore, the reductions in cryptophyte biomass in recent decades may also, partially, reflect a habitat shift. As discussed in section 5.3.4, it is possible that diatoms have also experienced a habitat shift in most recent decades, an occurrence that has been regularly experienced in the Windermere catchment. Therefore, the cryptophyte community may have shifted to more deeper blooming taxa in response to elevated UV exposure.

In Blea Tarn, there is a general trend of cryptophytes expanding while diatoms decline during the 20th century. In the Windermere catchment the upland tarns experienced concurrent declines in both cryptophytes and diatoms whilst lowland lakes experienced increases. This places Blea Tarn in a unique position in the Windermere catchment, with Blea Tarn the only lake experiencing this trend (Moorhouse, 2016). There is no clear period since at least 1600 when both diatoms and cryptophytes have sustained periods of enhanced biomass. The lack of concurrent increases between these spring blooming taxa may suggest that while Blea Tarn has experienced some of the same drivers of change as the lowland lakes, there is potentially greater competition for resources in the spring months. Greater competition may have restricted the biomass of these taxa, with a competitive dynamic between diatoms and cryptophyte responding to changes in environmental conditions. However, the decline in diatoxanthin could also represent a habitat shift. In Sky Pond, USA there was a shift towards more planktonic taxa, with a decline in overall diatom abundance during the second half of the 20th century (Oleksy *et al*., 2020). These changes were likely driven by a combination of N deposition and rapid warming, and are probably responsible for the changes in Blea Tarn. The decline in $\delta^{13}C_{org}$ at Sky Pond since the 1950s (1.5‰) is also comparable to the ~1.8‰ reduction in Blea Tarn.

In Blea Tarn, the mean chlorophyte derived pigments are 308% and 344% higher in the 21st century than they are in the 1960s (lutein and chlorophyll-*b* respectively). This is comparable to the change experienced in Sky Pond, USA by Oleksy *et al*. (2020). They found that chlorophyte pigments increased by 200-300% in both lakes and the increase in chlorophytes continuing to the present day. With the decline in benthic diatoms there was an increase in the abundance of benthic chlorophytes. The increase in benthic chlorophytes likely reflects the change in nutrient availability and temperature that allowed them to colonise benthic habitats and outcompete the slower growing diatoms (Oleksy *et al*., 2020). The trends in Blea Tarn broadly follow those in Sky Pond and were attributed to the combined impacts of increased temperatures and atmospheric N deposition. Additionally, zeaxanthin concentrations in Sky Pond, USA increased in line with lutein and chlorophyll-*b* during the second half of the 20th century, indicating a concurrent increase in cyanobacteria and chlorophytes (Oleksy *et al*., 2020). Chlorophytes and non-heterocystous cyanobacteria can often both respond strongly to increased nutrient availability (Herrero *et al*., 2004). For example, the addition of urea to well-lit, P rich mesocosm experiments in the bay Wascana Lake, Canada stimulated non-heterocystous cyanobacteria and small celled chlorophytes (Finlay *et al*., 2010).

Nutrient supply is often the largest controlling factor on cyanobacteria growth. Lurling *et al*. (2018) collected freshwater samples from 39 sites in the Netherlands and subjected them to warming experiments. They found that there was no overall trend in cyanobacteria biomass from warming alone. However, when nutrients were elevated, warming had a clear impact on cyanobacteria growth. In general, they found marginal impact from temperature, with nutrient pulses causing significant increases, especially in already eutrophic waters. It is possible therefore that for Blea Tarn the trends in picocyanobacteria biomass are dominated by changes in nutrient supply.

Moorhouse (2016) found similar increases in lutein and zeaxanthin concentrations at Blea Tarn. Most lakes in the Windermere catchment exhibited a trend of increasing chlorophytes and cyanobacteria during the 20th century, indicating a regional driver of change. Only Easedale and Stickle Tarn showing a significant decrease in concentrations over time which was attributed to a recovery from acidification in these upland lakes. For the lowland lakes, the change varied considerably between lakes. For Blelham Tarn, sedimentary zeaxanthin concentration increased since the start of the 1970s. This increase occurred concurrently with an increase in livestock densities in the catchment and increasing $\delta^{15}N$ values until the 1980s, indicative of enhanced eutrophication from animal sources (Moorhouse *et al*., 2014). For Lake Windermere, zeaxanthin concentrations increased in the North Basin from around ~1920 and the South Basin in ~1860 and ~1987 (McGowan *et al*., 2012). These trends were attributed to sewage influx and agricultural intensification, causing an increase in P enrichment. In general, the broadly consistent increase in cyanobacteria and chlorophytes between the lowland lakes of the Windermere catchment during the 20th century indicate a regional driver of change, with the growing dominance of summer blooming taxa (Moorhouse *et al*., 2014). Atmospheric N deposition and climate warming has likely contributed towards algal community change in all lakes within the catchment, however for the lowland lakes the impacts are likely confounded by high nutrient inputs from direct sources (Moorhouse *et al*., 2014).

The relatively muted increases in canthaxanthin during the 20th century was also recorded by Moorhouse (2016) with non-significant trends overall. This is in contrast to many of the lakes in the Windermere catchment, in particular the lowland lakes (e.g. Lake Windermere, Grasmere, Esthwaite Water) which have experienced significant increases in canthaxanthin during the 20th century, likely as a result of anthropogenic activities (Moorhouse, 2016). Despite the muted response, there does appear to be a detectable impact of temperature on filamentous cyanobacteria, at least from the second half of the 20th century. Jeppesen *et al*. (2009) found that higher temperatures resulted in the increasing dominance of cyanobacteria, in particular N-fixing taxa, in 250 Danish lakes. This resulted in the increase in overall algal biomass (chlorophyll-*a*) with concurrent declines in diatoms.

In general, there has been a muted response of filamentous cyanobacteria, a stronger response of other algae and declining P concentrations since the 1970s. These trends would suggest that the increase in nutrients is due to N based compounds and may potentially indicate that Blea Tarn was previously N limited. Algae have been shown to respond strongly to N loading, even in the absence of P. In littoral enclosure experiments in shallow mountain lakes (Wyoming, USA), Nydick *et al*. (2004) showed that both N and N with P treatments resulted in greater algal biomass, but enrichment of N alone caused considerable change in the algal community structure. Algae shifted to greater proportions of pelagic phytoplankton with more variable or no response by benthic algae. This was likely due to the greater photosynthetic efficiency of phytoplankton compared to benthic algae, with this difference increasing with enrichment. This would be consistent with the interpretation of the lack of increase in chlorophyll-*a* from the 1980s representing a habitat shift towards greater pelagic production. Therefore a proportion of the increase in algal biomass from the 1970s may be related to greater N loading and may represent a lake that was N limited indicated by its high SRP concentrations (Moorhouse, 2016), despite sedimentary TP declining since the 1950s.

5.5 Summary

Overall, Blea Tarn appears to have remained relatively stable over much of the recent past although there are some clear periods of change within the algal community from the start of the 17th century. One of the more notable trends is the changing proportions of diatoms and chlorophytes over time (Fig. 5.29). Pigments from these two taxa dominate the sediment but show the trend of diatoms largely being replaced by chlorophytes over time with an inverse relationship. There is evidence of a strong competitive dynamic in Blea Tarn at various points in the time series, between spring blooming taxa such as diatoms and cryptophytes and to the summer blooming taxa. These relationships are likely controlled by nutrient availability although the impact of light availability appears to be a secondary control. Whilst the impacts are less prominent in the isotope data, periods of anthropogenic activity have had a clear impact on the algal community in Blea Tarn. Intense mining activity likely reversed the trend of declining diatom abundances while deforestation in the catchment appeared to broadly stimulate all algal taxa. While both cyanobacteria and cryptophytes increase and decline in relative abundances from the 1970s, chlorophytes continue to become more dominant in the algal community. This indicates that Blea Tarn is most likely getting progressively more productive despite the reductions in sedimentary P concentrations.

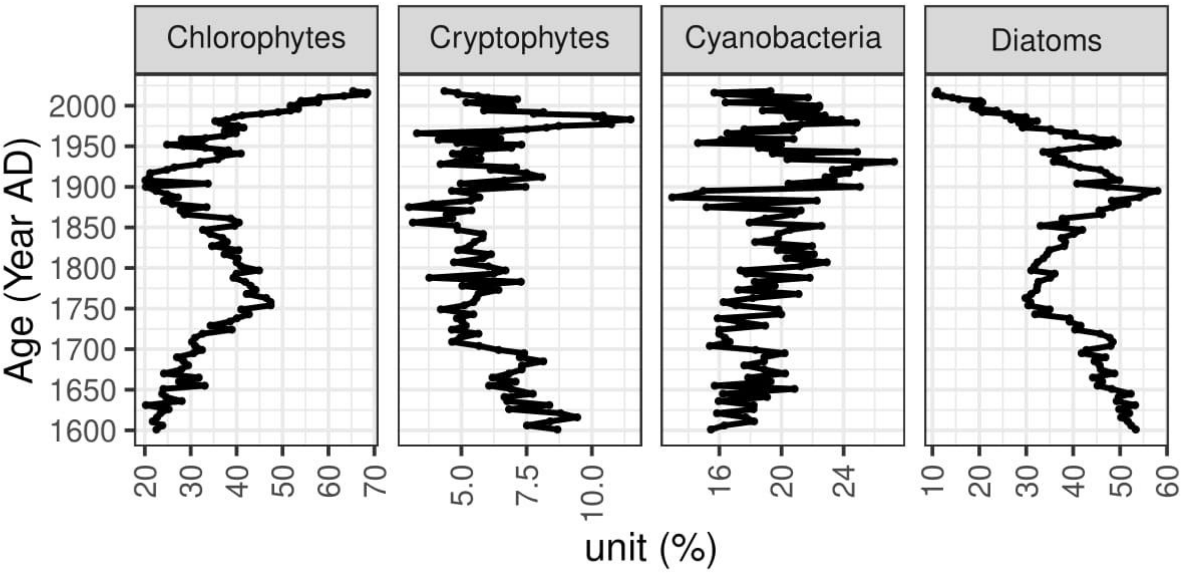

Fig. 5.29 Change in the relative abundances of dominant algal groups in Blea Tarn

The drivers of change in Blea Tarn from the 1970s are likely to be predominantly associated with increased N supply, although the direct impacts of temperature also appear to be stimulating chlorophyte growth. It is likely that much of the change in the lake is being driven by changes in the catchment, considering the timing shifts in $\delta^{13}C_{org}$ and $\delta^{15}N$. The relatively large size of Blea Tarn, coupled with its moderate altitude may present a lake in a more unique position in the Windermere catchment, where the catchment is relatively productive without being impacted by direct inputs of human and animal waste. Whilst it is likely that N deposition is also impacting Blea Tarn, most of the impact is likely to be moderated by the catchment.

It is likely that there has been an increase in N availability and temperature since the 1970s which has enhanced productivity in the catchment of Blea Tarn. The enhanced biomass and organic matter mineralisation rate would provide the lake with a greater supply of nutrients, which would be a prerequisite to support a lake in which chlorophytes become a dominant algal taxa. The declining trend in diatoms since the 1970s may reflect the indirect impacts of increased temperature caused by increased competition in benthic environments.

6. Sunbiggin Tarn

This chapter presents the results and interpretations for the data generated from Sunbiggin Tarn. It will discuss a timeline of events and explore the causes for any such changes, along with an assessment as to the impact of 20th century climate warming.

Fig. 6.1 Photograph of Sunbiggin Tarn taken from the western bank, August 2018.

6.1 Background

6.1.1 Historical land cover and vegetation

As a result, Sunbiggin Tarn and the surrounding Little Asby Scar is part of a SSSI and designated as a Special Area of Conservation (SAC) as an example of hard oligo-mesotrophic waters with benthic vegetation of *Chara* species (Bennion *et al*., 2017). Sunbiggin Tarn is of great geological interest being considered the most important site in Britain for petrifying springs with tufa formation (Natural England, 2008). Tufa formation occurs due to groundwater rich in calcium bicarbonate coming to the surface. The interaction of these calcium rich waters with the atmosphere leads to the loss of CO_2 from the water and results in the precipitation of calcium carbonate as tufa (Pentecost, 2009). The flushes of Sunbiggin Tarn also support two very rare species of snail with the only known

British location for *Vertigo geyeri* and one of three British sites supporting *Catinella arenaria* (Natural England, 2008).

The area has a long history of livestock grazing but sheep have been excluded from a substantial area of the fen surrounding the tarn since the 1960s (Holdgate, 2016). Livestock pressures reduced further since the site came under the management of the Cumbria Wildlife Trust who negotiate with livestock owners to reduce the number of sheep and cattle grazing in the summer months (Natural England, 2008; Pentecost, 2009). Most of the catchment currently comprise of heather grasslands (53%) and acid grasslands (32.8%; Fig. 6.2) with areas of rock outcrop (7.2%), improved grassland (4.1%) and heather (2.7%) (Morton *et al*., 2011). In some parts of the heathland there is high grazing pressure which has led to degradation into areas of grassy heath. Amongst the heather there are a range of species not normally associated with heathland in northern Britain, such as bird's-foot trefoil (*Lotus corniculatus*), salad burnet (*Sanguisorba minor*) and the lady's bedstraw (*Galium verum*) (Natural England, 2008).

There are extensive areas of swamp and fen around the tarn forming a wetland area of great biological interest. The fen is dominated by bottle sedge (*Carex rostrate*) along with species of tussock sedge (*Carex lasiocarpa* and *C. paniculate*), common spike-rush (*Eleocharis palustris*), soft rush (*Juncus effuses*), water horsetail (*Equisetum fluviatile*), bog bean (*Menyanthes trifoliata*) and mare's-tail (*Hippuris vulgaris*) (Natural England, 2008). Within the tarn the dominant submerged macrophytes are *C. contraria*, *C. curta*, *C. vulgaris*, *C. virgata*, *Potamogeton crispus* (Pentecost, 2009). These *Chara* species have a large impact on the lake driving marl deposition through photosynthesis (Holdgate, 2016).

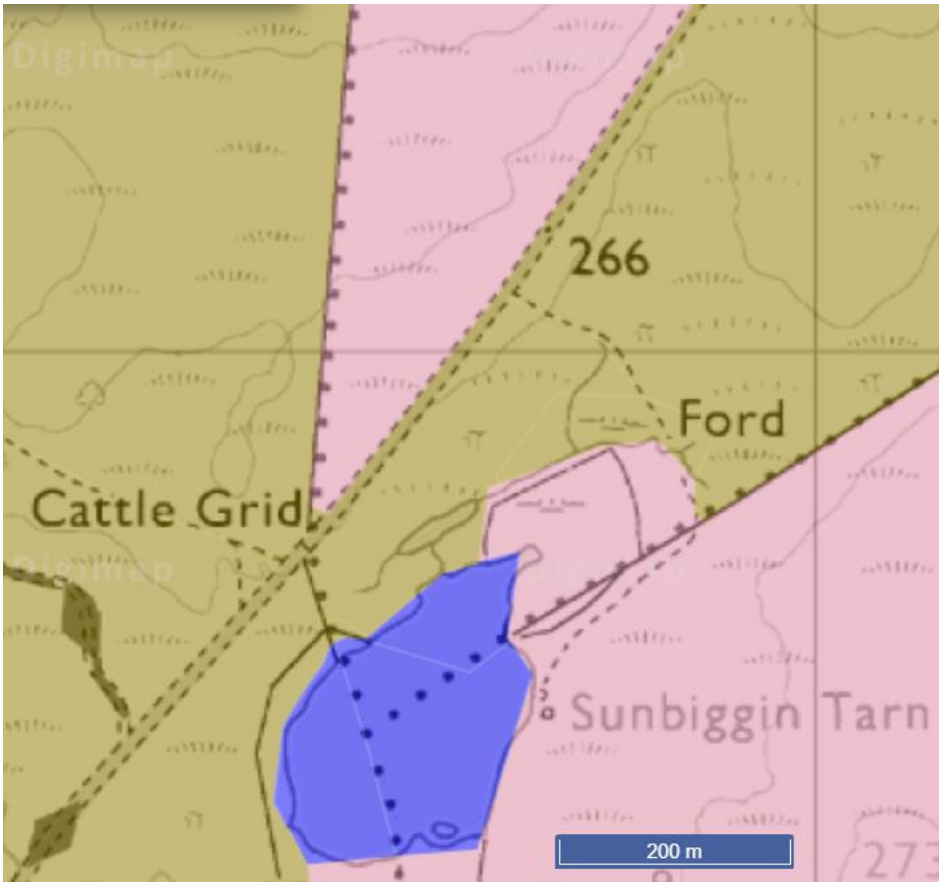

Fig. 6.2 Land cover map of Sunbiggin Tarn catchment showing areas of acid grassland (light brown) and heather grassland (pink).

The presence of a charophyte community has been documented from sedimentary records since 1900, with remains of *C. vulgaris*, *C. rudis* and *C. aspera* detected in 1900 (Bennion *et al*., 2017). In the mid-1940s *Chara* sp. remains were almost absent with only *C. rudis* present in low abundance and the pondweed *P. crispus* in high abundance. In 1950 there was substantial aquatic vegetation dominated by *Potamogeton sp* and *Myriophyllum spicatum* in the deeper section of the tarn and *Chara* sp. with *Zanichellia palustris* in the shallower sections (Holdgate, 2016). Since the 1950s there has been a decline in macrophyte species richness, possibly through eutrophication caused by presence of the black-headed gulls with the nutrient tolerant species *Zannichellia palustris* appearing from 1982 (Bennion *et al*., 2009). *Chara* sp. seemed to have recovered by 1982 (Bennion *et al*., 2017) and a macrophyte survey in 2002 showed a healthy community of flora typical for an upland marl lake, although with fairly low diversity, with *C. vulgaris*, *C. contraria* and *Z. palustris* dominating (Goldsmith *et al*., 2003).

For the surrounding catchment, prior to 1950 there appeared to be a dominance of terrestrial mosses and *Juncus* which have since gradually declined in abundance (Bennion *et al*., 2017). The broad vegetation pattern around the tarn changed relatively little from 1953 to 1969, however some reedswamp (*Phragmites*) and the small areas of *Carex elata* tussock at the fen edge reduced through damage by nesting gulls. In the fens north of the tarn there were signs of eutrophication with increased nettles, docks and *Juncus effuses* (Holdgate, 2016). By 1985-1986 the northern fens had been considerably eroded by the gull population resulting in a major extension of open water in the north of the tarn which continued in the 1990s where the whole tarn area appeared to have experienced eutrophication with reductions in reedswamp and sedge fen (Fig. 6.3; Holdgate, 2016). By the turn of the century the fens had made a recovery in response to the decline in gull population with macrophyte species returning to a similar composition seen prior to the gull expansion, indicating regeneration (Bennion *et al*., 2009). However, since the recovery of the fen there has been a further expansion of *Typha* which indicates that there could be a persistent nutrient source (Holdgate, 2016).

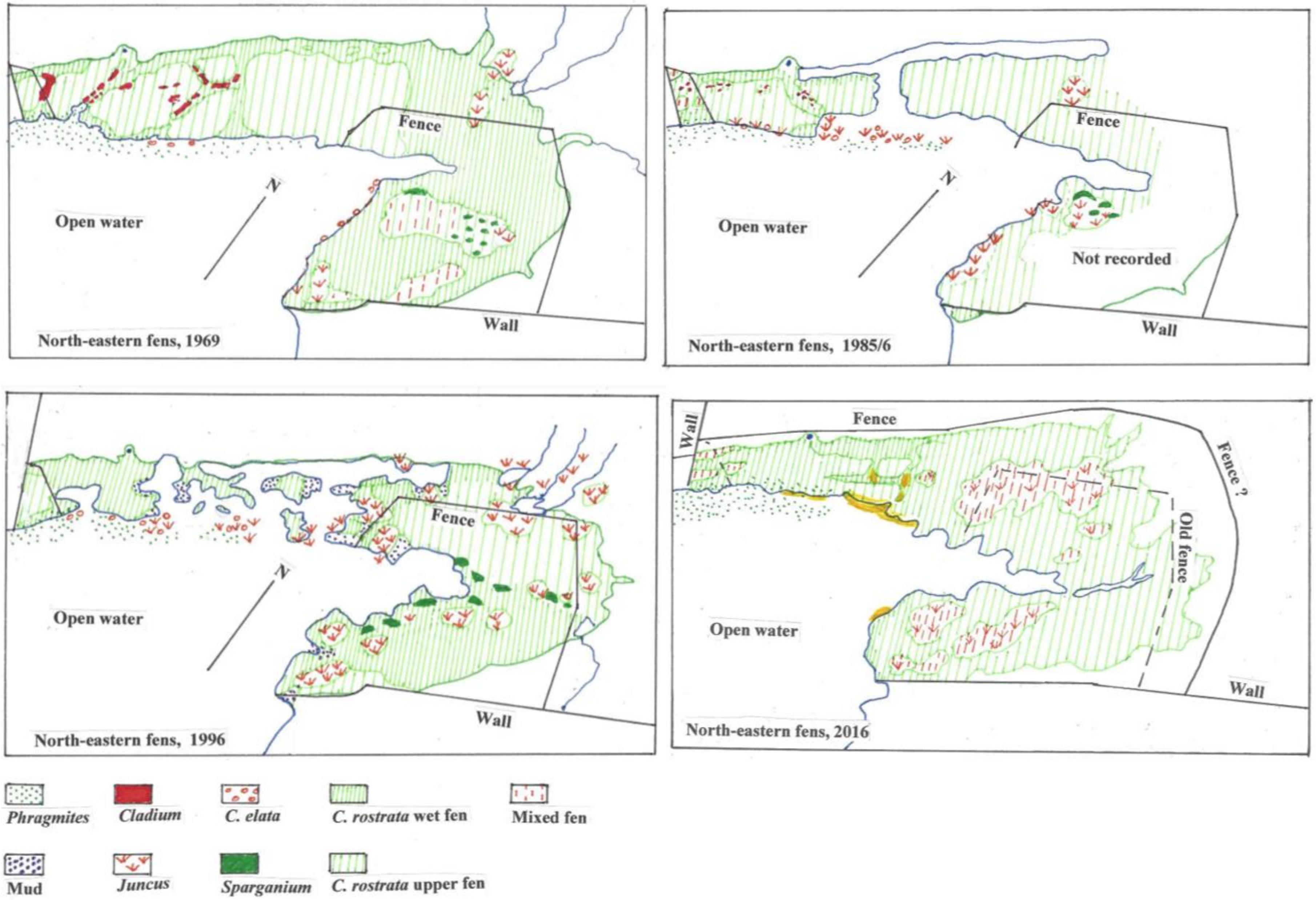

Fig. 6.3 Changes in the extent of open water/fen degradation in Sunbiggin Tarn from 1969 to 2016, as documented by Holdgate (2016).

6.1.2 Black-headed gulls

One of the greatest influences on the Sunbiggin Tarn catchment over time has been the water bird community with the lake providing an important habitat for nesting birds, in particular black-headed gulls (Natural England, 2008). A small black-headed gull colony (400-600 pairs) was present until the 1950s when it increased to around 1,000 pairs (Goldsmith *et al*., 2003). The population was partially managed by the resident gamekeeper who prevented pairs from establishing in the north of the tarn. After the gamekeeper retired in the early 1960s the colony rapidly expanded with a population explosion from 1975 (Holdgate, 2016) to around 10,000 pairs by the 1980s and 12,500 in 1988 representing the largest breeding population in the north of England (Bennion *et al*., 2017; Holdgate, 2016). There was still a substantial breeding colony in 1996 but this declined abruptly and was completely gone by 2005 (Holdgate, 2016). The numbers of black-headed gulls today are now negligible at this site, with no gulls present in 2016 (Bennion *et al*., 2017; Holdgate, 2016). The population decline is likely to have been due to food limitation as in 1988 the measured body weight of birds declined as the breeding season progressed and resulted in substantially lower hatchlings survival rates resulting in a subsequent population crash (Holdgate, 2016).

6.1.3 Water quality and monitoring

Diatom analysis of sediment cores has shown no conclusive signs of eutrophication although habitat shifts in the diatom species in the early 1990s suggest a possible physical disturbance (Goldsmith *et al*., 2003). In the summer of 2008, there were abundant phytoplankton populations of diatoms (e.g. *Fragilaria capucina*), chlorophytes (e.g. *Eudorina elegans*), cyanobacteria (e.g. *Anabaena flosaquae* and *Microcystis aeruginosa*) and zooplankton (Pentecost, 2009). In general, the tarn is species rich in zooplankton, benthic invertebrate and diatoms which dominate available surfaces and organic sediments (Pentecost, 2009). Zooplankton remains of the littoral-benthic species *Chydorus sphaericus* dominated the pre 1950 sections with *Simocephalus* spp also present. From 1982 *C. sphaericus* was no longer present and there was a large increase in pelagic species (e.g. *D. hyalina* agg. and *D. pulex* agg) but little remains are found in more modern samples (Bennion *et al*., 2017). The major increase in open water *Daphnia* taxa between 1950 and 1980, along with the shift to greater *Chara* sp. abundances indicate higher pelagic production (Bennion *et al*., 2009).

Sunbiggin Tarn is a hard oligo-mesotrophic lake with a mean alkalinity of 3 meq L^{-1} and a Secchi depth of 2 m (Bennion *et al*., 2017; Pentecost, 2009). In the early 1950s the pH of the tarn was around 8.2 with a measured pH of 8 in 2009 (Holdgate, 2016; Pentecost, 2009). The mean calcium carbonate concentrations in the water column were 121 mg L^{-1} in the summer of 2009 (Pentecost, 2009). Nutrient concentrations have been declining during the 21st century, with mean TP of 33.6 µg L^{-1} in 2003 (Goldsmith *et al.*, 2003), 28.6 µg L^{-1} in 2004-2006 (Environment Agency, 2008) and 13.0 µg L^{-1} in 2019-2020 (Maberly *et al.*, 2020). Environment Agency sampling between 2004-2006 (Table 6.1) also measured an SRP of 10ug L^{-L}, nitrate of 0.29 mg L^{-1} with a mean TN of 0.50 mg L^{-1}. The mean TN was recorded as 0.43 mg L^{-1} in 2019-2020 (Maberly *et al.*, 2020).

Table 6.1 Mean water quality parameters for Sunbiggin Tarn, 2004 to 2006 with standard deviation in brackets (Environment Agency, 2008).

Parameter	**Summer**	**Winter**
pH	8.5 (0.3)	8 (0.3)
Water temperature (°C)	15.4 (1.9)	6 (2.4)
Conductivity	258 (48.5)	164 (42.3)
Hardness ($CaCO_3$)	82.4 (52.9)	160 (7.3)
Turbidity (NTU)	4.3 (0.6)	3.2 (3.3)

An NTU of between 3 and 4 would indicate the lake to be of fairly low turbidity and the reduction in lake water hardness likely reflects enhanced carbonate ($CaCO_3$) precipitation in the summer months. The dissolved oxygen saturation exceeds 100% saturation in summer months, reducing from 14.6 mg L^{-1} to 8.9 mg L^{-1} by the autumn driven by high phototrophic activity, and indicating oxygen depletion in the summer months (Environment Agency, 2008). DOC concentrations between January and March (3.2 mg L^{-1}) is around half that present between October and December (6.1 mg L^{-1}).

6.1.4 Weather and climate

Little site-specific information exists for Sunbiggin Tarn, but due to its upland location and proximity to the Lake District it would be expected to experience a similar climate to that in the Windermere catchment. Due to its small size Sunbiggin Tarn would also be expected to regularly freeze over in winter months and this has previously been documented by site observations (Holdgate, 2016). The closest continuous weather monitoring station to Sunbiggin Tarn is Newton Rigg (~18 miles NW), with the data previously described in section 5.1.2.

6.2 Results

6.2.1 Sediment chronology

The equilibrium depth of total ^{210}Pb activity with supported ^{210}Pb activity was not attained at the base of the core (Fig. 6.4a). Unsupported ^{210}Pb activities decline with depth with some sharp fluctuations, suggesting considerable changes in sedimentation rates (Fig. 6.4b), for example at 18.63 cm and in the 20.38 – 21.38 cm section. The ^{137}Cs activity versus depth profile shows a possible peak around 32.13 – 33.38 cm. The detected ^{241}Am activities in the basal section of the core would indicate that the high ^{137}Cs activities at the base were derived from fallout of atmospheric testing of nuclear weapons with a maximum level in 1963 (Fig. 6.4c). The non-monotonic variation in unsupported ^{210}Pb activities of the core precluded the use of the CIC model. The CRS dating model places 1963 between 26 and 30 cm, and dates 32.13 cm to 1929. However, these are not in agreement with the ^{137}Cs and ^{241}Am records. The final CRS chronologies were corrected by assuming that the sediment at 33 cm was formed in 1963, as indicated by the peaks in ^{137}Cs and ^{241}Am activity. The ^{210}Pb chronologies and sedimentation rates are shown in Fig. 6.5.

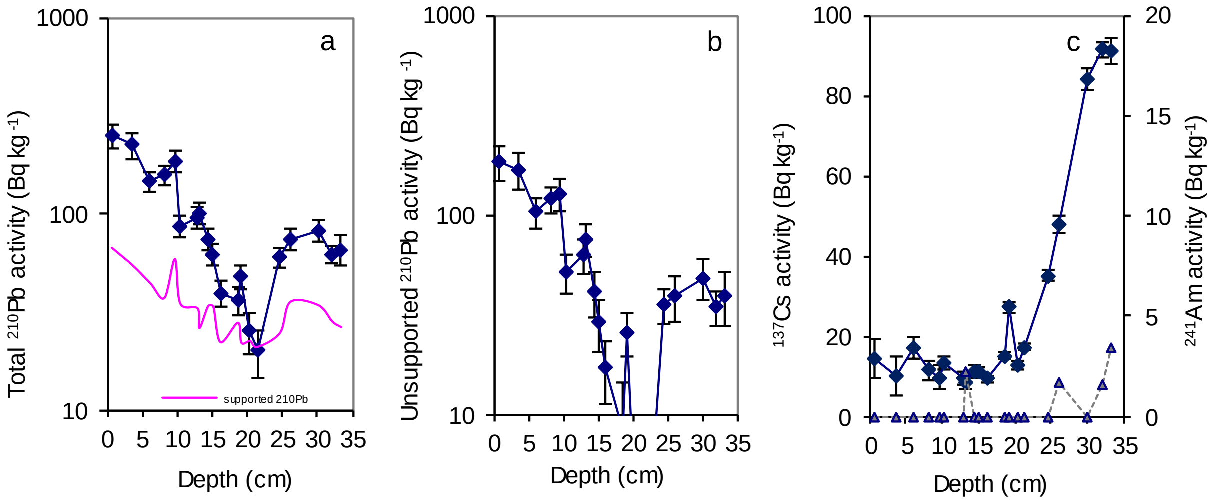

Fig. 6.4 Fallout radionuclide concentrations in core taken from Sunbiggin Tarn, showing (a) total ^{210}Pb (blue line) and supported ^{210}Pb (pink line), (b) unsupported ^{210}Pb, and (c) ^{137}Cs (solid line) and ^{241}Am (dashed line) concentrations against depth.

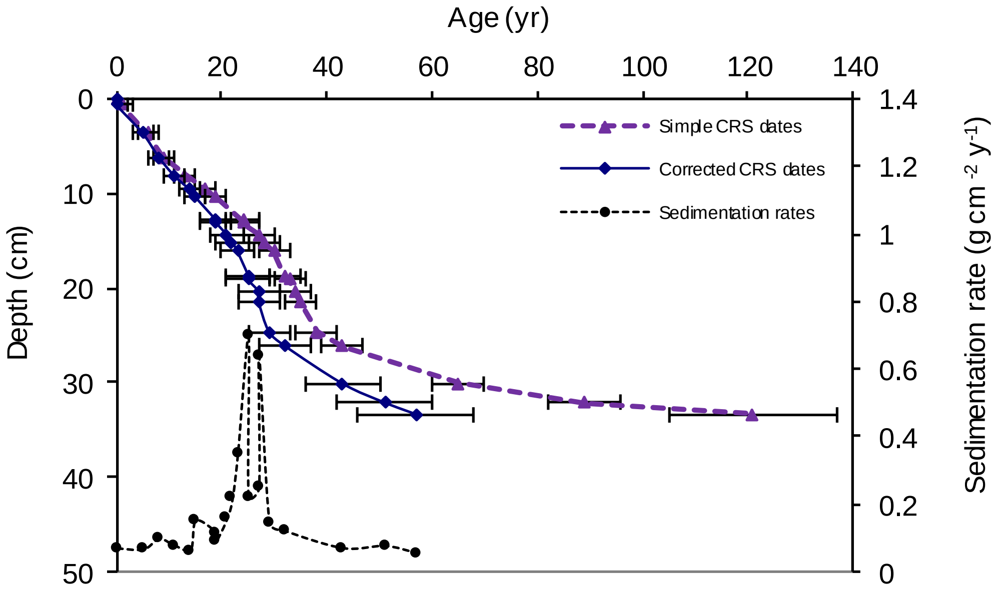

Fig. 6.5 Radiometric chronology of core taken from Sunbiggin Tarn, showing the CRS model ^{210}Pb dates and sedimentation rates.

In general, sedimentation rates in the core are relatively high and have large fluctuations through time. The sedimentation rate increases slightly during the 1960s from 0.19 cm yr^{-1} in 1961 to 0.26 cm yr^{-1} in 1975 and continues to rise through the 1980s to 0.53 cm yr^{-1}in 1989. The sedimentation rates then increase dramatically up to 1.52 cm yr^{-1} in 1991 and 1.51 cm yr^{-1} in 1993 before reducing to 1.17 cm yr^{-1} in 1995 and falling to 0.76 cm yr^{-1} by 1997. Sedimentation rates remain relatively stable through to the present, although with some slight decline with 0.84 cm yr^{-1} in 2003 and 0.67 cm yr^{-1} in 2013. While absolute ages are used in the following text, they represent the corrected CRS model's estimated age with uncertainty increasing with depth

6.2.2 Sediment lithology

The OM content increases gradually from 17.2% in 1964 to 23.7% in 1984 (Fig. 6.6a). OM content declines thereafter with a more rapidly shift to lower values after 1988, reaching a low of 11.2% in 1991. %OM increases to 22.3% in 1997 and continues to increase thereafter to 30.8% in 2010. The minerogenic content slightly increases from the 1960s to the 1980s with a peak of 48.2% in 1988 before declining to 44.8% in 1989 (Fig. 6.6b). The decline in minerogenic content continues to 41.6% in 1999 reaching 40.0% in 2016. The carbonate content (%$CaCO_3$) gradually decreases from the 1960s to the 1980s with 32.1% in 1988, increasing rapidly to 39.6% in 1989 (Fig. 6.6c). The carbonate content continues to increase into the start of the 1990s, reaching a peak of 45.4% in 1991. Carbonate content declines to 39.4% in 1996 after which there is a more gradual decline to a minimum of 26.7% in 2017.

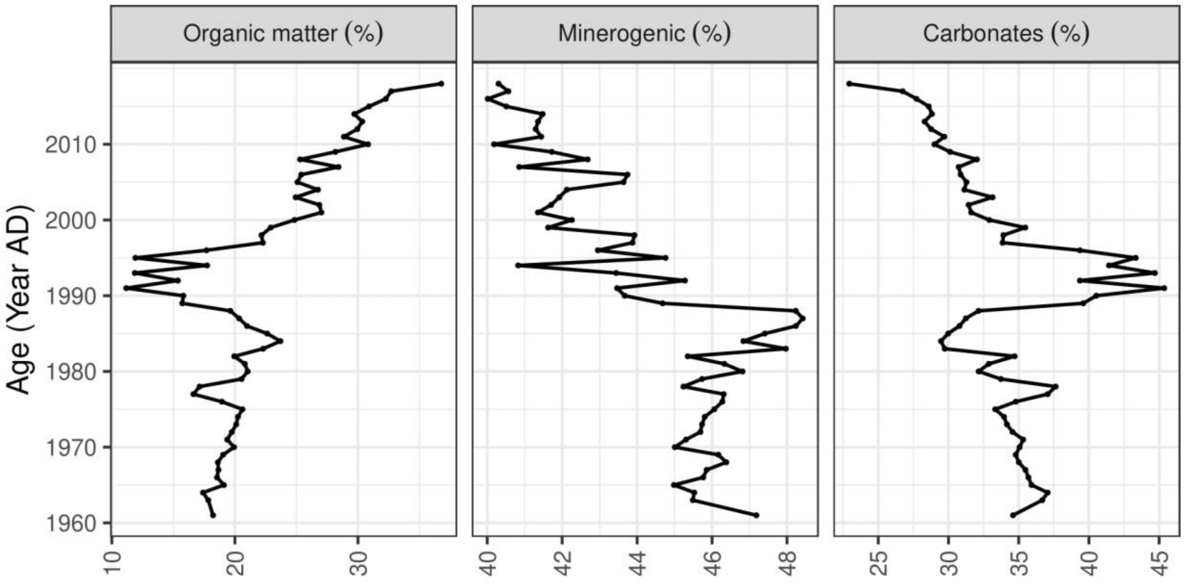

Fig. 6.6 Main sedimentary parameters from loss on ignition analyses: organic matter content (a), minerogenic content (b) and carbonate content (c) for Sunbiggin Tarn.

6.2.3 Sedimentary trace elements

The concentrations of lithogenic elements (Al, Li, Mg, K) all show similar trends (Fig. 6.7). While Li remains broadly stable from the start of the 1960s to the middle of the 1980s, K and Mg increase slightly. There is a greater increase in Al during the same time period reaching a peak of 4.3 mg g^{-1} in 1986. All lithogenic elements experience a decline from 1988, although this is of greater magnitude in Al and Mg, with Mg reaching a low of 0.89 mg g^{-1} in 1990. While concentrations of Li quickly recover, Al and Mg experience a period of prolonged lower concentrations before increasing to 3.0 mg g^{-1} and 1.1 mg g^{-1} respectively in 1997. All lithogenic elements then gradually increase from the start of the 21st century. Heavy metals (Cu, Cd, Zn, Pb, Cr, Ni) all follow very similar trends to each other, as well as to Fe and Al. All these elements experience a peak in concentration around 1986, followed by a rapid decline to the start of the 1990s. All heavy metals experience prolonged lower values until the second half of the 1990s. Following this period of low concentrations, Fe, Cu, Cr and Ni increase from the start of the 21st century, with a slow rate of increase in Zn. Both Cd and Pb remain broadly stable during the same period, with concentrations of 1.7 µg g^{-1} and 31.8 µg g^{-1} respectively in 2015.

P and Ba concentrations follows similar trends to many of the heavy metals (e.g. Fe and Cr), with a consistently increasing trend during the 21st century with 844.3 µg g^{-1} and 36.0 µg g^{-1}, respectively, in 2014. Mn and Ca follow similar trends for most of the sediment core, having broadly stable concentrations until the end of the 1980s, and increases to 494.1 µg g^{-1} and 286.7.3 µg g^{-1}, respectively, in 1990. Concentrations stay relatively high until the middle of the 1990s, after which they decline to the start of the 21st century. During the 21st century, the trends start to diverge with a slight increase in Mn and a decline in Ca. Na concentrations are largely inconsistent with the trends of the other elements, with fluctuations between a low of 128.1 µg g^{-1} in 1995 and a high of 262.2 µg g^{-1} in 1975. All elements are positively correlated on the PCA axis 1 which explains 91.4% of the total variation (Fig. 6.8). There are some relatively minor divergences on PCA axis 2 (4.2%) with Al, Zn, Pb, Zn, Cu having positive scores.

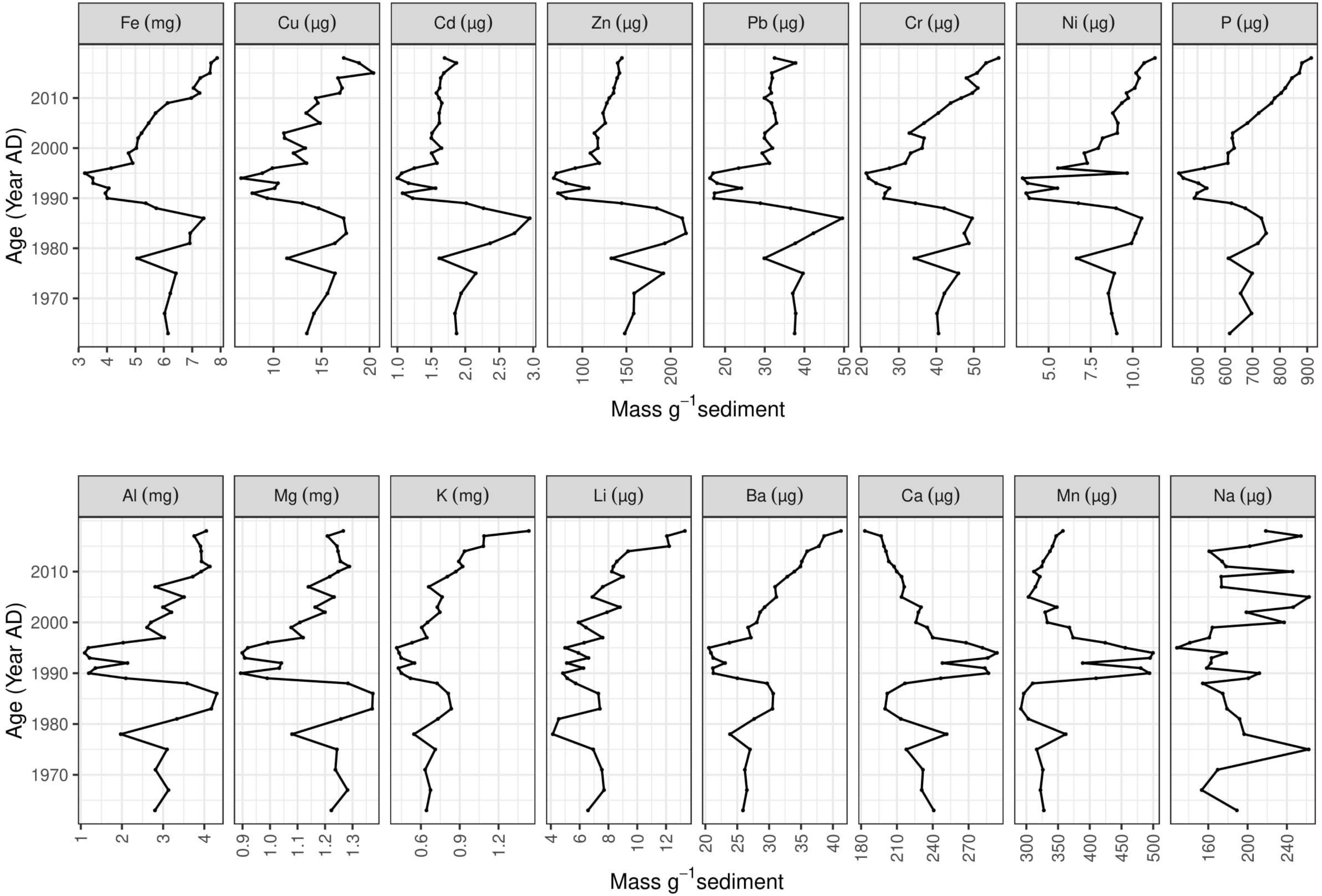

Fig. 6.7 Sunbiggin Tarn sedimentary trace elements.

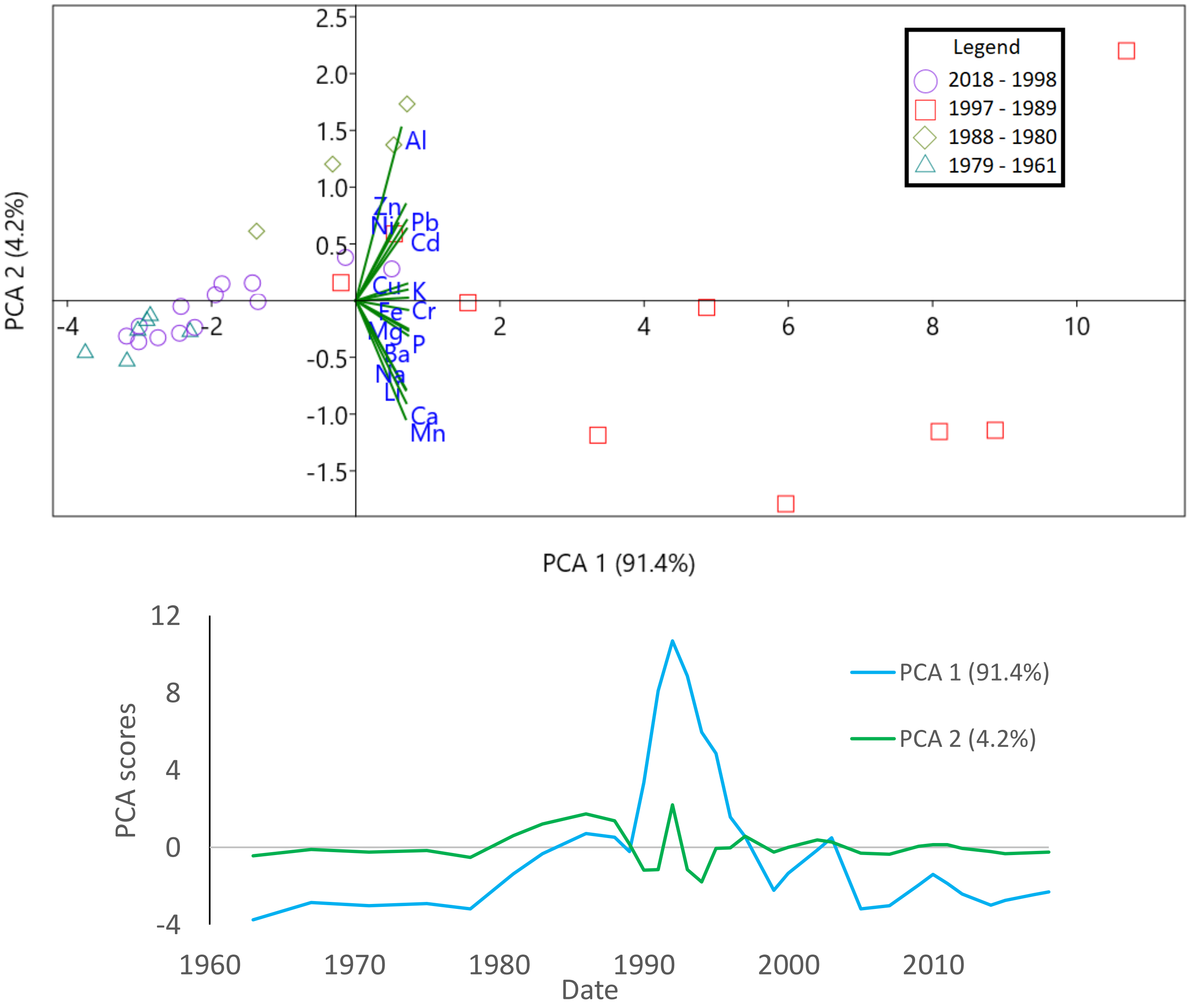

Fig. 6.8 Biplot of PCA scores and graph of change over time for sedimentary trace element concentrations in Blea Tarn.

6.2.4 Sediment C/N mass and stable isotopes ($\delta^{13}C$, $\delta^{15}N$)

Sedimentary %C and %N values slightly decrease from the start of the 1960s (25.9% and 2.3%, respectively), to 20.4% and 1.54% in 1989 (Fig. 6.9a). This is followed by an increase in concentrations of both, with %C increasing to 26% in 1990. This is followed by a decline to 17.8% in 1995. %C and %N both increase for the rest of the time period reaching 30.7% and 2.7% in 2016 respectively. C/N decrease slightly during the 1960s and 1970s before increasing at the start of the 1980s to 12.3 in 1982. C/N continues to increase during the rest of the 1980s, reaching 13.4 in 1990 after which C/N declines to 11.8 in 1992. C/N remains relatively stable to the start of the 21st century with a slight decline during the 2010s to 11.3 in 2016. $\delta^{13}C_{org}$ values increase gradually from −29.2‰ at the start of the 1960s, increasing more rapidly from 1976 to a peak of −28.0‰ in 1981. After this peak, $\delta^{13}C_{org}$ values remain relatively stable through to the middle of the 1990s where the start to decline to the 21st century, reaching a low of −29.9‰ in 2017 and 2018. $\delta^{15}N$ follows a similar trend to $\delta^{13}C_{org}$, increasing from 4.4‰ at the start of the 1960s to 5.2‰ in 1977. The greater increase during the end of the 1970s results in $\delta^{15}N$ values that reach 6.1‰ in 1981, after which they remain relatively high to the start of the 1990s. $\delta^{15}N$ decline from the middle of the 1990s to a value of 4.3‰ in 1998. $\delta^{15}N$ continues to decline during the 21st century reaching a minimum of 2.6‰ in 2018.

6.2.5 Sedimentary pigments

Chlorophyll-*a* concentration remains relatively stable between the start of the 1960s and end of the 1980s, with 311.1 nmole in 1988 (Fig. 6.9c). Chlorophyll-*a* concentrations decline around the start of the 1990s, although with some increased variability, reaching a low of 136.8 nmole in 1994. From the start of the 21st century, the chlorophyll-*a* concentrations increase to 598.5 nmole in 2011 after which it remains relatively stable before increasing to 820.0 nmole in surface sediments. The initial trends in phaeophytin-*a* largely follow that of chlorophyll-*a* with a relatively stable concentration until the end of the 1980s. Phaeophytin-*a* declines from the start of the 1990s, reaching a low of 591.5 nmole in 1994. The phaeophytin-*a* increase from the start of the 21st century is relatively muted in comparison to chlorophyll-*a* which results in an increase in preservation conditions (Fig. 6.9b) increasing largely in line with chlorophyll-*a*. Chlorophyll-*b* increases from the start of the 1960s to the end of the 1980s, before declining from 1989 and the shift to lower values continues to the start of the 21st century with 77.4 nmole recorded in 2000. Concentrations of chlorophyll-*b* increase during the 21st century, largely in line with chlorophyll-*a*. Lutein, zeaxanthin and alloxanthin all share similar trends to chlorophyll-*b*, except the increase in concentrations since the start of the 21st century is less prominent. While diatoxanthin also increases from the start of the 1960s, the concentration largely declines from the end of the decade through the 1970s and 1980s. The decline from the end of the 1980s mirrors that of most of the other carotenoids, however the concentration remains relatively low from the start of the 1990s to the most recent sediments. Canthaxanthin and echinenone concentrations share similar trends to each other but are largely different to the other carotenoids. These concentrations of canthaxanthin and echinenone are largely variable through the time series with a notable increase in concentrations from the middle of the 1990s with 34.1 and 23.6 nmole respectively in 1997. The UV index increases from the start of the 1980s to 34.1 before gradually declining to the start of the 1990s, reaching a low of 3.8 in 1993 (Fig. 6.9b). The UV index increases during the rest of the 1990s and 21st century to a peak of 41.2 in 2018.

PCA axis 1 (55.2%) and PCA axis 2 (24.6%) scores account for almost 80% of the total variance in the pigment dataset (Fig. 6.10). The PCA biplot shows that all pigments are well correlation on PCA axis 1. There is some divergence along the PCA axis 2 with chlorophyll-*a*, echinenone and canthaxanthin having positive values.

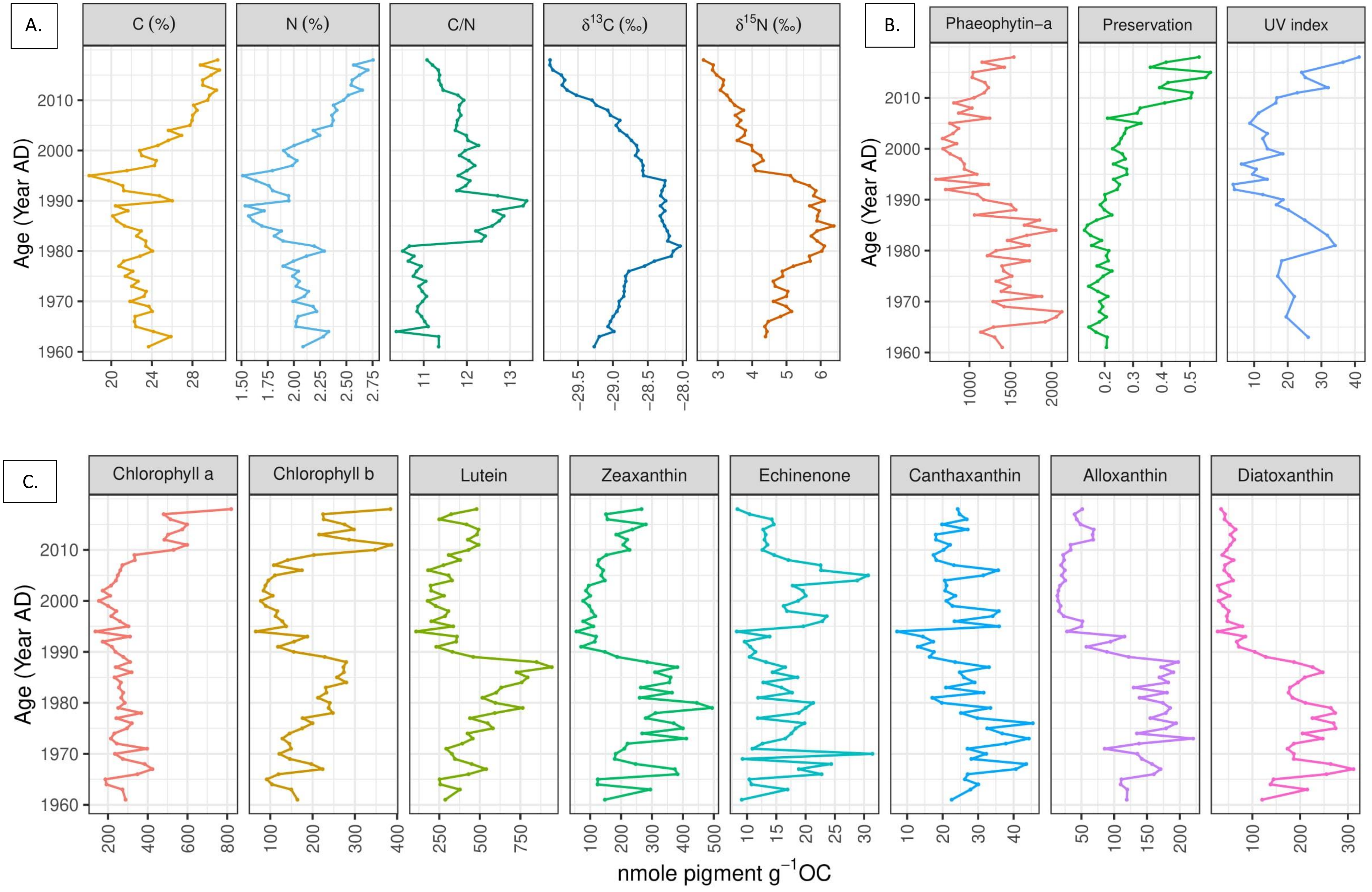

Fig. 6.9 Changes in Sunbiggin Tarn bulk organic C, N and their isotopes (A), pigment preservation condition and UV index (B), sedimentary chlorophylls and carotenoids (C).

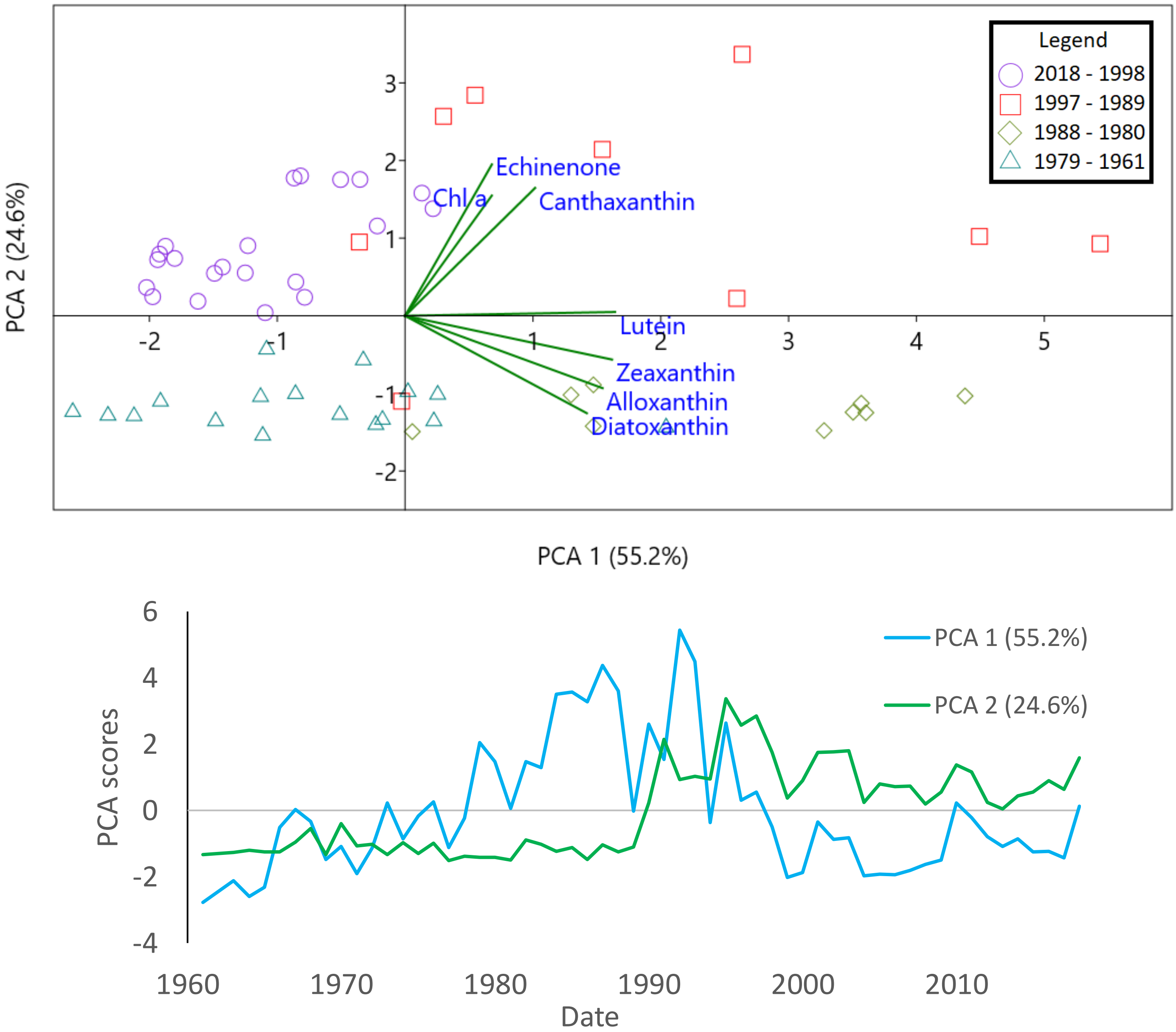

Fig. 6.10 Biplot of PCA scores and graph of change over time for sedimentary pigment concentrations in Blea Tarn.

6.2.6 Stable isotopes ($\delta^{13}C$, $\delta^{18}O$) from carbonates

$\delta^{18}O$ stays relatively stable during the time period, with slight increases from −6.3‰ in 1973, 1985 and 1989 to −6.0‰ in 2003 and 2006 (Fig. 6.11). The $\delta^{18}O$ in the most recent sample of 2012 is the same value as the earlier sample in the time series with a 6.2‰. $\delta^{13}C$ is recorded at −4.3‰ in 1965 and remains at similar values until a relatively rapid decline from 1989 to −5.7‰ in 1991. $\delta^{13}C$ stays relatively low to the middle of the 1990s when it increases to −5.4‰ in 1997 and remains relatively stable, with a slight decline to −5.6‰ in 2012.

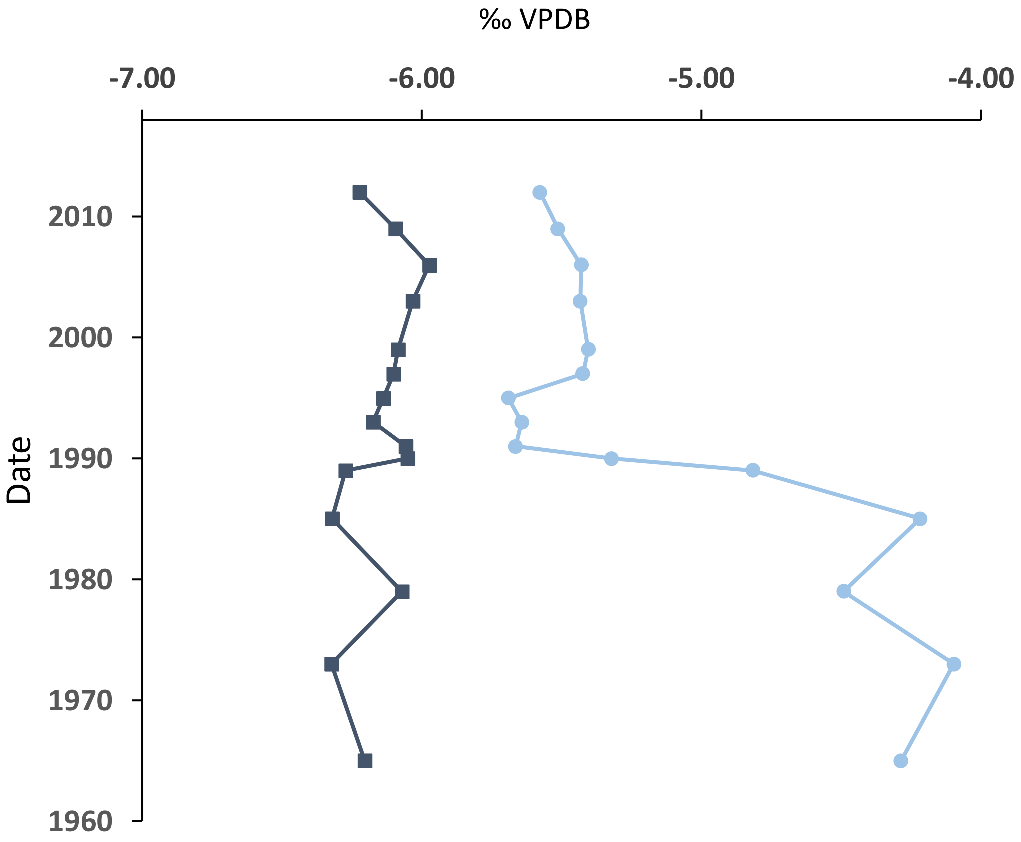

Fig. 6.11 Plot of $\delta^{13}C$ (dark blue) and $\delta^{18}O$ (light blue) change from carbonates in Sunbiggin Tarn.

6.2.7 Regression analysis of meteorological data and sedimentary pigment concentrations

The mean daily maximum temperatures recorded at the Newton Rigg weather station had no significant impact ($p>0.05$, $n=57$) on any of the sedimentary pigment concentrations. The lack of a relationship between pigment concentrations and meteorological data was also apparent for summer temperatures ($p>0.05$, Fig. 6.12) with multiple linear regression also showed there to be no relationship to any of the sedimentary concentrations (Table 6.2).

Table 6.2 Regression analysis statistics (r^2, p value) of sedimentary pigment concentrations at Sunbiggin Tarn with meteorological data from Newton Rigg (n=57).

Pigment	*Temperature*	*Precipitation*	*Temp and Precipitation*
Diatoxanthin	0.03 (p=0.19)	0.05 (p=0.08)	0.07 (p=0.14)
Lutein	0.002 (p=0.77)	0.003 (p=0.21)	0.03 (p=0.46)
Zeaxanthin	0.005 (p=0.60)	0.003 (p=0.20)	0.03 (p=0.43)
Canthaxanthin	0.008 (p=0.50)	0.02 (p=0.36)	0.030 (p=0.44)
Alloxanthin	0.017 (p=0.34)	0.05 (p=0.096)	0.056 (p=0.21)
Chlorophyll-*a*	0.002 (p=0.37)	0.002 (p=0.72)	0.015 (p=0.66)

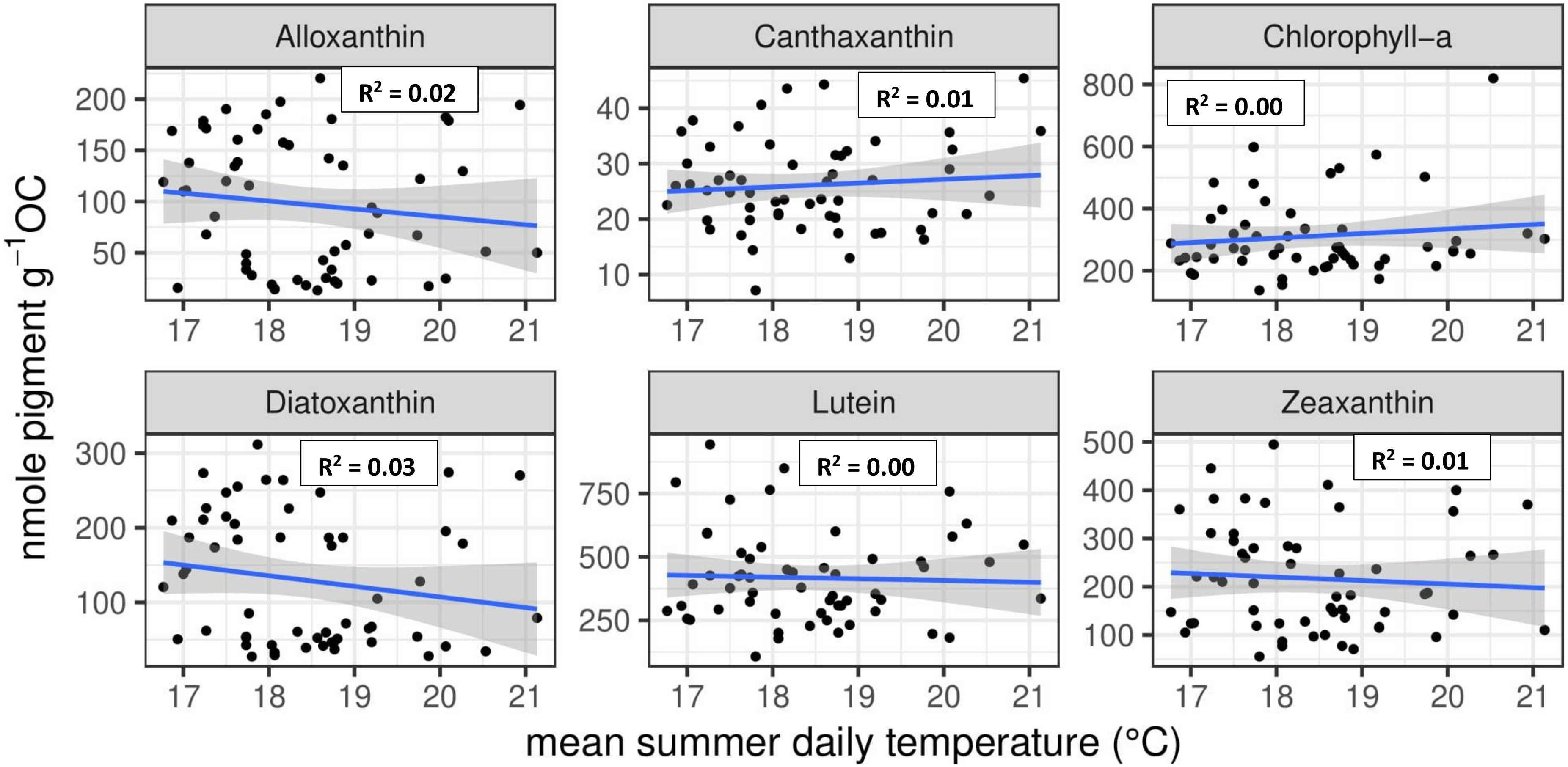

Fig. 6.12 Regression analysis of dated sedimentary pigment concentrations and mean summer daily temperature recorded at Newton Rigg weather station.

6.3 Interpretation

Sedimentation rates vary dramatically through the core, with a period of rapid change during the first half of the 1990s. This change to higher sedimentation rate is positively correlated to the carbonate content of the sediment (r^2=0.63, p<0.0001), which indicates that this change is likely the result of an increase in carbonate deposition between 1989 to 1996. Due to the variable sedimentation rate, flux rates (µg X cm^{-2} yr^{-1}) were calculated for OM (Fig. 6.13), key algal pigments (Fig. 6.15) and trace elements (Fig. 6.14), to account for any dilution effects.

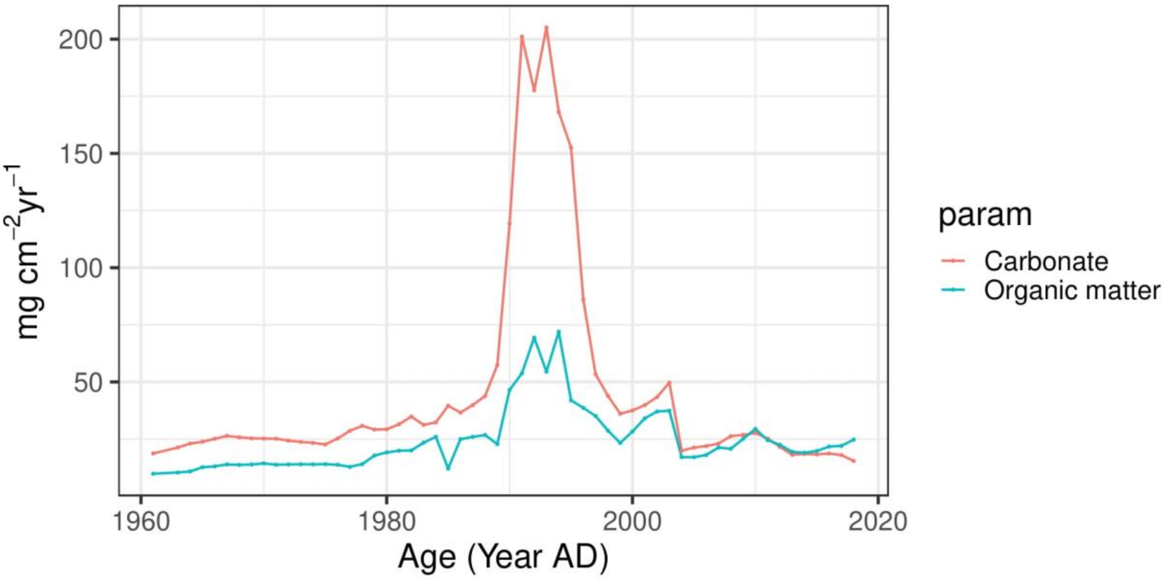

Fig. 6.13 Flux (mg cm^{-2} yr-1) of carbonates ($CaCO_3$) and organic matter to Sunbiggin Tarn sediment.

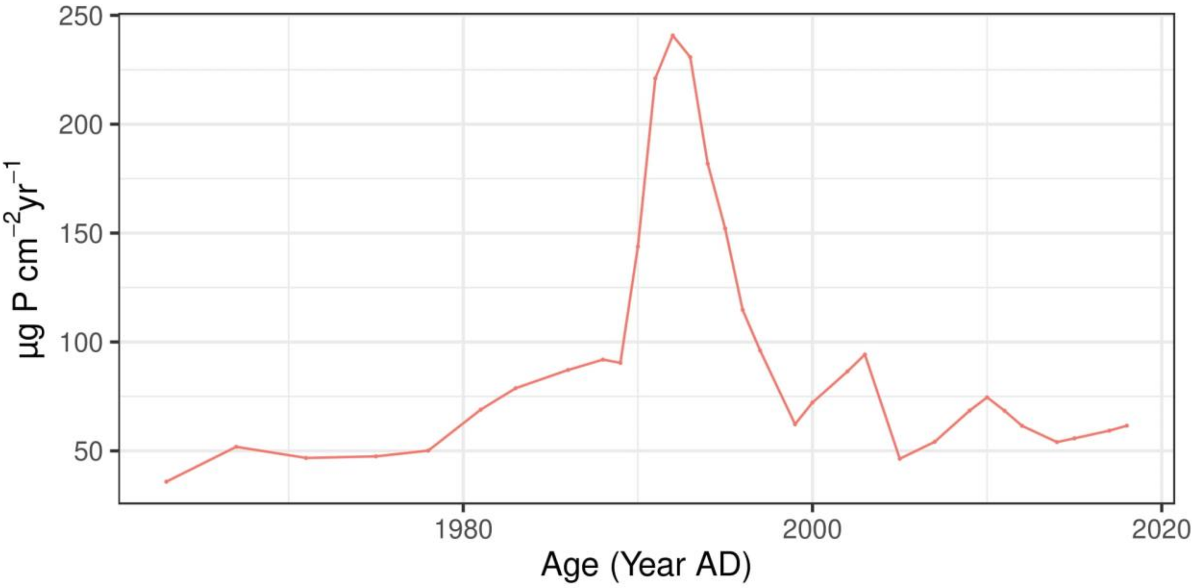

Fig. 6.14. Flux (μg cm^{-2} yr-1) of P to Sunbiggin Tarn sediment.

An increased flux of carbonates to the sediment contributed towards the rapid increase in sedimentations rate from the end of the 1980s. As a result, flux of most elements were highly correlated, for example P flux was particularly highly correlated to Fe ($r^2 = 0.98$), Cu ($r^2 = 0.94$) and Ca ($r^2 = 0.94$). The concurrent increases in flux of all the elements analysed demonstrates that while there is evidence that carbonates were diluting the relative proportions of the other elements in the sediments, the absolute quantities of these elements increased.

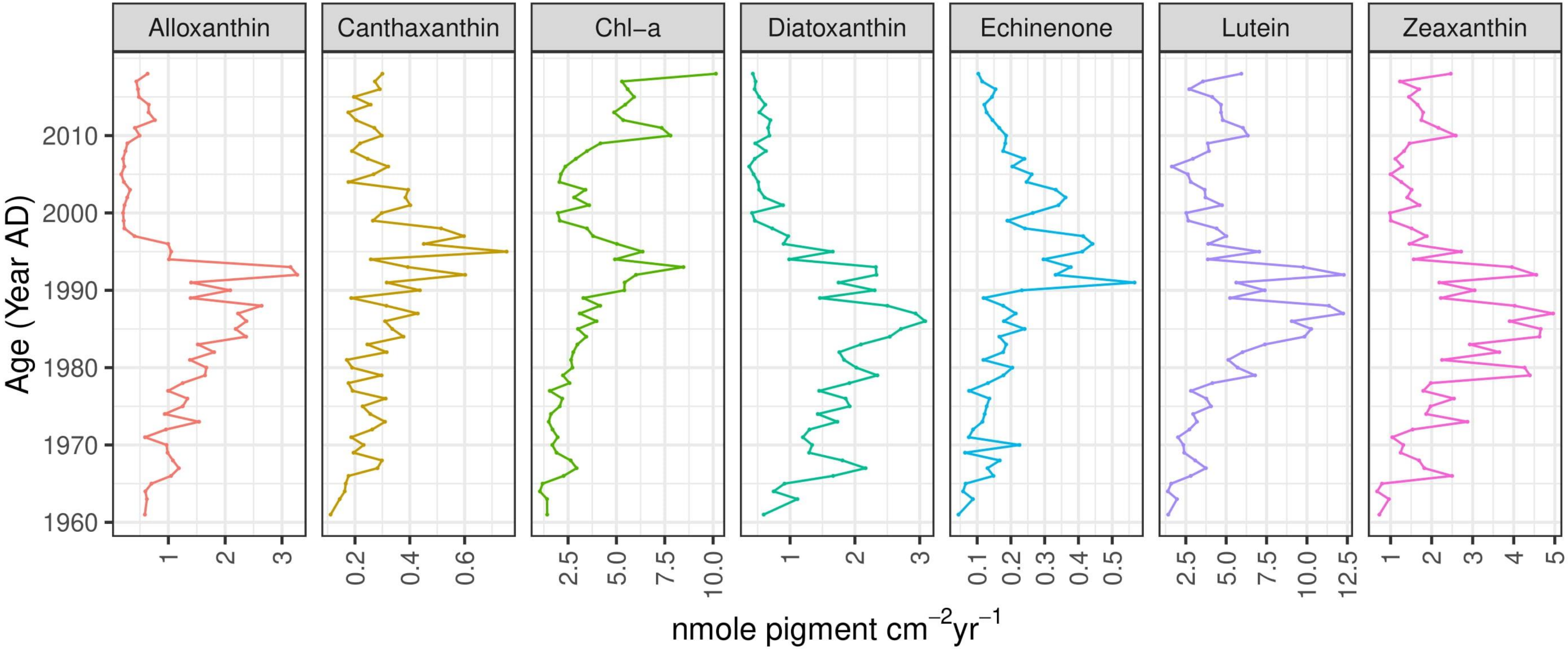

Fig. 6.15 Changes in flux (nmole pigment cm^{-2} sediment yr^{-1}) of key chlorophylls and carotenoids in Sunbiggin Tarn.

6.3.1 δ^{13}C indicating different carbon sources

δ^{13}C$_{org}$ broadly follows the trend in %C although there are some periods which indicate changes in the source of organic matter to the sediments (Fig. 6.16). From the 1960s to the middle of the 1970s there is a slight increase in δ^{13}C$_{org}$ (0.4‰) along with a decline in %C of 1.5%. The increase in δ^{13}C$_{org}$ is relatively small, possibly reflecting some minor changes in catchment derived material, which is supported by a decline in %C during the same period and an increase in chlorophyll-*a* flux potentially indicating a response from enhanced nutrient loading.

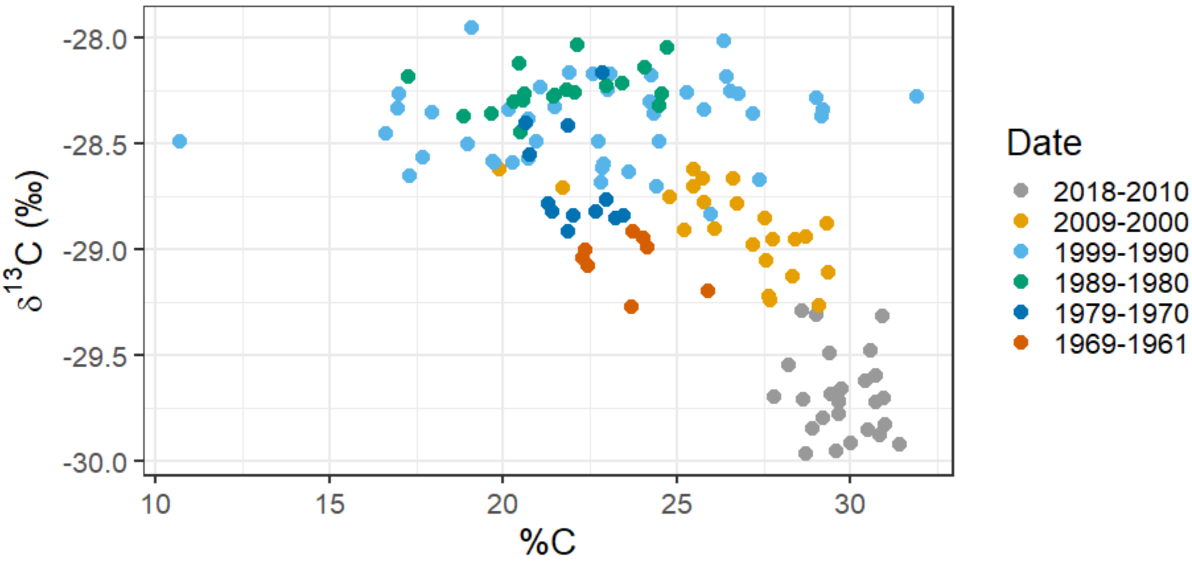

Fig. 6.16 Cross-plot of δ^{13}C$_{org}$ and %C for the Sunbiggin Tarn sediment core.

There is a slightly more rapid increase in δ^{13}C$_{org}$ from 1977 along with a slight increase in %C. This is followed by a relatively rapid shift towards increasing C/N values around the start of the 1980s which could indicate relatively more macrophyte production (Fig. 6.17). The increase in macrophytes may also be indicated by the increase in water clarity from the start of the 1980s. Marl lakes are characterised by their clear waters which enables high macrophyte colonisation at depths (Wiik *et al*., 2015a). However, such a rapid shift in C/N is unlikely to be just related to an increase in macrophyte abundance, especially considering the 1980s was a period of increasing algal production (inferred by increases in pigment flux) which would have contributed lower C/N OM to the sediments. Therefore, the changes in C/N could reflect a period of increased catchment derived inputs, which continues during the 1980s with a progressive increase in C/N.

The period of increased $\delta^{13}C_{org}$, C/N and chlorophyll-*a* flux during the 1980s coincides with the documented rapid increase in black-headed gull populations (Coulson, 1988; Holdgate, 2016). The dramatic increase in gull population would have a large impact on the lake, increasing nutrient inputs due to increased excrement being transported to the lake. Therefore, the expansion of the gull population during this period may have driven the changes in $\delta^{13}C_{org}$ and C/N. The C/N ratio reaches their maximum values during 1989 to 1990 (Fig. 6.17), which is also around the time when the gull population peaks indicating that they may be driving the trends in C/N. The increase in C/N probably reflects the onset of the documented degradation of the surrounding fenland, which would transport increased quantities of organic rich material to the lake.

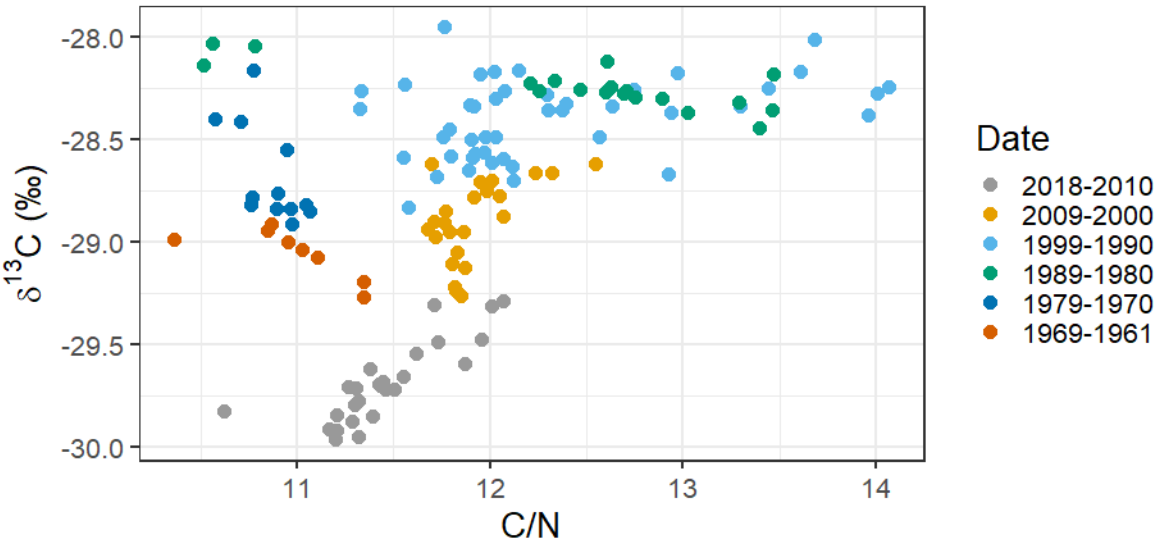

Fig. 6.17 Cross-plot of $\delta^{13}C_{org}$ and C/N for the Sunbiggin Tarn sediment core.

C/N values decline rapidly from the start of the 1990s, driven by a rapid increase in sedimentation rate. Sedimentation rate during this period more than triples, from 0.53 cm yr^{-1} in 1989 to 2.24 cm yr^{-1} in parts of 1991 and remains high until the mid-1990s. A rapid increase in sedimentation rates was also recorded by Goldsmith *et al*. (2003) who reported episodes of very rapid accumulation on top of a baseline of around 1 cm yr^{-1}. While sedimentation rates more than triple, the carbonate content of the sediment increases by ~50%. Considering the rapid expansion of the gull population at Sunbiggin Tarn around the time of the rapid increase in carbonate sedimentation, it might be expected that eutrophication has driven an increase in calcite precipitation. However, there is a strong negative relation between sedimentary Ca and P concentrations (r^2=0.89, p<0.0001). Therefore, the increase in carbonates during this period is likely to be diluting sedimentary P, along with most other elements (e.g. all heavy metals, Mg, Ba). The dilution of P indicates that the additional carbonates are not contributing P to the sediment pool and that the source of carbonates are not, primarily, biogenic calcite. Therefore it is likely that the increase in carbonates are precipitates such as tufa rather than primarily biogenic calcite. There is also strong correlation between Ca and Mn concentrations during the 20th century ($r^2=0.94$, $p<0.0001$). Both Ca and Mn rapidly increase from 1989, coinciding with the period of enhanced sedimentation. The concurrent increases in Ca and Mn during the period of increased sedimentation may suggest that the increased carbonates were derived from Mn-carbonates, possibly reflecting diagenitic processes

The increase in carbonates may represent a terrestrial source, which is supported by an increase in OM flux during the period of enhanced carbonate flux (Fig. 6.13). While there has been an increase in carbonates during this period of enhanced sedimentation, more than half of the sediment is still derived from organic and minerogenic sources. However, there have been even greater increases in non carbonate material to the sediment. Pigment concentrations are expressed to the OM content of the sediment (largely to mitigate against any dilution effects from minerogenic inputs) and they also appear to have been diluted during this period of enhanced sedimentation. The dilution of pigment concentrations suggests that there is also a large non-algal OM source, possibly a terrestrial source.

An increase in terrestrial inputs is likely derived from enhanced inputs from the surrounding fenlands and banks of Sunbiggin Tarn. The cause of such rapid increase in terrestrial material is also likely connected to the extensive black-headed gull populations during the 1980s. Such large gull populations clearly led to degradation to the fen surrounding the Tarn (Fig. 6.3). Sunbiggin Tarn likely experiences a degree of regular bankside erosion as the exposed nature of the site will result in substantial wave action (Goldsmith *et al*., 2003). However, coupled with such extensive degradation of the fenland and bankside by the large gull populations this would likely have enhanced sedimentations rates. The erosion of the immediate fenland and lake bank could have produced the rapid decline in C/N from 1990 to 1992. The C/N values of OM derived from a catchment is largely dependent on the degree of degradation (Rumpel and Kögel-Knabner, 2011). In highly degraded soils C/N values can be particularly low and of similar, or lower, values to those from algal derived material (Paul, 2016). Although there is an indication of an increase in algal pigment flux during the period of rapid sedimentation, it is likely that any in-lake signal is overwhelmed by the increase in allochthonous inputs. Therefore the changes in C/N are more likely to reflect an increase in degraded catchment material as opposed to enhanced algal production.

The $\delta^{13}C_{org}$ values remain largely stable during the 1980s and the first half of the 1990s, which may indicate no major change in the OM source. Considering the large increase in sedimentation during the late 1980s and early 1990s, this may suggest that $\delta^{13}C_{org}$ values at Sunbiggin Tarn are dominated by the $\delta^{13}C$ of the fen material, with increases in quantity having little impact on values. There is more variability in %C during the same period, which would be expected considering the fenland degradation and enhanced sedimentation rates. There are clear outliers during the 1990s, with very low %C during 1994 and a period of higher %C during 1990-1992. The periods of higher %C at the start of the 1900s likely reflects enhanced input of degraded fen material being transported to the lake. This is relatively short lived and %C rapidly declines during the middle of the 1990s, likely representing a reduction in fen erosion. Some of the particularly low %C may also be influenced by seasonality. The sedimentation rate was ~2cm yr^{-1} during parts of the early 1990s. Therefore, the lower %C in some of the samples may reflect some variation in conditions that reduced quantities of catchment material being transported to the lake.

A decline in water clarity at Sunbiggin Tarn is likely to have resulted from the extensive bank erosion. While the UV index has declined from the middle of the 1980s, values decline to record lows from 1989, reaching minimal values between 1992 and 1993. The greater decline in water clarity coincides with the period of enhanced sedimentation, indicating fenland degradation to be controlling water clarity during this period. There is an indication of some improvement in light conditions in Sunbiggin Tarn around turn of the 21st century. Whilst there is some variability at the start of the 21st century, there is a trend of improving water quality to the present, in particular during the 2010s. The more recent improvements in water quality may reflect a combination of improvements to the tarn with declining nutrient loads, the recovery of the fenland or potentially greater *Chara* sp. abundances.

One of the most striking features of the sediments during these periods of enhanced sedimentation are the visible increases in quantities of shell material and many whole snail shells. While this remains unquantified, it appears evident that there was a large increase in the deposition of shell material during this period of enhanced sedimentation. The fenland of Sunbiggin Tarn is known to contain populations of snails, including some particularly rare and endangered species in the UK (*Vertigo geyeri*, *Catinella arenaria;* EN, 1994**).** Therefore, the extensive degradation of the fen and lake bank could have transported large quantities of organic and minerogenic material, along with snails to the lake. This influx of material would then be deposited in the sediments, dramatically increasing sedimentation rates during this period.

The stabilisation of C/N values from 1993 to the end of the 20th century likely reflects the end of fenland degradation and the start of the recovery. This is likely driven by the dramatic reduction in the black-headed gull population, which reduced from 9,000 pairs in 1990 to 1,400 by 1996 (Goldsmith *et al*., 2003). The reduction in gull population may be reflected in the $\delta^{13}C_{org}$, which show a shift towards lower values from 1995. As site observations illustrate, the extent of the fenland degradation persisted for several years after the gulls declined, with the first improvements recorded in 1996 (Fig. 6.3). The noted recovery of the fenland coincides with the period in which sedimentation rates start to decline from a peak of 2.27 cm yr^{-1} in 1993 to 0.87 cm yr^{-1} in 1996. Therefore, the decline in gull populations appears to have reversed the degradation of the fenland.

The decline in $\delta^{13}C_{org}$, C/N and increase in %C from the start of the 21st century may reflect increasing algal productivity. Mean $\delta^{13}C_{org}$ is lower and %C higher during the 2010s (−29.7‰ and 29.8% respectively) than at any other decade during the time series. While this may indicate algal productivity is currently greater than since at the least the 1960s, pigment flux data would indicate this is unlikely to be the case considering the large and rapid increases during the period of enhanced sedimentation. It is more likely that the organics data have been heavily impacted by terrestrial inputs that complicate the use of $\delta^{13}C_{org}$ to indicate relative changes in algal productivity. However the increase in chlorophyll-*a* during the 21st century supports that while $\delta^{13}C_{org}$ may be primarily driven by catchment inputs it is likely to be a period of increasing algal biomass.

While C/N values are generally higher in the 21st century than those recorded in the 1960s and 1970s, this may reflect the recovery of the submerged macrophyte populations or the absence of gull pressure, which are currently at negligible numbers (Holdgate, 2016). Considering the gulls were likely enhancing the loading of catchment material to the lake, their absence may explain the higher C/N values. The more recent shift to lower C/N in the 2010s likely reflects a period of increasing algal productivity, supported by the increase in chlorophyll-*a* flux during this decade. Considering the 21st century is largely absent of the gull pressures that defined the 1980s, the increase in algal biomass indicates an alternative driver for this change.

It must also be noted that $\delta^{13}C_{org}$ values have not been corrected for the Suess effect which can produce progressively more negative values during the second half of the 20th century (Verburg, 2007). However, the relatively small change in $\delta^{13}C_{org}$ suggest that the Suess effect is not a dominant process in this lake.

6.3.2 δ^{15}N indicating different N sources

Changes in δ^{15}N are very similar to that of $\delta^{13}C_{org}$ (Fig. 6.18) with values slightly increasing from the 1960s before increasing more rapidly from 1976 to the start of the 1980s. As with the trend in $\delta^{13}C_{org}$, δ^{15}N likely reflects a change in organic matter source, possibly reflecting an increase in macrophyte abundances or catchment inputs.

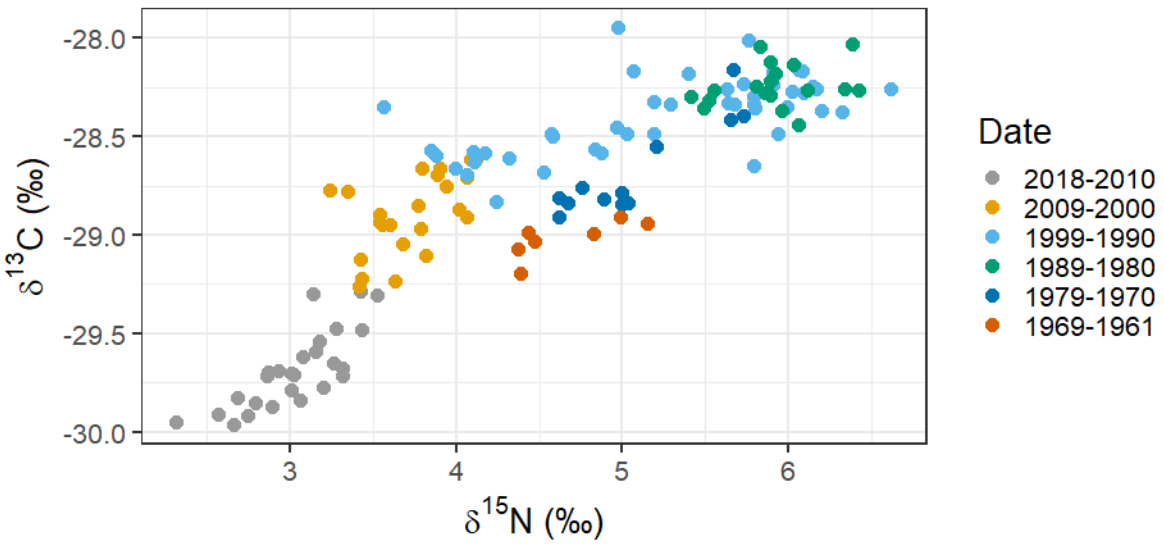

Fig. 6.18 Cross-plot of δ^{15}N and $\delta^{13}C_{org}$ for the Sunbiggin Tarn sediment core.

The changes in nutrient loading to the lake have likely led to a notable impact on the δ^{15}N values. The increases in δ^{15}N (and by extension $\delta^{13}C_{org}$) broadly follow the observed increases in gull population, likely reflecting the changes in gull excrement entering the lake. The gull population explosion occurred after 1975 reaching 10,000 pairs by the 1980s (Holdgate, 2016). The impact of the expanding gull population is further indicated by the P flux, which consistently increases during the 1980s along with most algal pigments. These very large populations coincide with the observed increase in δ^{15}N from 1977 to 1981 with δ^{15}N remaining high through to the end of the 1980s when gull populations peak.

The subsequent reduction in δ^{15}N broadly follows the gull population decline, although possibly with a delay of a few years. There is an indication of a decline in δ^{15}N from 1991 (when gull populations had reduced to 9,000 pairs) although the decline does not become consistent until 1994. A relatively rapid decline in δ^{15}N from 1995-1996 also coinicides with a rapid decline in gull population to 1,400 by 1996 and both δ^{15}N and the gull population continue to decline there after. It is possible, therefore, that the variations in sedimentary $\delta^{15}N$ are reflecting tracking changes in the gull population.

The changes in the gull populations may also be reflected in the elemental data. While there are large declines in almost all elements during the second half of the 1980s, this likely reflects dilutation from carbonates and fen material. As a result, the flux of heavy metals (e.g. Cu, Cd, Zn, Pb) increase rapidly from the start of the 1990s, along with the increase in sedimentation. Prior to this period, heavy metals flux had been increasing from the start of the 1980s. The increase in these heavy metals may reflect enhanced inputs from the expanding gull population at the time, either directly through excrement or thorugh enhanced catchment erosion. Therefore the gulls around Sunbiggin Tarn would likely have been driving a relatively large proportion of the loading in trace elements to the lake, prior to the 1990s. Following the collapse of the gull populations, the flux of sedimentary heavy metals decline to lower values, with Cd and Zn flux in the 21st century ~61% and ~50% lower, respectively, than in the 1980s.

$\delta^{15}N$ continues to decline after the gull population reduces to negligible numbers by the start of the 21st century (Goldsmith *et al.*, 2003). The continued decline in $\delta^{15}N$ after the gull populations decline to negligible numbers could represent the relatively slow recovery of the tarn from eutrophication. With the immediate catchment so heavily polluted by the extensive gull populations, high nutrient loading to lake may have persisted for many years after the gull populations declined. Despite the potential for marl lakes to recover more rapidly than non-calcareous lakes, the continual decline in in lake water TP indicates that Sunbiggin Tarn may still be recovering from the extensive eutrophication during the 1980s.

It is possible that the sediments of Sunbiggin Tarn are anoxic, which is supported by the complete absence of purpurin-18-phytyl ester in any section of the sediment core. This chlorophyll transformation product is formed in the presence of oxygen during the early stages of chlorophyll diagenesis (Naylor and Keely, 1998). There is a strong correlation between Fe and P concentrations ($r^2=0.91$, $p<0.0001$), which may represent a high proportion of P bound to Fe. Anoxia can drive the re-release of Fe-bound P, which may lead to enhanced bottom water P concentrations. However, the relationship of many elemental concentrations are likely to be heavily confounded by dilution, driven by inputs from catchment material.

Whilst the decline in $\delta^{15}N$ is likely to reflect the reduction in the gull population, there may be additional drivers to the decreasing $\delta^{15}N$ values during the 21st century. Along with a recovery from eutrophication, the concurrent decline in $\delta^{13}C_{org}$ and $\delta^{15}N$ during the 21st century could reflect an increase in algal biomass (Meyers and Teranes, 2001). The decreasing trend may also be amplified by low N availability in Sunbiggin Tarn, as low δ^{15}N can often be symptomatic of N limitation (Jones *et al*., 2004). Along with this, some of the decline in δ^{15}N may be driven by diagenesis and the preferential transformation of N bearing compounds. However, δ^{15}N values increase ~1.5‰ within the first 22 years after burial and ~3.5‰ after 28 years, much larger than the 1-2‰ expected from diagenesis alone (Brahney *et al*., 2014). In addition, the trend in δ^{15}N closely follows that of δ^{13}C$_{org}$, which is not substantially impacted by diagenesis. Therefore, it seems unlikely that diagenesis is a primary driver of the observed change in δ^{15}N.

6.3.3 Total algae (chlorophyll-*a*, phaeophytin-*a*)

While chlorophyll-*a* concentrations experience little overall change between the 1960s to the end of the 1980s, the doubling of chlorophyll-*a* flux rate, to 3.3 nmole in 1989, indicate that total algal biomass has increased substantially over the same time period (Fig. 6.19). This is also shared by the trends in phaeophytin-*a* indicating a progressive increase in lake algae, such as between the 1970s to 1980s increasing to 221.5 nmole in 1989 (Fig. 6.20).

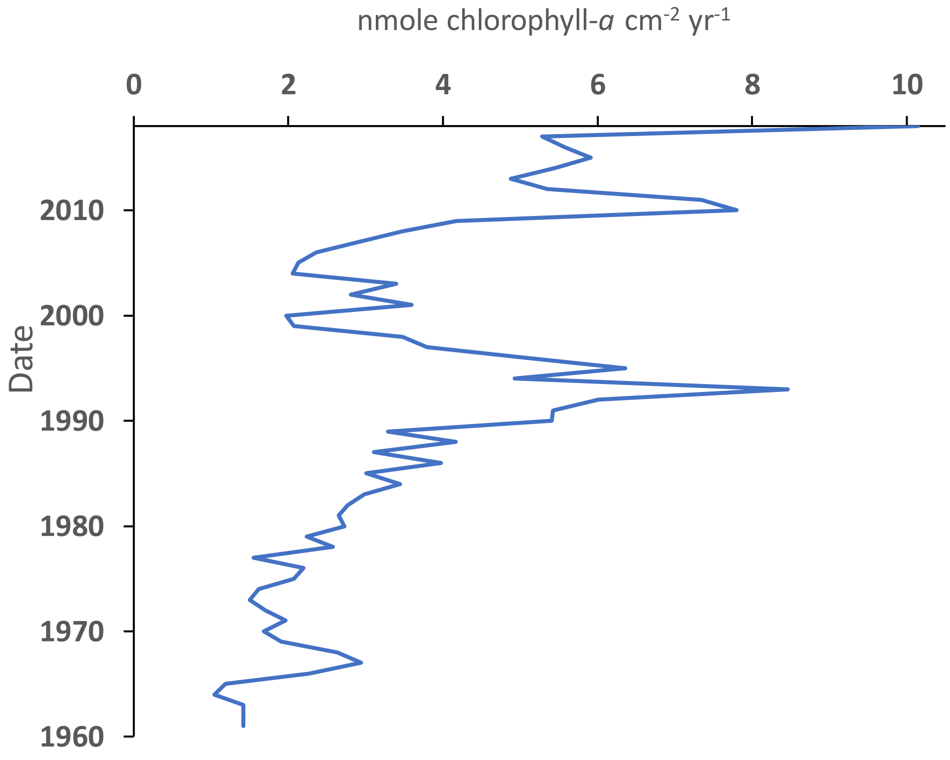

Fig. 6.19 Chlorophyll-*a* flux to Sunbiggin Tarn sediments.

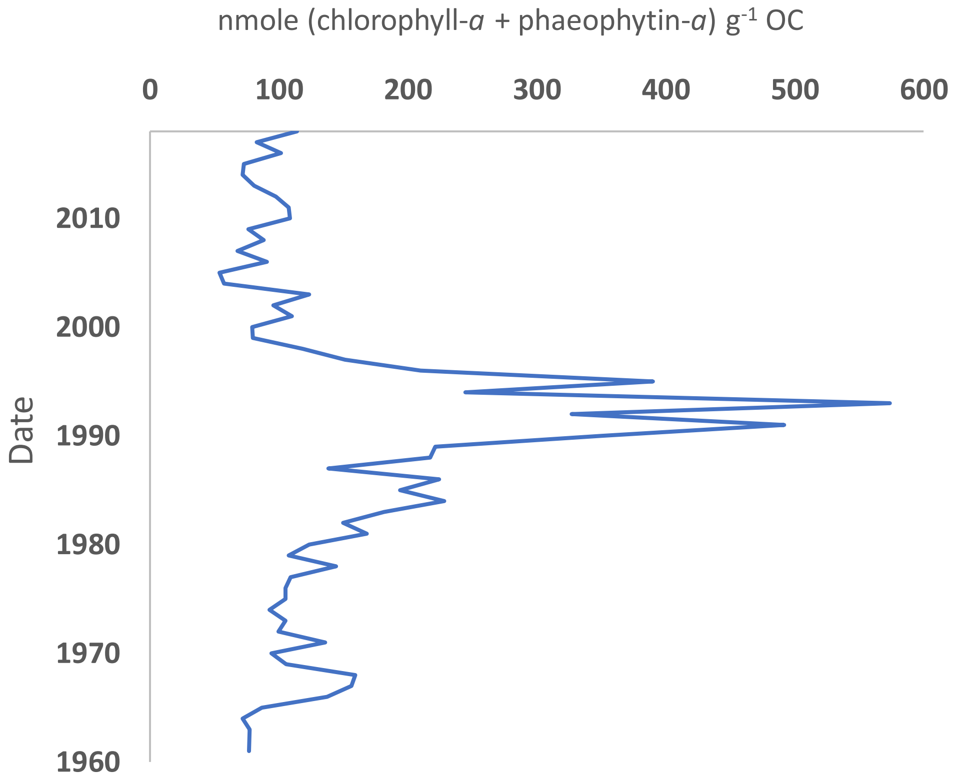

Fig. 6.20 Chlorophyll-*a* and phaeophytin-*a* flux to Sunbiggin Tarn sediments.

Chlorophyll-*a* (Fig. 6.9c) and phaeophytin-*a* concentrations (Fig. 6.9b) largely follow opposite trends to flux of these pigments during the 1970s and 1980s. This divergence likely reflects increasing contributions of catchment derived OM. Terrestrial OM would be largely absent of pigments as most of them will be degraded in the catchment or before they reach the sediment (Leavitt, 1993). Considering chlorophyll-*a* and phaeophytin-*a* concentrations are corrected for the organic content of the sediments, increased terrestrial OM would dilute their concentrations. Therefore, the dilution of pigment concentrations from terrestrial OM would largely obscure the increase in algal biomass. The progressive increase in total algal biomass from the 1960s to the end of the 1980s probably reflects the impact of the expanding gull population. The gulls would have directly increased nutrient and sediment loading to the tarn which is likely to be reflected in the increase in P flux during the 1980s. In comparison to the P flux associated with the period of enhanced sedimentation, the impact from the gulls is relatively minor. Therefore, while direct nutrient inputs from bird excrement have likely had a large impact on nutrient loading to the lake, the impact from catchment erosion was of a much greater magnitude, albeit over a reduced time frame. In general, the 1960s to the end of the 1980s represents a progressive increase in algal biomass in Sunbiggin Tarn, driven by increased nutrient loading from the growing gull population.

The declining water clarity from the middle of the 1980s (Fig. 6.9b) occurs at least 5 years before the period of increased sedimentation. At the same time the flux and concentrations of algal pigments continue to increase, indicating that the lake may have been progressing towards a more turbid state following the enhanced nutrient loading of the 1980s. While eutrophication of the tarn by the gulls was relatively gradual, the rapid increase in sedimentation of fenland material would have had a dramatic and rapid impact. As the fenland itself was likely to be heavily polluted by the extensive gull population this would have resulted in a dramatic increase in nutrient loading to the tarn at the time. P flux shows that the period of enhanced sedimentation resulted in a tripling of P delivered to the sediment (Fig. 6.14). Both chlorophyll-*a* and phaeophytin-a flux show that from 1989 there is a rapid, but relatively short-lived increase in algal biomass to a peak in 1993, with these pigments returning to lower quantities by 1997. The rapid increase in chlorophyll-*a* and phaeophytin-*a* flux coincides with the changes in sedimentation rate. Therefore, it is likely that the period of rapid sedimentation led to an equally rapid increase in algal biomass, although this was relatively short lived.

Along with the rapid increase in catchment inputs and algal biomass, there is a concurrent reduction in water clarity, with minimum values of the UV index in 1993. The shift from relatively clear waters to low water clarity and high algal biomass was rapid, driven by the increase in sedimentation. However, there were indications that during most of the 1980s the shift to a more turbid phytoplankton dominated state was already occurring, although at a slower pace. Therefore it is possible that the rapid sedimentation from the end of the 1980s accelerated the shift towards a phytoplankton dominated turbid state.

Considering the rapid reductions in water clarity and increases in total algal biomass, it is likely that planktonic biomass increased to such an extent that it masked any benthic losses during this period. The decline in water clarity along with the rapid increase in phytoplankton indicates more turbid conditions. This indicates that Sunbiggin Tarn had shifted to another ecological state during this period. Such shifts can occur rapidly in marl lakes as a result of disturbance events, such as a rapid increase in sedimentation (Connell and Sousa 1983) and extensive nutrient loading (Wiik *et al*., 2015b). Prior to the rapid increase in sedimentation, nutrient loading was likely particularly high (as indicated by observed gull populations and high $\delta^{15}N$). However, it is likely that any threshold response occurred largely through the input of catchment material. Considering an extensive area of the fenland was used by the gulls to roost, the fenland would have experienced substantial eutrophication (Holdgate, 2016). Therefore, a rapid increase in allochthonous inputs from a heavily polluted fenland would be expected to deliver an increase in nutrients to the lake. As a result, these additional nutrients could stimulate algal biomass to such a magnitude where the lake shifts towards a turbid state.

Following the period of rapid sedimentation there were declines in total algal biomass to 79.9 nmole in 1999, indicating a reduction in nutrient loading. The black-headed gull population has remained low since the start of the 21st century, with only 46 pairs recorded in 2000 (Goldsmith *et al*., 2003). However, since the start of the 2010s, there has been an increase in chlorophyll-*a* flux. While the larger impacts of the gull derived eutrophication ended around the turn of the 21st century, the continual decline in $\delta^{15}N$ and P flux indicates that the lake may still be recovering from eutrophication. P flux in the 2010s is slightly higher than in the 1960s and 1970s, which may indicate P loading to tarn is still elevated. Therefore, it is likely that the heavily eutrophicated tarn catchment has continued to supply Sunbiggin Tarn with elevated nutrient concentrations long after the gull populations had declined.

The 21st century increases in chlorophyll-*a* flux to 7.8 nmole in 2010 occurs with increased lutein and zeaxanthin and small increases in alloxanthin. This indicates that chlorophytes are likely to be the predominant contributor the increase in algal biomass. However, the increase in chlorophyll-*a* flux is greater than the other algal pigments and there is no concurrent increase in phaeophytin-*a*. The lack of increase in phaeophytin-*a* indicates that it may reflect more of a habitat shift than an increase in total algal biomass. Therefore it is possible that the increase in preservation conditions during the 21st century (Fig. 6.9b) represents greater benthic production. A greater proportion of benthic production during the 21st century may be a response to the increase in water clarity (Fig. 6.9b). In clear water shallow lakes, benthic algae often dominate primary production (Vadeboncoeur *et al*., 2008). Therefore, any increases in water clarity are likely to impact on the benthic environment, resulting in a greater colonisation depths and production for benthic algae (Pukacz et a., 2014; Reuss *et al*., 2009). Therefore, considering the decline in nutrient concentrations and increasing water clarity, the increase in chlorophyll-*a* flux during the 21st century may primarily be driven by benthic taxa.

There was no correlation between chlorophyll-*a* concentrations and summer temperatures, with variations in chlorophyll-*a* clearly heavily impacted by eutrophication and physical disturbance. Considering the nutrient loading and rapid increase in sedimentation experienced in Sunbiggin Tarn, it seems likely that any climate impact is largely being obscured in this lake. Typically, lakes that have been subjected to high anthropogenic nutrient inputs often have a muted signal of climate impact

(Leavitt *et al*., 2009). It is possible, however, that the increase in chlorophyll-*a* flux during the 21st century may be related to climate warming, as increased summer temperatures can create more favourable conditions for phytoplankton growth (Dupuis *et al*., 2009; Whitehead *et al*., 2006).

There was also no detectable impact of precipitation on algal biomass in Sunbiggin Tarn despite observations of water level fluctuations (WLF). An observed rise of 30-40cm above the minimum in June was recorded after two days of heavy rain in 1953 (Holdgate, 2016). In 2008 the water level was higher by approximately 0.5 m due to recent heavy rainfall (Bennion *et al*., 2009). Water clarity has been increasing since the 2010, which may be related to increased WLF. However, it is most likely to be due to changes in DOC concentrations. In general, catchment exports of OM vary depending on vegetation cover, air temperature and runoff (Hope *et al*., 1994; Tranvik and Jansson, 2002). Considering the recovery of the fenland and macrophyte community, along with reductions in nutrient loading to Sunbiggin Tarn, improvements in water clarity is an expected response.

6.3.4 Diatoms (diatoxanthin)

The increase in diatom flux from 1.1 nmole in 1963 to 3.1 nmole in 1986 indicates an expanding diatom biomass during this period (Fig. 6.21). This increase likely reflects the positive impact from the expanding gull population delivering greater quantities of nutrients to the lake. There is also a large spike in diatoxanthin flux in 1967 of 2.2 nmole which is present in most other algal taxa, including chlorophyll-*a*. However, the increase in diatoxanthin flux is of greater magnitude than the other taxa which may indicate a greater expansion of benthic taxa. An expansion of benthic taxa is supported by the relatively muted response of cryptophytes during this same period. The increase in diatoms may also reflect a greater macrophyte coverage, providing a greater habitat area for some diatom taxa. Sunbiggin Tarn has populations of *Amphora pediculus* which attach themselves to hard surfaces, such as the reed stems of macrophytes (Goldsmith *et al*., 2003). Therefore, increased nutrient loading may also be stimulating diatom biomass indirectly, through enhanced growth of some macrophyte species. In general, it is likely that the combined impacts of changes in macrophyte abundance and nutrient availability have increased diatom biomass in Sunbiggin Tarn between the 1960s and 1980s.

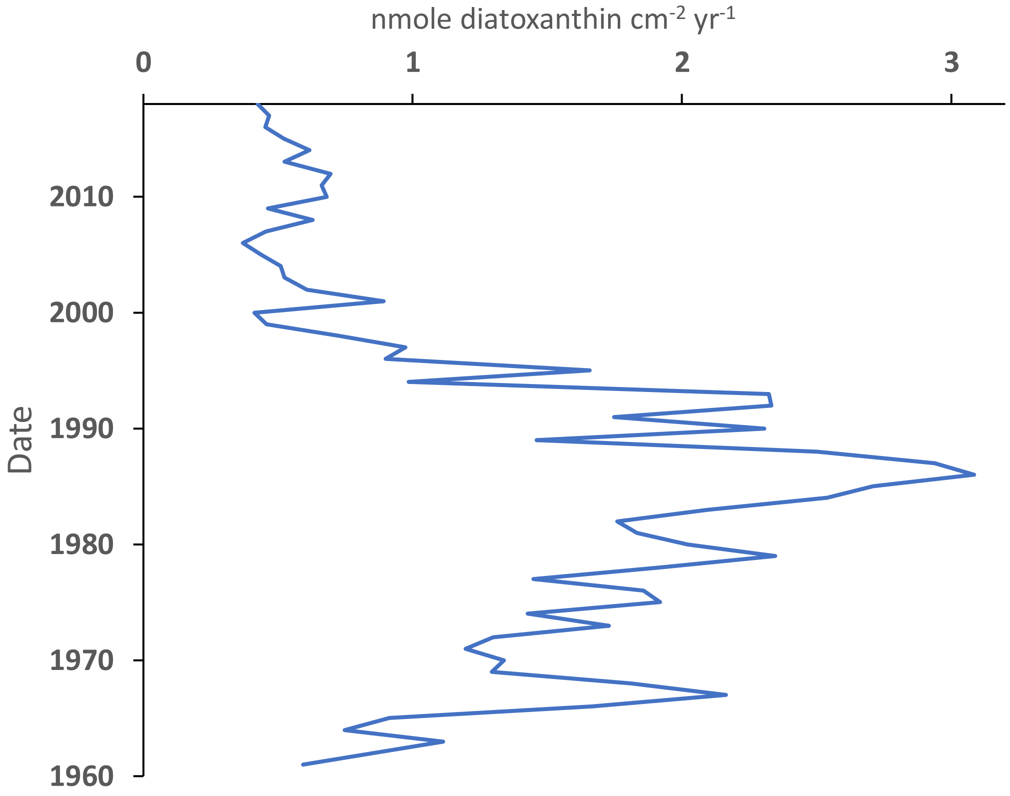

Fig. 6.21 Diatoxanthin flux to Sunbiggin Tarn sediments.

While changes in water clarity typically have an impact on diatom growth, it does not appear to have an overriding control in Sunbiggin Tarn during this period. While the UV index is recorded at a coarser resolution, the trend is largely variable up to the start of the 1980s where there is a notable increase. The apparent lack of influence on diatom biomass of water clarity may suggest that it remained high enough not to restrict diatom growth. While water clarity between the 1960s and the start of the 1980s has likely increased, the variability and relatively few data points make this assessment uncertain. However, there has likely been a substantial increase in nutrient concentrations in the tarn during the same period, indicating it to be a dominant driver of increased diatom biomass.

The 1980s is a period of sustained decline in water clarity in Sunbiggin Tarn, likely reflective of the enhanced algal biomass and allochthonous inputs. Diatoxanthin flux continues to increase to a concentration maximum in 1986 and then declines throughout the rest of the decade. Therefore, it is unlikely that water clarity at the start of the 1980s was impacting diatom biomass, although it is possible that it started to by the end of the decade. A decline in both diatoxanthin flux and water clarity continues into the 1990s, with water clarity reaching lows around 1992-1993. This is a period of rapid increase in algal biomass in Subiggin Tarn, indicated by the peak in chlorophyll-*a* flux. In contrast, the response of diatoxanthin during this period is relatively muted with the lowest increase out of any of the algal pigments to 2.3 nmole.

The muted increase during this period may reflect a suppression in benthic taxa as a result of severe reduction in light availability. The increase in diatoxanthin flux, while lower than the peak in the late 1980s, may reflect some planktonic taxa that responded positively to the increase in nutrients and were still able to maintain adequate light conditions for growth. Planktonic diatoms may have been stimulated by a rapid increase in nutrient loading, that would have been offset by the loss of benthic taxa. Therefore the period of rapid sedimentation may represent a habitat shift, from relatively more benthic to planktonic diatom taxa. The shift towards more planktonic taxa is supported by the rapid increases in cryptophyte flux during the early 1990s.

Diatoxanthin flux declines from the second half of the 1990s, in line with total algal biomass and most other algal taxa, to 0.4 nmole in 2000. This likely reflects the recovery of the fen and reductions in OM and nutrient loading. By the start of the 21st century, diatoxanthin flux had reduced to comparable values to those recorded from the start of the 1960s. This may indicate the recovery of the tarn to conditions prior to the expansion of the gull population. While the improvement in water clarity during the 2010s likely reflects the tarn retuning to a more benthic dominated system, diatom abundances have not recovered. Both the flux and concentrations of diatoxanthin continue to remain low during the entirety of the 21st century, while total algal biomass increases. The lack of response in diatom biomass to improvements in water clarity during the 21st century may indicate a return to conditions more similar to those experienced during the 1960s and 1970s, with comparable diatom biomass and an apparent lack of control from changes in water clarity.

Diatom biomass during the 21st century is lower than during the start of the 1960s. Additionally, as with the 1960s and 1970s, water clarity improvements during the 21st century do not appear to be impacting diatom biomass. Therefore the lower diatom biomass in Sunbiggin Tarn during the 21st century is likely controlled by other factors, such as nutrient availably and submerged macrophyte type or cover. Low abundances of diatoms may reflect the availability of Si in the tarn. During the growing season, recorded SiO_2 concentrations have been low in Sunbiggin Tarn, with most months <1 mg L^{-1} (Environment Agency, 2008). This likely reflects the limestone catchment of the tarn, delivering limited Si to the waters. Although the impact from the gull and catchment pressures makes the assessment of the impact of climate change difficult, it is possible that more recent changes represent the impact of increased temperatures. Enhanced temperatures may have increased the colonisation range of other algal taxa, providing increased competition for diatoms suppressing their growth.

6.3.5 Cryptophytes (alloxanthin)

Alloxanthin flux increases substantially from the start of the 1960s to 2.4 nmole in 1984 (Fig. 6.22), indicating a similar increase in biomass to that of diatoms, most likely indicating that enhanced nutrient loading was having a broadly positive impact on lake algae. The increase in cryptophytes during this period indicates an expanding planktonic community. Compared to the relatively muted increase in total algal biomass, this suggests that enhanced nutrient loading resulted in a habitat shift leading to greater proportions of planktonic taxa. The trend of increasing cryptophyte biomass in Sunbiggin Tarn suggest that eutrophication was progressive, likely reflecting the expansion of the gull population. Coupled with the relatively long WRT of Sunbiggin Tarn, high nutrient concentrations would have been maintained allowing for algal blooms to develop.

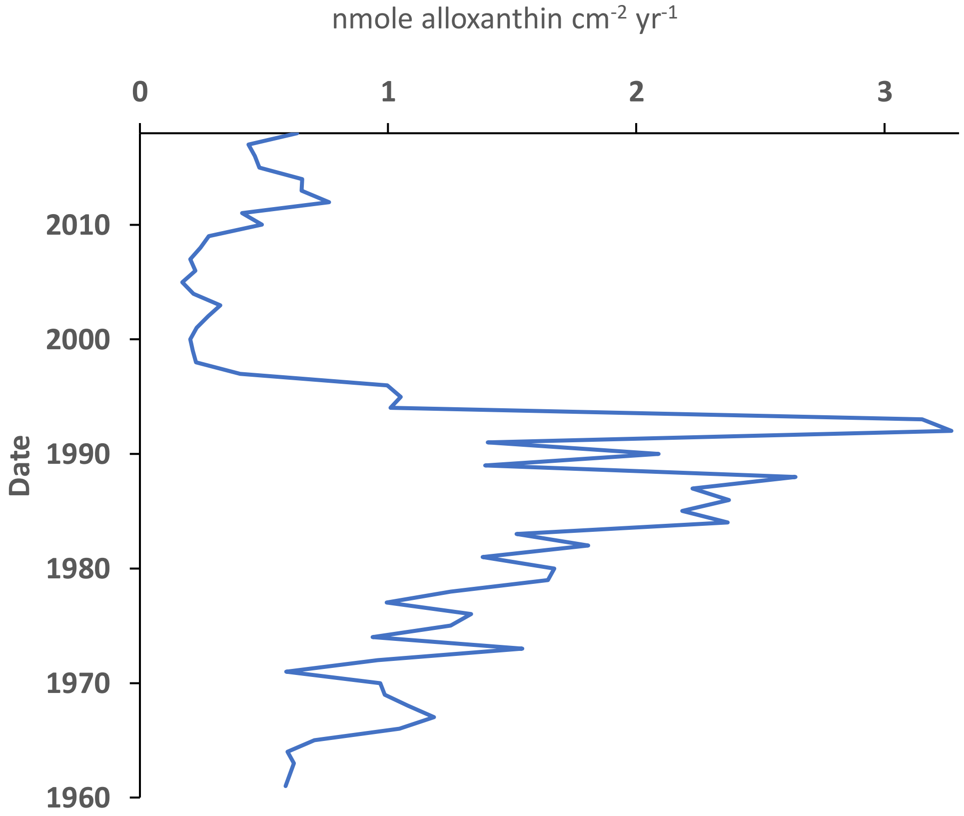

Fig. 6.22 Alloxanthin flux to Sunbiggin Tarn sediments.

The expansion of cryptophyte biomass occurs alongside declining water clarity during the 1980s. This could represent the phytoplankton community starting to have an impact on light availability, shading benthic environments (Paerl and Huisman, 2009). A reduction in light reaching the benthic zone can inhibit the growth of benthic algae and submerged macrophytes (Paerl and Huisman, 2008). A decline in the concentrations of diatoxanthin and canthaxanthin indicates that there may have been a reduction in benthic taxa during the 1980s, although the flux of these pigments increased. This likely reflects a shift towards greater proportions of phytoplankton while the overall lake productivity increases.

Following a brief decline in alloxanthin flux from the start of the 1990s there is a short-lived but rapid increase in to 3.3 nmole in 1992. This increase occurs at the same time as the relatively muted increase in diatoxanthin flux, potentially indicating that cryptophytes were outcompeting diatoms during the spring growing season. The peak in alloxanthin flux coincides with the peak in chlorophyll-*a* flux, which indicates that during this period of extensive catchment input cryptophytes were substantial contributors to the OM pool. The greater response of cryptophytes compared to most other algal taxa during the early 1990s likely reflects the low light availability at the time. As indicated by the UV index, light availability was probably reduced in the early 1990s and this would have favoured motile taxa which can migrate to parts of the lake with more optimal UV conditions. In addition, a large increase in OM would provide an enhanced energy source for the cryptophytes, providing them with a competitive advantage over diatoms.

For Sunbiggin Tarn, it is likely that the early 1990s represented more turbid conditions and potentially a shift in lake state induced by the rapid catchment erosion and eutrophication. While the rapid increase in algal production was relatively brief, the UV index indicates that these more turbid conditions lasted for around decade, recovering from the lowest values by the end of the 20th century. In such conditions, the algal community is typically dominated by planktonic taxa. However, whether Sunbiggin Tarn was dominated by planktonic taxa during this period is uncertain. High abundances of benthic organisms are often a feature of marl lakes, which are characterised by their extensive macrophyte abundances and high water clarity.

Following the shift towards greater pelagic production, subsequent to the period of enhanced eutrophication and sedimentation, there is a rapid decline in alloxanthin flux from the middle of the 1990s. By the end of the 20th century, alloxanthin flux had stabilised at values comparable to those experienced at the start of the 1960s with 0.2 nmole in 1998. This rapid return to levels of cryptophyte biomass prior to the expansion of the gull population may reflect a relatively rapid recovery of the lake and its algal community.

The decline in cryptophyte biomass may indicate that environmental conditions in the lake had returned to those more reflective of a benthic system. However, the delayed increase in water clarity suggests that it is likely to be driven by a decline in nutrient and OM loading. The lower stable cryptophyte biomass at the start of the 21st century indicates that the tarn had returned to a more stable condition. There are signs of increasing cryptophyte biomass during the 2010s with 0.8 nmole in 2012, however the increase in alloxanthin flux is relatively muted compared to lutein and zeaxanthin. The muted increase in alloxanthin, with a period of increasing UV index indicates Sunbiggin Tarn has likely become increasingly dominated by benthic taxa during the 21st century.

6.3.6 Chlorophytes (lutein and chlorophyll-*b*)

Lutein flux increases from the 1960s to 10.3 nmole in 1985 (Fig. 6.23), similar to the trends with zeaxanthin and alloxanthin. The change in lutein flux is notably more pronounced than the change in chlorophyll-*a* flux, which may reflect that the increase in chlorophytes is caused predominantly by increases in planktonic taxa. It appears that chlorophytes were progressively becoming more dominant in Sunbiggin Tarn during this period. This is particularly notable during the 1980s, when concentrations of most other pigments stabilise (alloxanthin) or slightly decline in concentration (diatoxanthin, zeaxanthin), lutein continues to increase to peak at concentrations of 12.3 nmole in 1987. With other pigment concentrations remaining stable or slightly declining during the 1980s, this could represent a degree of growth suppression by chlorophytes. While this could result from high nutrient uptake, it may also occur through shading by an extensive chlorophyte biomass (Vadeboncoeur *et al*., 2008). Shading by algae is supported by the decline in the UV index during the 1980s, many years before the rapid sedimentation of catchment material.

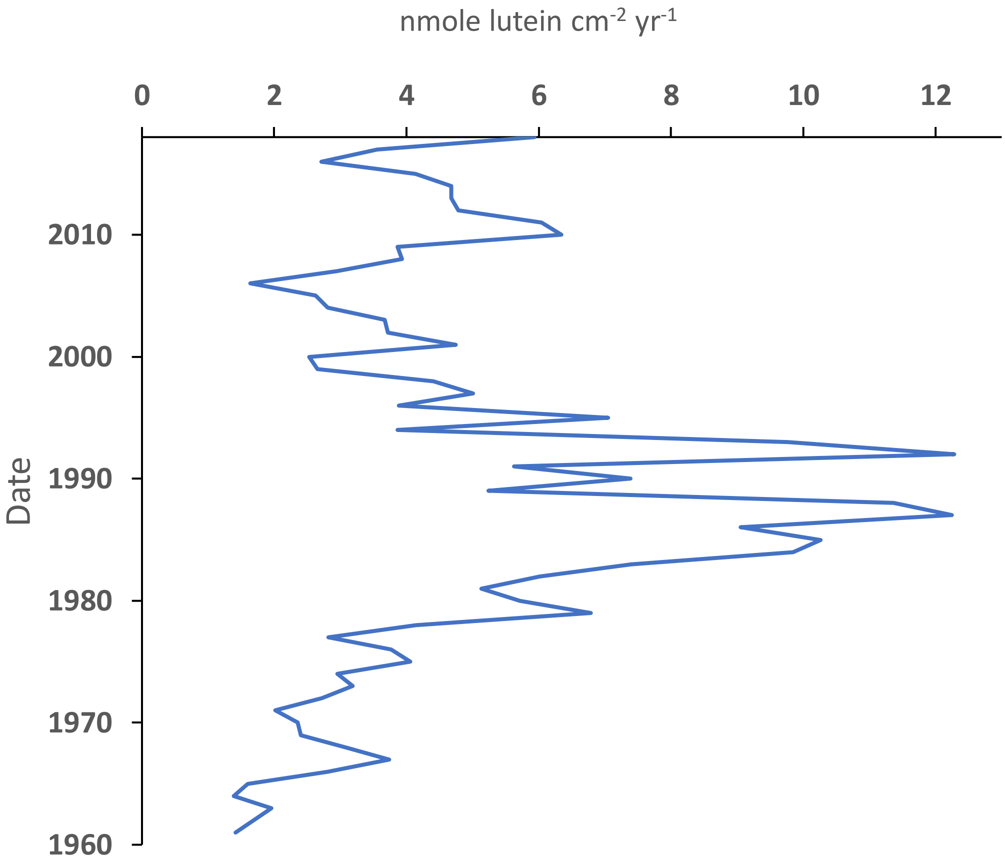

Fig. 6.23 Lutein flux to Sunbiggin Tarn sediments.

The peak in lutein flux occurs in 1992 at 12.3 nmole, with similar values to the previous peak towards the end of the 1980s. There is also a concurrent peak in alloxanthin flux in 1992, indicating that chlorophytes and cryptophytes were particularly stimulated during the period of rapid sedimentation. However this shift was relatively short lived as the flux in lutein, and other pigments associated with potentially planktonic taxa, rapidly declined after 1993 to 2.5 nmole in 2000. The trends in chlorophytes show that there have been multiple periods of environmental change occurring in Sunbiggin Tarn. The most notable periods being a result of the progressive eutrophication of the tarn due to the expanding gull population and through rapid inputs of catchment material. Therefore, it appears that these pressures far exceed the capability of the lake to mitigate against the increased nutrient levels.

There is an increase in lutein flux and concentration during the 21st century to 6.3 nmole in 2010 which may indicate a return to greater chlorophyte dominance. This increase in chlorophytes occurs while most other taxa decline or remain relatively low (e.g. diatoms, cryptophytes, cyanobacteria). The most recent period of increase in chlorophytes also occurs with higher UV index values, indicating recent improvements in water clarity. The values for the UV index suggest that light penetration during the 2010s are likely to have been one of the highest since the 1960s. Such an increase in water clarity may be driven by the continued recovery of the tarn catchment, resulting in reduced erosion. A reduction in catchment inputs is supported by a reduced flux of lithogenic elements (Al, Li, K, Mg) which have all broadly declined since the start of the 21st century (Fig. 6.7).

Considering the improvements in water clarity during the 21st century and the more muted increases in alloxanthin, the recent increase in chlorophytes may represent enhanced benthic abundances. This would contrast with previous periods of enhanced chlorophyte biomass, when chlorophytes were likely to have been predominantly planktonic, considering the concurrent increases in cryptophytes with low or declining water clarity. Therefore it appears that the 21st century represents a return to a more benthic dominated clear water lake. However the lack of response in diatoms and muted increase in cryptophytes indicate that chlorophytes may become more dominant in the benthic zone during the last decade. This indicates a habitat shift in Sunbiggin Tarn, potentially related to climate change. However due to the confounding influences of the extensive periods of eutrophication, the impacts of meteorological change will be largely obscured, resulting in no correlation between lutein concentrations and temperature.

6.3.7 Cyanobacteria (echinenone, zeaxanthin, canthaxanthin)

Echinenone flux gradually increases from the start of the 1960s, quadrupling in concentration to 0.2 nmole in 1987 (Fig. 6.24) with canthaxanthin (Fig. 6.26) and zeaxanthin increasing by a comparable amount to 0.4 nmole and 5.0 nmole respectively (Fig. 6.25). The similar trends in these cyanobacteria pigments suggest a broad increase in all taxa, likely stimulated by enhanced nutrient loading. These peaks occur during the period when the gull population rapidly expands, reflecting the impact of enhanced nutrient loading to the tarn. The increase in cyanobacterial pigments during the 1980s is relatively muted compared to lutein, which may indicate that chlorophytes were beginning to dominate in this high nutrient environment.

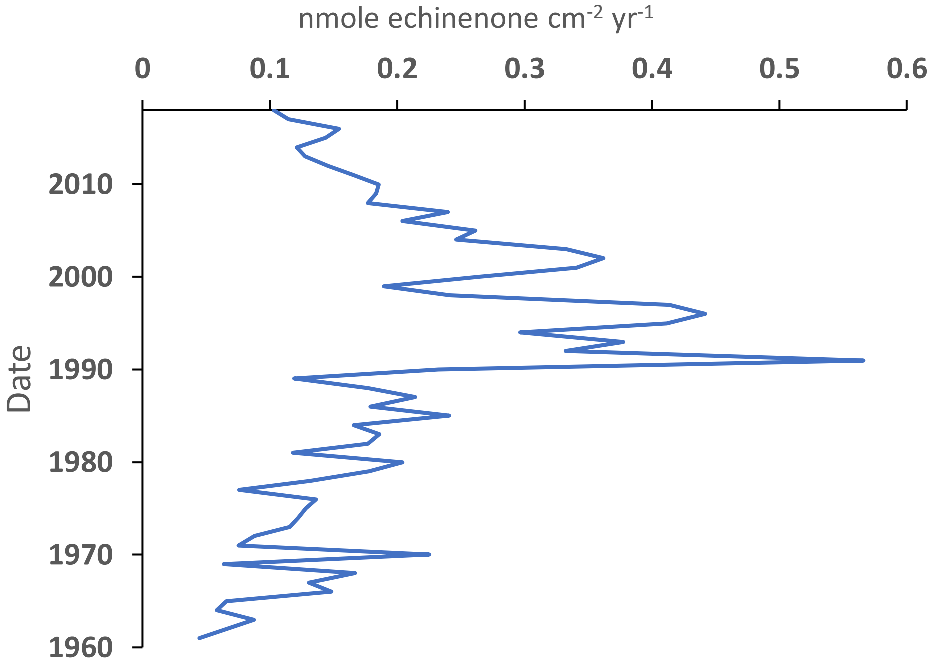

Fig. 6.24 Echinenone flux to Sunbiggin Tarn sediments.

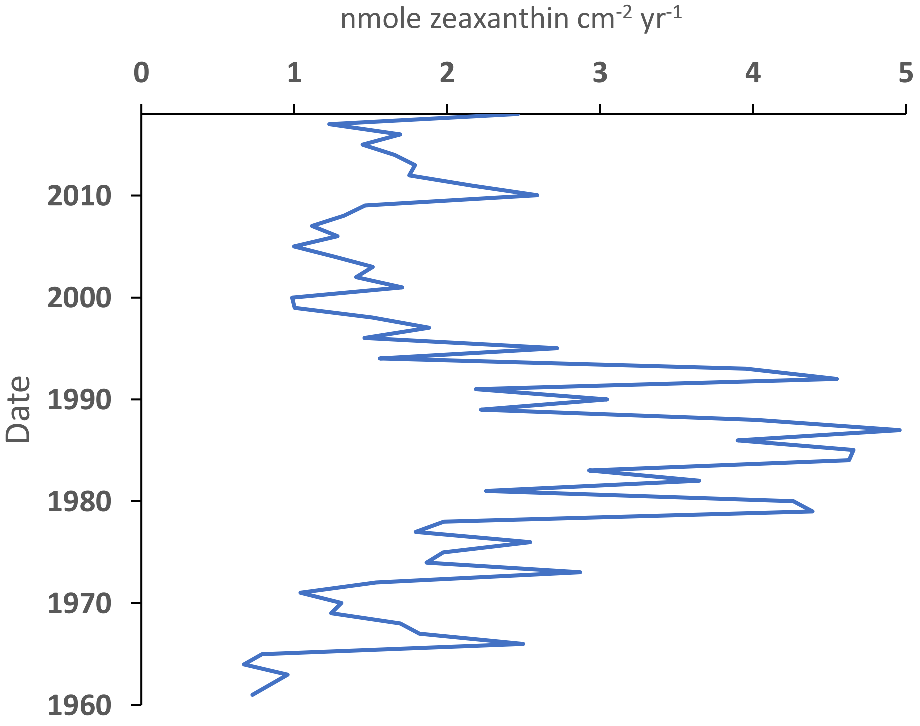

Fig. 6.25 Zeaxanthin flux to Sunbiggin Tarn sediments.

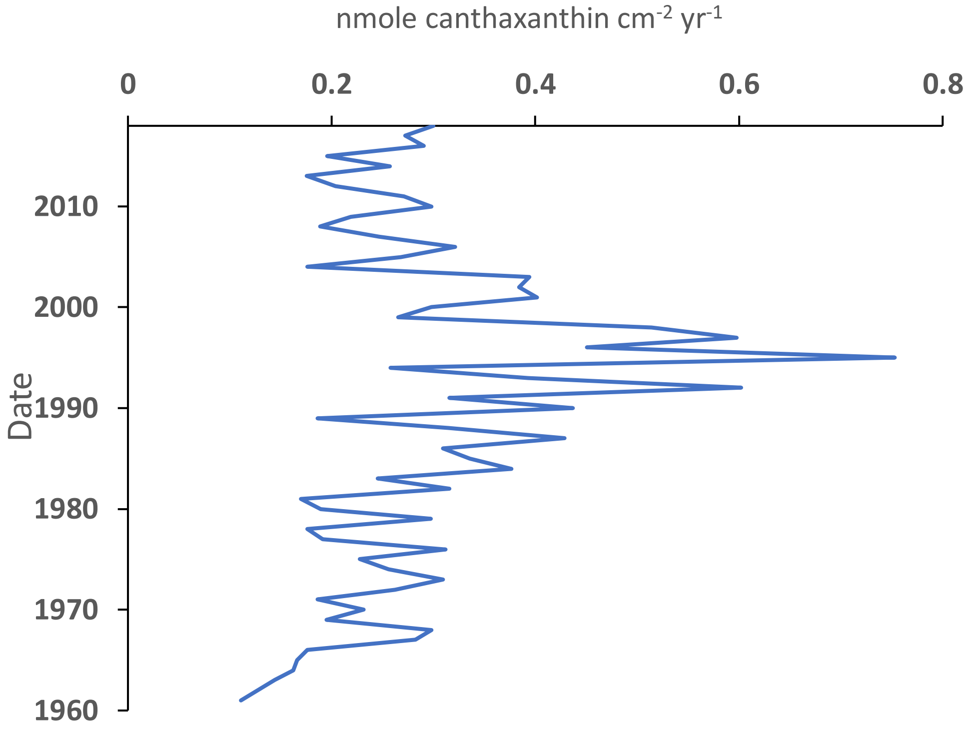

Fig. 6.26 Canthaxanthin flux to Sunbiggin Tarn sediments.

Within the period of gradually increasing cyanobacteria biomass there is a relatively brief but rapid increase in zeaxanthin flux. Zeaxanthin increases to 2.5 nmole in 1966, which is also present for most other pigments, including alloxanthin, diatoxanthin, lutein and chlorophyll-*a*. This increase likely represents a period of enhanced cyanobacteria production in the lake, although it is not present for both echinenone and canthaxanthin which may also represent a shift in community composition. Considering there was not a concurrent increase in canthaxanthin flux during this period, it is likely there was an increase in nutrient loading which would favour non-N-fixing cyanobacteria. Increased nutrient availability may have reduced the competitive advantage of N-fixing cyanobacteria and led an increase in algae with high nutrient demands, such as chlorophytes.

Another period of increased zeaxanthin flux occurs around 1979 with 4.4 nmole and is also present for diatoxanthin and lutein although not for chlorophyll-*a* flux. Therefore, this is likely more representative of a community shift than an increase in lake productivity during this period. These relatively brief periods of enhanced picocyanobacteria biomass occurring as algal biomass is increasing may represent annual changes in weather conditions or gull populations, which heavily influence nutrient loads to the tarn.

All three cyanobacteria pigments decline during 1989, with canthaxanthin flux of 0.2 nmole and zeaxanthin of 2.3 nmole. These declines occur along with the rapid increase in sedimentation, which resulted in further declines in water clarity. A decline in pigment flux is largely shared across all algal groups, indicating a broad suppression of lake algae, although some algal groups appear more affected than others. Picocyanobacteria appear to have been moderately impacted with zeaxanthin flux reduced by 50% from that recorded during the second half of the 1980s for a 2-3 year period. During this period of supressed zeaxanthin flux, there is a sharp increase in echinenone in 1991 to 0.6 nmole representing a substantial increase in total cyanobacteria in Sunbiggin Tarn. The magnitude of increase during this period far exceeds that of chlorophyll-*a* and all other pigments. Whilst there are some increases in zeaxanthin to 3.0 nmole and canthaxanthin to 0.4 nmole, they are not of the same magnitude to echinenone flux which far exceeds previous values. This would indicate that it is not picocyanobacteria or filamentous cyanobacteria driving most of increase at this time, but colonial and non-heterocystous taxa.

This rapid increase in total cyanobacteria biomass also occurs with a rapid decline in water clarity, likely through the inputs of catchment material. Cyanobacteria are often dominant in low light conditions. Therefore, it may represent a rapid, but ultimately brief, expansion of a particular taxon of cyanobacteria which were able to exploit these more favourable conditions. The rapid increase in total cyanobacteria biomass, catchment inputs and decline in water clarity indicates that this may represent a shift to a period of turbid conditions, albeit one that was relatively brief. These shifts are typically driven by nutrient loading and for Sunbiggin Tarn nutrients were likely derived from the extensive gull populations and catchment erosion. Given that the rapid decline in cyanobacteria biomass largely followed the trends in sedimentation, it may indicate enhanced sedimentation to be the primary driver of change. However, considering the tarn itself would have experienced substantial eutrophication by the gull population, enhanced nutrient and sediment loading are both likely to be important drivers.

The peak in echinenone is followed by a rapid decline and an equally rapid increase in zeaxanthin flux to 4.5 nmole in 1992. This indicates that while there is a clear increase in picocyanobacteria, following the rapid increase in sedimentation, it may have been of slightly lower biomass than compared to the end of the 1980s. Following this period of increased picocyanobacteria biomass there is a rapid decline to 1.6 nmole in 1994. If N is a limiting factor in the lake, then increasing N inputs will make N-fixation a less advantageous adaptation. The initial period of sedimentation would have delivered large quantities of nutrients and OM to the lake. However, following the end of the period of rapid sedimentation, much of the additional N would be transformed, deposited in the sediment and flushed out. Therefore, it is possible that the lake became more nutrient limited after this point which may help to explain why canthaxanthin flux peaked in 1995 at 0.8 nmole, ~3 years after most other algal taxa. The peak in canthaxanthin flux occurs as the sedimentation rate declines, which would result in reduced nutrient loading to the lake. A decline in nutrient loading, along with high utilisation from the expanded algal population could have resulted in a large amount of nutrient depletion at the time. Coupled with the low water clarity, these conditions would likely have favoured N-fixing cyanobacteria.

Following the increase in these cyanobacterial pigments they all decline during the 1990s with zeaxanthin to 1.0 nmole and canthaxanthin to 0.3 nmole in 1999. While echinenone and canthaxanthin flux decline after their peaks in 1991 and 1995 respectively, they both remain relatively high for the rest of the 1990s. Considering nutrient concentrations are likely to have been declining since the period of rapid sedimentation ended it might be expected that filamentous cyanobacteria would have a competitive advantage. P flux indicates that, while reduced from its peak, values at the start of the 21st century were comparable to the period of rapid gull expansion during the 1980s. Considering the 1980s was a period of high nutrient loading to the lake caused by the gull population, this demonstrates that nutrient loading likely remained high for many years after the gulls declined. This period of relatively high filamentous cyanobacteria biomass is also likely maintained by the low water clarity during this period, as the UV index starts to increase around the same time that canthaxanthin flux declines. Filamentous cyanobacteria are likely to have a competitive advantage in an environment of low water clarity, low N but relatively high P availability.

Whilst there is a brief period of decline in echinenone flux at the end of the 1990s, it returns to relatively high values by the start of the 21st century with 0.4 nmole in 2002. From the start of the 21st century there is a consistent decline in echinenone flux towards the present with 0.1 nmole in 2017. Canthaxanthin flux during the 2010s remains comparable to the 1970s, which likely represents a recovery of the lake environment, although one which may still experience a degree of eutrophication from historic enrichment of the catchment material. While this decline likely reflects the decline in gull population and recovery of the tarn, the increase in zeaxanthin flux to 2.6 nmole in 2010 is likely due to a different driver. This increase in shared by chlorophytes and cryptophytes which may reflect more beneficial meteorological conditions. However, as previously mentioned, any impact of climate change is likely to be largely obscured in Sunbiggin Tarn due to the extensive nutrient loading and catchment degradation.

In general, zeaxanthin and lutein flux correlate well (r^2=0.80, $p<0.05$). Therefore, it is possible that a proportion of zeaxanthin is derived from chlorophytes (Krajewska *et al.*, 2019). However, zeaxanthin also shares a strong relationship to cryptophytes ($r^2=0.73$, $p<0.05$) so it is also possible that the similarities are more reflective of a general trend in algal biomass across multiple taxa. While the driver of increase in zeaxanthin during the 2010s is uncertain, it is likely to be related to enhanced N availability, which is being utilised by the superior competitiveness of chlorophytes and non heterocystous cyanobacteria.

6.4 Discussion

6.4.1 Zone 1 (1961 - 1979)

As recorded by Holdgate (2016), prior to the 1960s, Sunbiggin Tarn contained several macrophyte taxa, including *Chara* species and two elodeids. The elodeids (*Myriophyllum spicatum* and *Potamogeton crispus)* disappeared from the fossil record from the 1960s indicating a decline or total loss of these taxa (Bennion *et al*., 2009). The loss of species richness and macrophyte cover occurred along with an increase in algal biomass in Sunbiggin Tarn, which has progressively increased during the 1960s and 1970s. Typically, algae will compete with submerged macrophytes for light and nutrients, as recorded in shallow Danish lakes, in response to increased water clarity (Jeppesen *et al*., 2005). Therefore the low abundance of macrophtes may have allowed the expanison of the algal community in Sunbiggin Tarn.

In two shallow hypertrophic lakes in Denmark (Lake Lading and Lake Søbygaard), past algal abundance and community composition was correlated mainly to changes in macrophyte abundance (McGowan *et al*., 2005). At Cunswick Tarn, in the early 1900s a period of high charophyte abundances occurred along with a scarcity of algal pigments in the sediment core, indicating low pelagic production. Charophyte abundance declined around the 1910s, which resulted in a progressive increase in algal pigments from the rest of the 20th century (Wiik *et al*., 2014). The decline in *Chara* sp. and the following increase in algal abundance was attributed to a progressive eutrophication from the surrounding catchment.

Nutrient additions can often have a positive impact on macrophyte growth. However, when nutrient loading gets too high it can have negative impacts on the growth and diversity of macrophytes, including *Chara* species (James *et al*., 2005). Considering the gull population at Sunbiggin Tarn expanded since the 1960s, it is likely that nutrient loading increased as a consequence. A clear decline in *Myriophyllum* and *Potamogeton* indicate that nutrient loading may have had a detrimental impact on lake macrophytes and reduce species richness (Bennion *et al*., 2009).

Higher planktonic production is a typical response in lakes experiencing nutrient enrichment. Following experimental nutrient additions, Nydick *et al*. (2004) found a strong response by planktonic phytoplankton to N and N + P but a more variable, or absence of, response by benthic algae. This was likely due to the greater photosynthetic efficiency of phytoplankton than benthic algae, with this difference increasing with enrichment. In general, N and N + P enrichment increased algal biomass and transferred more productivity to the water column. Lakes often respond strongly to N additions, with minimal phytoplankton response in P treatments. Lafrancois *et al*., (2004) conducted enclosure experiments with N additions resulting in increased chlorophyll-*a* photosynthetic rate but P addition resulted in a muted response. ^{15}N tracer applications indicated that a considerable fraction of the NO_3-N added to enclosures was immobilised in the benthos, making it unavailable to phytoplankton (Lafrancois *et al*., 2004). This large removal process resulted in N being the limiting factor for algal growth and as a result P addition alone had little impact (McGowan *et al*., 2005).

It appears that there was a general increase in lake productivity during this period, as a result of progressive enrichment from the growing gull population. The muted increase in canthaxanthin during this period is unsurprising, considering it has been shown to have little response to added N (Donald *et al*., 2011). Between the 1950s and 1980s there was an increase in pelagic production, indicated by a major increase in open water *Daphnia* spp. (Bennion *et al*., 2009). Similar trends were experienced in British marl lakes, with Wiik *et al* (2014) reporting an increase in *Daphnia* spp. in Cunswick Tarn, Hawes Water and Malham Tarn, with an increase in cryptophytes. These increases in planktonic taxa indicate a shift from benthic to increasingly pelagic-dominated production during the second half of the 20th century in these lakes (Wiik *et al*., 2015a). These changes are most likely driven by eutrophication, with Malham Tarn losing eight macrophyte species during the 20th century, including six *Potamogeton* species which are typically associated with nutrient-poor marl lakes (Wiik *et al*., 2014). There were concurrent increases in zeaxanthin and diatoxanthin in these lakes (Wiik *et al*., 2014) and increasing chlorophytes in Hawes Water (Wiik *et al*., 2015a).

Following the decline in macrophyte densities in Lake Lading and Lake Søbygaard, Denmark, there were increases in the proportions of chlorophytes, cyanobacteria and cryptophytes in the algal community (McGown *et al*., 2005). This shift was reflective of a habitat change from benthic to pelagic and was not associated with an increase in total algal abundances (chl *a,* pheophytin *a*), in contrast to Sunbiggin Tarn. The increases in these pigments are also what has been experienced in Sunbiggin Tarn from the 1960s as a result of eutrophication. This suggests that despite their high buffering capacity, marl lakes can be sensitive to nutrient enrichment.

6.4.2 Zone 2 (1980 - 1988)

The start of the 1980s likely represents an increase in macrophyte abundance in Sunbiggin Tarn, however species richness likely also declined. Around 1982, Bennion *et al*. (2017) recorded the first presence of *Chara* sp. remains since before the 1950s, along with the appearance of the nutrient tolerant pondweed *Zannichellia palustris* (Bennion *et al*., 2009). Whilst *Chara* likely increased during the early 1980s, there are indications that abundances were low and so the increase may have been relatively minor (Welsh, 1982). Increases in angiosperms, in response to eutrophication, have been observed in to occur in other UK marl lakes (Davidson *et al*., 2002; Davidson *et al*., 2008). However, their increase is typically associated with a decline in *Chara* indicating that the more nutrient tolerant species will typically outcompete *Chara* under elevated nutrient loadings.

Across 62 sites in the UK, N concentrations rather than P explained the presence or absence of *Chara* with a boundary occurring at concentrations of 2 mg L^{-1} (Lambert and Davy, 2011). The growth of charophytes was progressively impaired above this limit, through toxic effects and enhancing algal production, with reduced light and oxygen availability. However, the N concentration at which detrimental effects start to occur has been shown to be species specific in laboratory experiments (Simons *et al*., 1994). For Sunbiggin Tarn, there is the possibility that the lake may have naturally low N availability and therefore elevated concentrations may lead to positive effects on *Chara* growth.

While P concentrations are generally high in Sunbiggin Tarn, TN concentrations are low. Mean concentrations of 500 µg L^{-1} were recorded between 2004-2006 (Environment Agency, 2008) and 427 µg L^{-1} in 2019. (Maberly *et al*., 2020). In measurements by the Environment Agency between 2004-2006, total oxidised nitrogen (nitrate plus nitrite) was below the limit of detection (0.2 mg N L^{-1}) in the summer months, which may indicate that Sunbiggin Tarn is N limited, or at least co-limited with P (Environment Agency, 2008). The N concentrations in the tarn were also found to be lower than the inflows, indicating a large loss process, likely through extensive nitrogen uptake or denitrification (Maberly *et al*., 2020). While these concentrations were recorded over two decades after the increase in macrophytes at the start of the 1980s, the currently low N concentrations indicate how Sunbiggin Tarn likely has naturally low N availability. Therefore, increased N loading to Sunbiggin Tarn would initially be expected to produce a stimulating effect on lake biomass in general, including *Chara*.

The increase in *Chara* is potentially indicated by the increase in UV index from the start of the 1980s. *Chara* maintains the clear waters of marl lakes due to their high nutrient uptake (Vermeer *et al*.,

2003) and coprecipitation of P with Ca (Kufel and Kufel, 2002; Robertson *et al*., 2007)**.** As a result, increasing *Chara* cover was associated with a reduction in turbidity in Krankesjön, Sweden (Hargeby *et al*., 1994) and in Scharmützelsee, Germany (Hilt *et al*., 2010). Whilst it is possible that an increase in *Chara* abundance contributed to the increase in water clarity in the early 1980s, it is often difficult to assess whether high charophyte abundance is a result of clear water conditions rather than what caused them. While the increase in *Chara* abundances may be reflected in the increased UV index at the start of the 1980s, it declines for the remainder of the 1980s. The decline in water clarity may be related to the increase in algal biomass at the time, potentially indicating a progression to a more turbid state.

It is estimated that 14 – 23% of *Chara* associated P can be immobilised through coprecipitation, therefore a high charophyte biomass can effectively regulate in lake conditions and make marl lakes resilient to eutrophication (Wiik *et al*., 2013). Charophyte biomass is also resistant to decomposition, which can further immobilise nutrients (Krolikowska, 1997; Kufel and Kufel, 2002). In addition, large charophyte abundances can restrict sediment resuspension, which can release high concentrations of SRP and phosphate (Søndergaard *et al*., 1992; Gerhardt *et al*., 2010). Therefore, increasing *Chara* abundance can help to control nutrient concentrations and supress phytoplankton production in lakes (Vermeer *et al*., 2003). Considering algal biomass continued to increase during the 1980s, this would support the theory that *Chara* biomass was relatively low and/or the increase in eutrophication from the expanding gull population was an overriding factor.

The expansion of the black-headed gull populations in the 1980s likely lead to an increase in nutrient loading and phytoplankton biomass in Sunbiggin Tarn. At Hickling Broad in Norfolk, the winter roost of 50,000 black-headed gulls resulting in summer TP concentrations increasing to over 100 µg l^{-1} (Moss and Leah, 1982). Similar to the situation at Sunbiggin Tarn, increases in duck populations around Cunswick Tarn presented a major nutrient source, stimulating phytoplankton growth (Wiik *et al*., 2015b). Therefore the increase in macrophyte and algae during the 1980s are likely to be related to the rapid expansion of the gull population, which would have increased nutrient exports to the lake (Brimble *et al*., 2009).

The progress of eutrophication in Sunbiggin Tarn is likely reflected by the $\delta^{15}N$ profile. Animals produce faeces and urea which can be highly enriched in ^{15}N due to consumption of higher trophic organisms (Szpak *et al*., 2012). Hargan *et al*., (2018) analysised guano from water birds which nested in ponds on the islands of Lake Ontario and they found $\delta^{15}N$ values of 6.3‰ for cormorants and 8.6‰ for herring gulls. As bird guano is typically enriched in ^{15}N the presence of large population of birds can increase the $\delta^{15}N$ of catchment soils (Irick *et al*., 2015). As a result particularly large ^{15}N

enrichments in soils and plants (5–40‰) have been recorded in and around seabird nesting sites (Szpak *et al*., 2012). Consequently, enriched $\delta^{15}N$ values are often recorded in cores from lakes with higher seabird populations (Hargan *et al*., 2017; Michelutti *et al*., 2010).

Michelutti *et al*. (2008) showed the potential of using $\delta^{15}N$ shifts in sediment cores to track the population change of seabirds in a Canadian arctic pond in Nunavut. Increased $\delta^{15}N$ values suggested an increase in seabird populations. The considerably lower $\delta^{15}N$ levels (2.8–5.2‰) in the surface sediments likely reflected the absence of a modern seabird colony. The changes in gull population is also likely to be reflected in the sediments of Sunbiggin Tarn, when $\delta^{15}N$ reduced from 6.0‰ in the 1980s, when the gull populations peaked, to 3.0‰ in the 2010s when gulls were largely absent.

The impact of gulls is also likely to be reflected by the variations in heavy metal flux. Brimble *et al*. (2009) found elevated concentrations of sedimentary Cd, K, Zn and P in ponds closest to seabird colonies. This would have resulted from bird guano, which is enriched in nutrients and heavy metals, being transported to the lake. As these birds feed on organisms higher in the food web, they accumulate a range of contaminants and can present a large source of heavy metals to terrestrial and aquatic environments. When they form large breeding colonies, water birds can create hotspots of contamination via their guano and mortality (Blais *et al*., 2007). High sedimentary Fe concentrations have been recorded around seabird colonies (Hargan *et al*., 2017) and relatively high concentrations of Al, Mn, Ni, Pb measured in their body tissues, which they bioaccumulate (Borgå *et al*., 2006; Campbell *et al*., 2005; Mallory *et al*., 2004). While the soils and OM of lake catchments are a common source of these elements, the extensive gull populations at the time would have enhanced heavy metal flux during the 1980s.

Elevated Cd is often found in seabirds that feed on organisms higher in the foodweb (Campbell *et al*., 2005; Mallory *et al*., 2004) and as a result higher concenrations of this metal can also be recorded in the sediments of lakes receiving seabird inputs (Brimble *et al*., 2009). At Lake Windermere, an increase in $\delta^{15}N$ occurred together with increases in concentrations of Zn and Cu, linking metal enrichment to anthropogenic N sources, likely wastewater effluent (Fielding *et al*., 2020). A link between avian waste and metal enrichment is likely reflected in Sunbiggin Tarn, with the period of highest $\delta^{15}N$ (maximum extent of gull populations) occurring with a peak in Cd concentrations prior to the rapid increase in sedimentation.

While the 1980s was a period of generally increasing algal biomass, it appears that chlorophytes may have become increasingly dominant during this period. When nutrient availability is high, chlorophytes are fast growing and can outcompete other phytoplankton taxa (Fernandez and Galvan, 2007). In mesocosm experiments, the highest N treatment increased eukaryotic phytoplankton contribution to 53% of the total biomass (Vrede *et al*., 2009). In laboratory experiments, Ryan *et al*. (2017) found that chlorophytes (*Scenedesmus quadricauda* and *Chlamydomonas reinhardtii*) dominated over cyanobacteria (C. raciborskii) under high P conditions. Similar findings were reported by Bogard *et al*. (2020) for N. Under extreme N loading the phytoplankton community can be driven towards chlorophyte dominance. This suggest that these chlorophyte species were better competitors under high nutrient conditions, likely due to a higher nutrient uptake resulting in faster growth. Therefore, the 1980s may represent a period for Sunbiggin Tarn when nutrient availably was high and chlorophytes started to dominate.

The shift towards increasing chlorophyte dominance, in response to enhanced nutrient loading, has been experienced in Hawes Water. The fast-growing chlorophytes rapidly expanded as heterocystous cyanobacteria declined (Wiik *et al*., 2014; Wiik *et al*., 2015a). This was further demonstrated in the freshwater wetlands of the Florida Everglades, where algal community composition shifted from cyanobacteria and diatoms to chlorophytes with enhanced P availability (Waters *et al*., 2012; Gaiser *et al*., 2005). This has also been demonstrated across 35 shallow lakes in Denmark, where a continuous input of nutrients and carbon, both internally and externally, gave the faster growing chlorophytes a competitive advantage leading to their dominance (Jensen *et al*., 1994; Jeppesen *et al*., 2005).

The dominance of chlorophytes may be partly due to their ability to colonise pelagic and benthic environments, while diatoms are often considered benthic and cryptophytes pelagic (Buchaca and Catalan, 2007). Chlorophytes colonising pelagic and benthic habitats have been documented in two Welsh lakes (Llyn Peris and Llyn Padarn) where chlorophytes were present in both habitats in almost equal abundances (Ong and Happey-Wood, 1979). Chlorophyte dominance is often symptomatic of turbid conditions, as the cause of turbidity often relates to the input or release of nutrients to the photic zone (Jensen *et al*., 1994).

Chlorophytes can have a high tolerance to increased light exposure, with the chlorophyte *Zygnema* shown to be largely insensitive to experimental UV exposure (Holzinger *et al*., 2009). Therefore, in an environment of high nutrient availability and increasing light exposure they may be more adapted to growth than other taxa. When growth conditions are good benthic chlorophytes can form dense mats which can shade out other benthic algae and reduce their growth (DeNicola, 1996).

6.4.3 Zone 3 (1989 - 1997)

This period is defined by a rapid increase in sedimentation and enhanced by contributions from carbonates. A rapid increase in carbonates was also reported by Wiik *et al*. (2015b) in Cunswick Tarn around the start of the 20th century. The rapid increase in carbonates was likely caused by eutrophication, as this was a period of intensifying land management. There were concurrent increases in sedimentary Ca and P concentrations, indicating enhanced coprecipitation of these elements by *Chara*. While there was a positive relationship between Ca and P in Cunswick Tarn, for Sunbiggin Tarn the relationship was negative with carbonates diluting P concentrations. Therefore the increase in carbonates was not likely to be primarily derived from enhanced *Chara* co-precipitation. The increase in carbonates may related to the enhanced algal biomass, uptaking more CO_2 which increases the precipitation of other forms of carbonates, such as tufa (Arenas *et al*., 2013). The clear shift in the $\delta^{13}C_{carbonate}$ from the end of the 1980s, concides with the rapid increase in sedimentation (Fig. 6.5). Therefore it could represent a major change in the source of carbonates to the sediment and a shift in lake state.

The close correlation of Ca to Mn may reflect the formation of Mn-carbonates in the lake during this period. Mn-carbonates can be formed in lakes through redox reactions that occur in the pore waters of anoxic sediments and is may be linked to stratification (Stevens *et al*., 2000; Wetzel, 1983). Mn-carbonates typically have low $\delta^{13}C$ (Stevens *et al*., 2000) and may be reflected by the decline in $\delta^{13}C$ from carbonates during this period (Fig. 6.11). However Mn-carbonates can also originate from sedimentary rocks, such as limestone (Delian *et al*., 1992) and then be delivered to lakes through erosion and weathering.

The theory that the rapid increase in sedimentation is being driven by enhanced catchment inputs is supported by site observations. Periods of enhanced erosion of the surrounding fen led to dramatic change to the shorelines of Sunbiggin Tarn from the middle of the 1980s and into the 1990s (Fig. 6.3). The impact of the increased period of sedimentation was detected through a diatom habitat shift. Goldsmith *et al*. (2003) found that there was a decrease in the benthic *Fragilaria* taxa and increase in *Amphora pediculus* from relative abundances of around 10% to 40% during the 1990s. They attributed this to a physical disturbance as *Fragilaria* taxa are typically loosely attached to reed stems or on the surface of consolidated sediments (Hughes, 2002). When disturbed the *Fragilaria* can get dislodged and removed from the lake allowing *Amphora*, which are firmly rooted to hard substrates such as reed stems, to flourish. There was also a clear increase in motile diatom taxa during this period (e.g. *Navicula* spp) which live within loose sediments and can move to the surface

(Goldsmith *et al*., 2003). These adaptations may be particularly beneficial to the rapid sedimentation environment during the early 1990s.

Such a large increase in catchment derived inputs would have increased nutrient loading to Sunbiggin Tarn from the end of the 1980s. Typically marl lakes are thought to be resilient to eutrophication due to the ability of *Chara* to assimilate additional nutrients and precipitate them into the sediments, restricting phytoplankton growth (House, 1990; Robertson *et al*., 2007). While marl lakes can mitigate against the impact of nutrient loading, extensive eutrophication can exceed a loading threshold, potentially leading to rapid changes (Carpenter, 2003). An abrupt shift was experienced in Cunswick Tarn, where algal productivity rapidly increased in the 1930s in response to nutrient loading (Wiik *et al*., 2015b). This represented a rapid shift to a low macrophyte diversity and high pelagic production state, with a cessation of marl precipitation.

When nutrient concentrations are particularly elevated, they can start to block crystal growth sites on the charophytes, inhibiting co-precipitation with carbonates (House, 1990). In the highly eutrophic Feldberger Haussee in Germany, TP concentrations exceeded 1400 µg L^{-1} during the early 1980s (Krienitz *et al*., 1996). This led to a cessation of carbonate precipitation, which resumed in 1985 after a reduction in nutrient loading. In laboratory studies, phosphate concentrations above 300 µg L^{-1} inhibited carbonate precipitation due to a lowering of the pH, which in itself inhibits precipitation (Danen-Louwerse *et al*., 1995; Lin and Singer, 2006). Some short term inhibitions of carbonate precipitation may occur at concentrations around 100 µg L^{-1} (Teranes *et al*., 1999), until biological uptake in the summer months reduced P concentrations. Any reductions in P-coprecipitation will effectively increase lake water TP concentrations, therefore reductions in *Chara* abundance may result in conditions where nutrient loading exceed the lakes capacity to buffer against eutrophication. In the 1950s, a decline in the charophyte community coincided with a cessation of marl precipitation in Sunbiggin Tarn, indicating that the lake had reached a threshold response to nutrient enrichment (Bennion *et al*., 2017). Therefore changes in *Chara* abundance are an important factor in determining the impacts of nutrient loading to a marl lake, with changes potentially inducing rapid ecological shifts.

Such a shift was experienced in Lake Lading and Lake Søbygaard, Denmark during the 20th century, as a result of macrophyte loss (McGowan *et al*., 2005). The loss of macrophytes led to a decline in diatom abundance and a shift to planktonic diatoms, which can provide surfaces for some taxa to grow on (Goldsmith *et al*., 2003). The shift towards more planktonic taxa resulted in a shift from a clear water to turbid state, with high abundances of chlorophytes, cryptophytes and cyanobacteria. These were the taxa stimulated the most in Sunbiggin Tarn during the period of rapid sedimentation, indicating a turbid phase and potentially a state transition. While state transition brought about changes in the phytoplankton community of Lake Lading and Lake Søbygaard, the shift did not occur instantaneously and progressed over a number of years (McGowan *et al*., 2005). This may indicate that Sunbiggin Tarn was progressing towards a state shift, prior to the period of rapid sedimentation as indicated by the expanding phytoplankton biomass. It is possible that this transition would have occurred without the period of rapid sedimentation, and that it was accelerated by it. Often shifts to turbid states can be difficult to reverse once a threshold has been reached (McKee *et al*., 2003). However the eutrophication that resulted in the change would have largely reduced from the middle of the 1990s with the rapid decline in sedimentation and gull populations.

In Hawes Water there was a sub-decadal doubling of phytoplankton abundance between the end of the 1990s and 2010 (Wiik *et al*., 2015a). This was attributed to the lake reaching a nutrient loading threshold, which can occasionally lead to abrupt and rapid ecological shifts, often from clear water to turbid states (Scheffer and van Nes, 2007**;** Wiik *et al*., 2015b). A severe reduction in light availability from the extensive phytoplankton blooms was inferred by a substantial increase in *Daphnia* abundance and the absence of charophytes from higher water depths. Eutrophication driven reductions in light availability can have an impact on marl lakes as it limits the area of the benthos able to support *Chara* species (Wiik *et al*., 2015b).

Water clarity was likely also impacted by the rapid increase in sedimentation. In Cunswick Tarn, high duck populations led to bank erosion and resulted in the increase in DOC and suspended solid loads (Wiik *et al*., 2015b). Increases in DOC can severely reduce water clarity and supress benthic production. For Sunbiggin Tarn, the concurrent increase in phytoplankton biomass and catchment inputs likely explains the low UV index during the early 1990s, with the lowest values in 1993 corresponding to the peak in both chlorophyll-*a* flux and sedimentation rate.

The importance of light availability was demonstrated by Karlsson *et al* (2009) in lake in northern Sweden. They found that nutrients supply did not control algal biomass, with light attenuation and mean water depth explaining 73% of the benthic primary production. As benthic algae exploit nutrients from the sediments, light penetration to the sediment surface often controls their growth (Hansson, 1992). Therefore, in lakes which are dominated by benthic production, light availability may be more important than nutrients (Karlsson *et al*., 2009). Sunbiggin Tarn is likely to be dominated by benthic taxa, with high abundances of non-planktonic diatoms (>95%) found throughout most sections of the sediment core analysed by Goldsmith *et al*. (2003) indicating a clear water and plant dominated system. However, the progressive shift of *Fragilaria* to *Amphora* dominance from the 1960s to the start of the 21st century indicate that the diatom community of Sunbiggin Tarn has changed over time.

The dominance of non-planktonic taxa throughout the core reflects that despite the changes in water clarity, the lake has likely maintained relatively a clear water and a macrophyte dominated state during most of the second half of the 20th century. The period of rapid change around the start of the 1990s appeared to have shifted the lake to a more phytoplankton dominated and turbid state. However it is likely that the most dramatic impacts of this were relatively short lived as typical planktonic taxa (cryptophytes) decline rapidly around the middle of the 1990s. Therefore, while the tarn catchment may still be recovering from the impacts of eutrophication, the lake itself may have recovered more quickly with a greater ability to mitigate against the impacts of nutrient loading.

As previously demonstrated with the trends in diatom biomass, for Sunbiggin Tarn it appears that water clarity is not the dominant driver in determining algal biomass. It is likely nutrients are the dominant factor and the period of increased total algal biomass, along with low water clarity, suggests a large shift towards more planktonic taxa. The increase in planktonic taxa would have to have been high enough so that it compensated for any suppression of benthic production. Planktonic production is typically very high in turbid lakes, with modern monitoring of Lake Søbygaard showing that ~96% of annual algal production were planktonic rather than benthic algae (Liboriussen and Jeppesen, 2003). As Sunbiggin Tarn is typically benthic dominated (Goldsmith *et al*., 2003) such relative abundances of planktonic algae are unlikely to have been quite so high. However, particularly high planktonic production during the first half of the 1990s is supported by the rapid increase in cryptophytes, which far exceeded fluxes than at any other point in the time series. Typically, high planktonic algal production would be reflective of more eutrophic conditions, as recorded in Cunswick Tarn. Cryptophytes increased in the 1990s along with planktonic diatoms and *Daphnia*, with a decline in macrophyte species richness reflecting a decrease in benthic production (Wiik *et al*., 2015b).

From the start of the 1990s there appears to be a successional change in algal taxa with a peak in total cyanobacteria biomass (1991), followed by chlorophytes and cryptophytes (1992-93) and a peak in filamentous cyanobacteria (1995), which stayed relatively high until 1998. Ohtsuki *et al*. (2015) reported increased echinenone concentrations following nutrient loading in Lake Hataya Ohunma in Japan. The trophic state of the lake changed from oligotrophic to mesotrophic from the middle of the 20th century. Concentrations of echinenone increased from the 1970s to 2000s, in particular from the 1990s, due to a doubling of P loading between the 1980s and 1990s (Ohtsuki *et al*., 2015).

The shift to greater chlorophytes and cryptophytes in 1992-1993 likely reflects a dramatic increase in nutrient availability in Sunbiggin Tarn with high additions of nitrogen (ammonium, nitrate) shown to produce a shift towards greater chlorophytes and cryptophytes (Barica *et al*., 1980; Lepori and Robin, 2014). The transition between different taxa of cyanobacteria and chlorophytes in Sunbiggin Tarn is largely the reverse of what was experienced in Hawes Water. There was a decline in heterocystous cyanobacteria, followed by a rapid increase in chlorophytes and then by non heterocyctous cyanobacteria, many of which would have been pelagic taxa (Wiik *et al*., 2015a). A transition towards a pelagic dominated system had been occurring in the lake, relatively slowly, for around 100 years prior to the 1940s. The response of Hawes water indicated that nutrient loading had reached a threshold with excessive nutrients overwhelming the buffering capacity of the lake, leading to rapid ecological change. It seems likely that Sunbiggin Tarn has experienced a similar response considering the high nutrient exports from the black-headed gulls and sedimentation (Goldsmith *et al*., 2003), the relatively low abundance of *Chara* (Bennion *et al.*, 2017) and the rapid growth in chlorophyte biomass between the 1960s and 1980s. While the driver of change in Hawes Water represents increasing nutrient availability, the relatively rapid transition from greater chlorophytes to filamentous cyanobacteria dominance likely reflects a reduction in N availability.

Considering the peak in canthaxanthin flux occurs as the sedimentation rate declines it is likely that this trend represents a degree of N limitation that favoured N-fixing cyanobacteria during the second half of the 1990s. If N-exports decline then this can quickly lead to N limitation, especially in lakes with high denitrification rates (Hayes *et al*., 2015) or increased trophic status (Dolman *et al*., 2012), such as in Sunbiggin Tarn during the early 1990s. In Hawes Water there were relatively high abundances of N-fixing cyanobacteria in the early 1900s, when conditions were that of a nutrient poor, clear water marl lake (Wiik *et al*., 2014). Replacement of chlorophytes by N_2 fixing cyanobacteria was experienced in Lough Neagh and is common in lakes which experience N limitation but maintain a good supply of P (Bunting *et al*., 2007; Leavitt and Findlay, 1994). This would align with the previous water sampling, which provides strong evidence for naturally high P availability and possibly some periods of N limitation (Environment Agency, 2008; Maberly *et al*., 2020).

The impact of N limitation on community composition has been well demonstrated. In mesocosm experiments, N-fixing cyanobacteria comprised up to 50% of the total phytoplankton biomass with no N addition, and an inverse relationship between N addition and cyanobacteria biomass (Vrede *et al*., 2009). As cyanobacteria have a low competitive ability to use nitrate as an N source, eukaryotic phytoplankton dominate when there is increased nitrate availability (Hyenstrand *et al*., 1998). Therefore the start of the 1990s, and the period of rapid sedimentation, likely represents high nutrient loading. By the middle of 1990s N availability had declined substantially, potentially becoming a limiting factor. The decline in N availably is probably due to a combination of a reduction in external loading along with enhanced utilisation by a rapidly expanded chlorophyte population. In Hawes Water, eutrophication resulted in high pelagic productivity leading to nutrient depletion and reduced light availability for benthic cyanobacteria (Wiik *et al*., 2015a).

Lakes typically recover rapidly from enhanced N loading (<5 years) which can lead to rapid reduction in algal biomass once loading has been reduced (Jeppesen *et al*., 2005). The additional N is lost through denitrification rather than with P which is accumulated in the sediments and re-released to the water column. As a result, lakes which experienced a P driven increase in algal biomass typically have a delayed recovery, often 10-15 years due to period of extended high internal P loading (Jeppesen *et al*., 2005). Considering the rapid reductions in algal biomass from the middle of the 1990s and the high, potentially N-fixing, cyanobacteria biomass in the second half of the 1990s, this would further support N driving the period of increased algal biomass.

6.4.4 Zone 4 (1998 - 2018)

Macrophyte surveys conducted in 2002 indicated that while there were relatively few taxa of submerged macrophytes, there had been an increase in cover from the 1980s to the start of the 21st century (Goldsmith *et al*., 2003). Site observations recorded a submerged vegetation dominated by *Chara vulgaris, Chara contraria* along with *Zannichellia palustris*. The submerged vegetation in Sunbiggin Tarn during 2002 indicated a healthy flora, although it was of fairly low diversity, and a relatively rapid recovery likely accelerated through the absence of gull pressure (Goldsmith *et al*., 2003). Although there is uncertainty around the impact on the macrophyte community during the period of increased sedimentation, it appears unlikely to have resulted in large negative impacts.

The recovery of the tarn from eutrophication is indicated by the decline in P flux since the start of the 21st century. Additionally, lake water sampling measured TP concentrations at 33.6 µg l^{-1} in 2003 (Goldsmith *et al*., 2003), reducing to 28.6 µg l^{-1} in 2004-2006 (Environment Agency, 2008) and 13.0 µg l^{-1} by 2019-2020 (Maberly *et al*., 2020). These concentrations are similar to those in the calcareous Nagawicka Lake, Wisconsin, USA, which were measured at 14.0 µg l^{-1} TP between 2003 and 2004, a reduction from 38.0 µg l^{-1} in the 1970s. This decline was driven by a reduction in P loading between the late 1970s and early 1980s, rapidly shifting from a mesotrophic to oligotrophic classification. (Robertson *et al*., 2007).

The TP concentration in Sunbiggin Tarn indicate that nutrient concentrations may have been declining for ~25 years and are possibly still declining in the lake. The gradual decline in lake water TP concentrations likely reflects a slower recovery of the tarn catchment, which was subject to extensive eutrophication from the gull populations. A slower recovery of the catchment was highlighted by Holdgate (2016), as while the fenland clearly recovered from much of the gull pressures in the 1980s, the extension of patches of *Typha* in 2016 indicate that eutrophication may still be persisting. *Typha* dominance occurred in the northern Everglades, USA, as a result of increased P availability as sediment TP increased to 600–700 µg g^{-1} (Waters *et al.*, 2012). Typically, sediment TP above a threshold of 650 µg g^{-1} has been shown to accelerate *Typha* dominance (Wu *et al.*, 1997). Increasing sedimentary TP concentrations have been used to indicate higher nutrient status in other marl lakes, such as Malham Tarn when increases during the 20th century indicated eutrophication (Pentecost, 1998). For Sunbiggin Tarn, this threshold is exceeded in the majority of samples from the start of the 1960s to the end of the 1980s and all samples after 2003, with the sediments in between heavily affected by dilution from carbonates and catchment inputs.

P concentrations in Sunbiggin Tarn have been noted to be particularly high, with SRP concentrations of 298 µg L^{-1} recorded in the lower 1m of water (Maberly *et al.*, 2020)**.** The very high P concentrations may reflect an anoxic sediment surface, which would promote internal P loading and increase lake water P concentrations (Jensen *et al.*, 1992). Anoxic conditions can result from thermal stratification in the summer months. In summer 2019, Maberly *et al.* (2020) recorded a temperature difference of 6.1°C between the surface and bottom waters with low oxygen concentrations in the lower 1.5m of the water column (~1% air-saturation) indicating that some thermal stratification occurs.

Considering the relatively long WRT of Sunbiggin Tarn of ~300 days (Maberly *et al.*, 2020) it may be expected that internal P loading is having a large impact on lake water P concentrations, especially when stratification breaks down (Maberly *et al.*, 2020; Wiik *et al.*, 2015b). This was the case in Rostherne Mere, where substantial internal nutrient loading advanced eutrophication for several years after the diversion of sewage effluent (Lacey *et al.*, 2018). Concentrations of total P of the lake increased between 1992 and 1993 (Carvalho *et al.*, 1995) with only limited declines over the next decade (Moss *et al.*, 2005). As a marl lake, Sunbiggin Tarn precipitates carbonates in summer months (Maberly *et al.*, 2020). Due to the coprecipitation of calcite with P, this can accelerate the recovery from eutrophication in marl lakes (Robertson *et al.*, 2007). Pentecost (2009, 2013) made direct measurements of the content of phosphorus in calcite from Sunbiggin Tarn and from the sediment with values of 0.58 and 2.35 mg P g^{-1} Ca respectively. However, considering the negative correlation between P and Ca concentrations in Sunbiggin Tarn, calcite precipitation, and re-release, may be relatively minor in controlling in lake P concentrations. This is supported by the data from Maberly *et al*. (2020) who estimated P released from sedimentary calcite to account for only 7% of the high SRP concentrations at depth. Therefore, is seems likely that the high SRP in the bottom water column is driven by anoxia and Fe-bound P rerelease to the water column (Lake *et al*., 2007). This is supported by the strong positive correlation between Fe and P (r^2=0.91, p<0.0001)

As the stratification regime of Sunbiggin Tarn is unclear so is the impact of internal P loading. As the mean depth of the tarn is 4m, around half the lake area may be too shallow to stratify (Maberly *et al*., 2020). If the high concentrations of P in the bottom waters only represent a relatively small volume, the impact of internal P loading will be relatively small. As TP concentrations in the tarn are lower than most of the inlets that feed into the tarn, it is likely that external P loading is largely or wholly controlling P concentrations (Maberly *et al*., 2020). The lack of a rapid increase in P concentrations in the surface sediments also suggests that internal P loading is not a dominant process in Sunbiggin Tarn, at least compared to other lakes. Therefore it is likely that the catchment is controlling nutrient concentrations in the tarn and that eutrophication from the gulls has been persistent despite reducing to negligible numbers since the start of the 21st century. A continued impact from gull eutrophication of the catchment was highlighted by Goldsmith *et al*. (2003), who through modelling estimated that P loading at the start of the 21st century was 50% higher than in the 1930s, resulting in a doubling of in lake P concentrations. As the surrounding moorland is sparsely used, with some low intensity sheep grazing, the estimated nutrient load is low (Bennion *et al*., 2003). Therefore, it appears that the gull populations have had a dominant influence on the lake.

Along with a reduction in nutrient concentrations the lake has experienced an improvement in water clarity during the 21st century, in particular during the 2010s when there is a relatively rapid increase. An improvement in water clarity is supported by Secchi depths of 2.2m recorded in 2002 (Goldsmith *et al*., 2003) which increased to 3.2m in 2019 (Maberly *et al*., 2020). While there was an improvement in water clarity by the start of the 21st century, a Secchi depth of 2.2m represented a tarn with restricted macrophyte colonisation depth limits, compared to other marl lakes (Maberly *et al*., 2020). However, this did not represent turbid conditions during this period (Goldsmith *et al*., 2003) as demonstrated by the reduced phytoplankton biomass, compared to the early 1990s. Whilst it is difficult to extrapolate the precise impacts of water clarity prior to the Secchi depth measurements of 2002, the UV index strongly suggests that colonisation depths would have been lower during the 1990s.

Increased water clarity typically results from reduction in lake water DOC. Karlsson *et al*. (2019) found that DOC concentrations were highly correlated to light attenuation, (r^2=0.97) indicating that they were the overwhelming driver. Typically, DOC inputs are of a terrestrial origin and as a result light penetration to benthic habitats is controlled mainly by variations in the input of coloured terrestrial OM (Jones, 1992). In general, catchment exports of OM vary depending on vegetation cover, air temperature and runoff (Hope *et al*., 1994; Tranvik and Jansson, 2002). Therefore it is likely that the progressive recovery of the fenland and wider tarn catchment from the gull pressures has contributed towards the increase in water clarity. Although any impacts from changes in meteorological conditions are largely undetectable in Sunbiggin Tarn, it is possible that changes in precipitation have impacted water clarity during the 21st century. Schindler *et al*., (1997) found that decreased precipitation between 1970s and 1990s in the Experimental Lakes Area, north-western Ontario, Canada resulted in lower DOC concentrations. Reduced streamflow delivered less DOC and increased WRT enhanced DOC removal in the lake, which was further stimulated by increased temperatures. Therefore increased seasonality could impact DOC concentrations, such as through reduced summer precipitation. Changes in precipitation could also lead to changes in algal biomass. In Hawes Water, a lowering of water level reduced flushing rates in the lake. The increased WRT led to an enhanced phytoplankton bloom during the summer of 2013 (Wiik *et al*., 2014).

Despite the declining lake TP concentrations there has been an increase in algal biomass during the 21st century, as indicated by the increases in chlorophyll-*a* flux and likely driven by increases in chlorophytes and cyanobacteria. This increase in algal biomass is supported by previous water sampling data. There was a slight increase in mean chlorophyll-*a* concentrations from 2.4 µg L^{-1} in 2002 (Goldsmith *et al*., 2003) to 3.4 µg L^{-1} in 2019-2020 (Maberly *et al*., 2020). Therefore while the flux in pigment chlorophyll-*a* flux is relatively large during this period, the increase in algal biomass may be relatively small.

As for precipitation data, there was no detectable impact of changes in temperature on algal biomass in Sunbiggin Tarn. There was also no detectable impact on algal biomass, inferred from sedimentary pigment concentrations, in Cunswick Tarn despite an increase in in air temperature during the 20th century (Wiik *et al*., 2015b). The lack of a detectable relationship between temperature an algal biomass was attributed to other, more dominant, drivers of change obscuring the climate impact.

A lack of detectable climate impact was observed for many of the lowland lakes in the English Lake District (Moorhouse *et al*., 2018). These lakes have had a long history of anthropogenic activities in their catchments. As a result, algal communities in many of the lakes in the Windermere catchment were shown to be strongly controlled by external nutrient inputs, such as those from wastewater treatment facilities. However, there was clear evidence of algal communities responding to climatic variations in other lakes less impacted by anthropogenic activity within the Windermere catchment. The response of these more upland lakes highlights how the climate is likely impacting most lakes in the Lake District, but this signal can often be obscured by other drivers of change.

Synergistic effects of warming and eutrophication can lead to pronounced and rapid changes (Taranu *et al*., 2012) and may lead to a shift towards a new lake community composition (Bennion *et al*., 2011). Warming can also have a large impact on stratification, increasing water column stability (Wagner and Adrian, 2009). While increased temperatures lead to enhanced internal P loading, strengthening stratification can prevent the nutrient rich water mixing with the upper layers (Gibbons and Bridgeman, 2020; Jeppesen *et al*., 2005). Under these circumstances, enhanced stratification may increase nutrient availability for benthic taxa, but it would also increase the likelihood of oxygen depletion. An increase in water column stability can be beneficial to algal taxa that can regulate their buoyancy (e.g. cyanobacteria), giving them a competitive advantage for nutrients (Jöhnk *et al*., 2008). Due to the uncertainty around the stratification extent and regime of Sunbiggin Tarn, any impact from warming induced changes to stratification remains speculative. However, even in the absence of stratification, warming coupled with persistent eutrophication could lead to substantial algal stimulation.

Chlorophytes will often dominate during warm periods at the expense of diatoms (Florian *et al*., 2015). In Sky Pond, USA, concentrations of diatoxanthin decreased substantially from the start of the 20th century. While diatom abundances declined there was a concurrent increase in the abundance of benthic chlorophytes (Oleksy *et al*., 2021). The increase in benthic chlorophytes likely reflects the combined impact of N deposition and rapid warming since the 1970s that allowed them to colonise benthic habitats (Oleksy *et al*., 2020). As benthic diatoms typically outcompete chlorophytes when N concentrations are low, this indicates an elevated N supply (Oleksy *et al*., 2021).

Low diatom abundances during the 21st century is supported by Maberly *et al*. (2020) from water samples collected during 2019. The most abundant species was *Fragilaria capucina* with a similar level of dominance in the diatom community to that recorded in 2008 (Pentecost, 2009). Other species recorded included those typically attached to plants and hard surfaces e.g. *Synedra sp.* (Maberly *et al*., 2020). Despite the improvements in macrophyte coverage and light availability during the 21st century, diatoms do not appear to have been stimulated. This may represent them being outcompeted by other taxa, such as chlorophytes in benthic environments, or represent Si limitation restricting their growth.

This period of increasing algal biomass during the 21st century appears to be driven primarily by chlorophytes with some increase in zeaxanthin and alloxanthin pigments. In sediment cores from freshwater wetlands in the Everglades, USA, the marl sections had relatively high concentrations of alloxanthin, canthaxanthin pheophytin b, and scytonemin, indicative of periphyton mats composed of cyanobacteria and chlorophytes, along with a relatively large population of planktonic cryptophytes (Waters *et al*., 2012). However, despite similar increases in Sunbiggin Tarn the low concentrations of echinenone would indicate that the overall cyanobacteria abundances are relatively low during the 21st century and may be continuing to decline.

Low cyanobacteria abundances were also reported by Maberly *et al*. (2020) who found small amounts within the summer phytoplankton community during 2019. The exposed nature of the site may act to naturally restrict cyanobacteria growth, as wave action will induce turbulance that will break up cyanobacteria colonies, limiting their growth (Mur *et al*., 1999).

Cryptophyte biomass is substantially lower following the decline in the gull population, however there are indications of increases in alloxanthin flux during the 2010s. Modern water sampling suggests that the tarn still contains relatively large abundances of cryptophytes in the phytoplankton community. In 2019 the motile cryptophyte *Rhodomonas* sp. was the most dominant phytoplankton recorded by Maberly *et al*. (2020), with concentrations of *Rhodomonas* sp. over an order of magnitude greater than almost all other identifiable species, except the chlorophyte *Tetraspora lemmermanni* which was approximately one-third of the concentration.

6.5 Summary

The ecological community of Sunbiggin Tarn has clearly been heavily impacted by changes in gull populations since at least the 1960s. The extent of eutrophication from the gulls appears to have obscured any other drivers of change in the lake, making any assessment to the impacts of climate change highly confounded. Nutrient loading to the tarn was likely progressive with concurrent increases in algal biomass between the 1960s and 1970s, indicating an expansion of most algal taxa. The 1980s recorded the rapid expansion of the gull populations, reaching a peak of 12,500 pairs in 1988. Such large populations would have resulted in extensive eutrophication in the catchment, which would then be transported to the lake. During the 1980s water clarity started to decline and chlorophytes became more dominant indicating particularily high nutrient concentrations in the lake at the time. The extent of chlorophyte dominance may have led to the surpression of other taxa, potentially through the shading of benthic environments, indicated by the continual decline in water clairty. In general, the period from the 1960s to the end of the 1980s is indicative of a progressive increase in nutrient loading and trophic state driven by an expanding gull population.

A consequence of the expanding gull population was signficant degradation to the immediate surrounding fenland and catchment area. The shoreline was dramatically changed with a clear expansion of the open water area and loss of fenland in which the gulls roost. This degradation likely resulted in the rapid increase in sedimentation in Sunbiggin Tarn which lasted from the end of the 1980s to the middle of the 1990s. During this period there would have been a dramatic increase in nutrient loading from a heavily polluted catchment, with associated decline in water clarity. These pressures led to some equally rapid changes in the lake algal community with algal biomass rapidly increasing as a result. There is indication that the tarn may have gone through a relatively rapid successional shift during this period from fast non heterocystous cyanobacteria to chlorophytes and cryptophytes to heterocystous cyanobacteria. A prolonged period of enhanced heterocystous cyanobacteria during the second half of the 1990s indicated that the lake may have rapidly shifted from high N concentrations to N limitation within ~5 years (Fig. 6.27). This shift likely reflects a rapid decline in catchment inputs and the gull population leading to an equally rapid reduction in nutrient loading coupled with high nutrient uptake by an expanded algal biomass. These changes indicate a rapid shift in the lake evironment, which has been regularly experienced in marl lakes during the 20th century as a result of nutrient enrichment.

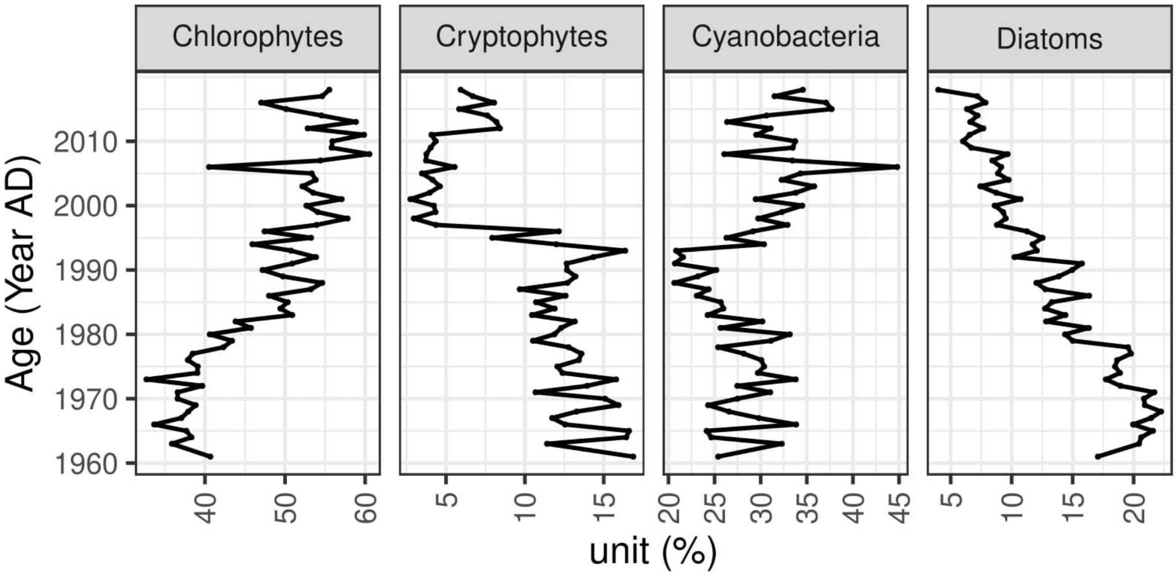

Fig. 6.27 Change in the relative abundances of dominant algal groups in Sunbiggin Tarn.

By the 21st century it appears that the lake has returned to conditions similar to those experienced in the 1960s. This highlights the natural capability of marl lakes to recover from eutrophication once the nutrient load has been reduced. However, lake nutrient concentrations, catchment vegetation and an increase in chlorophyte biomass indicates that eutrophication may still have impacted Sunbiggin Tarn after the gull populations declined to negligable numbers. Likely this reflects a slower recovey from a heavily polluted catchment. Although it is not possible to directly interpret any impacts on the lake from climate change, it is possible that some of the more recent increases in algal biomass is related to 21st century climate warming.

7. Synthesis of data and discussion of research outcomes

Climate change is likely to be impacting all lakes in the UK, although the extent of the impact is variable. Smaller lakes are generally understudied in the UK and around the world, especially in relation to climatically driven ecological change (Watts et al., 2015). Whilst there is relatively more data from larger lakes, the physical, chemical and ecological differences between the larger and smaller lakes means they are unlikely to be responding to climate change in the same way (Winslow *et al*., 2015). In general, smaller lakes are expected to be particularly sensitive to climate change, potentially resulting in earlier and more rapid ecological shifts (Arvola *et al*., 2010). The sensitivity of small lakes may also present the ability of these systems to act as early warning systems and provide environmental data of climate related impacts that may not yet have developed in other lakes. Therefore, an expanded body of research into the sensitivity of small lakes and how they are impacted by changes in weather and climate is needed for the UK. This research is necessary to assess both the risk of small lakes to climate change and their utility in being able to reflect future changes to other lakes, both regionally and nationally. The main aim of the research was to investigate the response of small lakes located in England to climate change from the mid-19th century to the present day. This chapter discusses the strengths and limitations of the data obtained, in the context of the original objectives, which are listed below:

Objectives

1. Establish changes in phytoplankton biomass and community composition in small English lakes since at least ~AD1850 using algal pigments as biomarkers.
2. Identify changes in sedimentary OM sources (e.g. %C) and cycling using bulk isotopes ($\delta^{13}C$ and $\delta^{15}N$).
3. Establish the impact of historic pollution events and changes in catchment inputs using trace element analysis.
4. Develop sediment core chronologies using ^{210}Pb dating in order to derive timings of algal community change over the 20th and 21st centuries.
5. Compare changes in sedimentary algal communities with meteorological records to identify the role of weather and climatic variations in driving algal community change over the 20th and 21st centuries.
6. Synthesise the impacts of multiple stressors on lake algae communities to help identify the impact of catchment changes, atmospheric and diffuse pollution on algal biomass and community change.

7. Assess differences in response between lake types and how that may impact their future ecological trajectories in response to projected 21st century warming.
8. Synthesise the data to suggest effective remediation measures to address current and future management concerns of small English Lakes.

7.1 Using photosynthetic pigments as biomarkers for lake algal biomass and community composition

Algal pigments proved to be generally well preserved in all three lakes. As Sunbiggin Tarn has been shown to stratify this may have improved pigment preservation through the reduction in oxygen availability in the bottom waters (Maberly *et al*., 2020). However, the extent and impact of stratification may be relatively minor. As most of the lake basin is relatively shallow (mean depth 4m), any long-lasting stratification is likely restricted to the relatively small area of deeper water in the lake. Similarly, while the stratification status of Lake Gormire and Blea Tarn is uncertain, they are presumed not to stratify due to their relatively small volume and depth. Additionally, these lakes contain high abundances of oxygenated forms of chlorophyll-*a* (hydroxyphaephytin-*a*, purpurin-18-phytyl ester) throughout the sediment cores indicating that if stratification does occur it is unlikely to impact oxygen availability substantially Therefore, these lakes appear to have well-preserved pigment records despite oxygenated conditions in the water column which would promote pigment degradation.

The presence of high pigment concentrations indicates either high preservation or high supply of pigments to the sediments. The presence of the relatively labile fucoxanthin in all the samples in sediment cores from the three lakes indicates that there is high preservation and high supply (McGowan *et al*., 1999). The shallow nature of these lakes most likely promotes rapid sedimentation compared to deeper lake environments, enabling higher quantities of pigments to be preserved (Leavitt, 1993). Additionally, considering the moderate altitude of these lakes they would be expected to have reasonably productive catchments and lake systems. Therefore, it would also be expected that these lakes would have a higher annual standing of algal biomass and their pigments would be more rapidly deposited in the sediment than more upland lakes.

The consistent presence of fucoxanthin in all three lakes indicate that the preservation of pigments is good. However, they failed to record some of the most labile pigments with a complete absence of peridinin (derived from dinoflagellates) in any samples from the three lakes. Dinoflagellate populations have been recorded in Lake Gormire (Scott, 1948) and Sunbiggin Tarn (Maberly *et al*.,

2020) meaning that a potentially important taxa of algae was not represented in the dataset. Additionally, there were no detectable concentrations of aphanizophyll that could have been used as a more specific marker for N-fixing cyanobacteria (e.g. Moorhouse, 2016). The complete absence of this pigment may be due to several reasons, including the extraction and HPLC technique, high lability, or lower production than other cyanobacterial pigments. Despite some of the pigments being absent, there was a generally wide range, high abundance and near consistent presence of algal pigments in all three lakes.

While pigments appear to have generally been well preserved in the three lakes, changes in pigment preservation do appear to have occurred in Blea Tarn in particular. The changes in preservation conditions between the 1970s and 1980s appear to have been related to the response of the algal community to a shift to more planktonic taxa. This indicates that whilst pigments are sensitive to changes in the algal community, there are limitations in using them for establishing changes in lake conditions. While chlorophyll-*a* is a commonly used marker for total algal biomass, its relatively high lability means that is can be affected by changes in preservation. As a result, β-carotene is also typically used as an indicator for total algae. However, for all three lakes the β-carotene peaks in the HPLC analyses often co-eluted with chlorophyll transformation products. This resulted in largely incoherent profiles for β-carotene and confounded their use in any interpretations of changes in lake algal biomass.

While the absence of some pigments prevented the reconstruction of certain algal groups, there was likely also an effect from pigments being derived from more than one algal group. Zeaxanthin can be produced by some chlorophytes as well as cyanobacteria (Brown and Jeffrey, 1992). As lutein and zeaxanthin are two of the most closely correlated pigments in all three of the lakes this may indicate a large chlorophyte source. However, there were high correlations between multiple algal pigments in all three lakes indicating periods of broad increases in algal biomass across multiple taxa. Therefore, it is difficult to establish how much (if any) zeaxanthin is being produced by chlorophytes as information is required about the lake algal communities at the time and the carotenoids that specific species produce.

Although algal pigments have been essential to understand community level impacts in the three lakes presented, they lack the ability to distinguish any species level change. This prevents a more detailed impact assessment for the algal communities. For instance, enhanced mining inputs led to an increase in Cu-resistant diatom species in Elterwater (Pickering, 2001). Considering the mining related inputs to Blea Tarn and the changes in diatom biomass during the 19th century, these taxa may have been stimulated in Blea Tarn to an extent. However, it is not possible to discern any such change from algal pigments alone, which highlights the limitation of using algal pigments in palaeolimnological studies without data on the dominant species which inhabit the lake through time. There is the potential that any species-specific changes could have been established though the identification of diatom frustules and changes through the core. The analysis of diatom frustules would have allowed for analysis of diatom community change at a much finer taxonomic level, potentially recording increases in metal resistant taxa during the period of mining activity at Blea Tarn. Diatom analysis would also have presented a way to corroborate the interpretations from the trends in diatoxanthin along with presenting the ability to determine the proportions of benthic and planktonic species.

7.2 Changes in algal biomass and community composition in small English lakes

All three lakes showed change in both algal biomass and community composition throughout the sediment cores. The greatest change has been experienced in the most recent decades, from the ~1970s, with periods of enhanced algal biomass (chlorophyll-*a*) associated with broad increases in planktonic taxa (cryptophytes) and fast-growing taxa which can inhabit both planktonic and benthic habitats (chlorophytes, picocyanobacterial). These increases likely represent a shift towards more planktonic taxa, which is consistent with observations from across the UK (e.g. Dong *et al*., 2011; Moorhouse, 2016) and at other sites globally (e.g. Oleksy *et al*., 2021; Sivarajah *et al*., 2016; Wolfe *et al*., 2001).

Whilst there have been observed increases in chlorophytes, cryptophytes and picocyanobacteria, the response of diatoms has been more variable. In Lake Gormire, diatom biomass increased during the 20th century at a comparable rate with the other algal taxa. In comparison, for both Blea Tarn and Sunbiggin Tarn, diatoms declined following a period of stimulation by atmospheric pollution and nutrients respectively, although over different timescales. The more variable response of diatoms indicates that the planktonic and faster growing algal taxa (e.g. chlorophytes) may have been responding to broader and more regional drivers, and the diatoms may be controlled by more local and site-specific factors. In general, the trends in diatoxanthin in the three lakes indicate that diatoms may be particularly sensitive to particular drivers of change, notably water clarity which had a clear impact in Lake Gormire and Blea Tarn. Additionally, Si availability was likely driving a period of increased diatom biomass in Blea Tarn which is typically one of the most common limiting factors for diatom growth (Billen *et al*., 2001; Kong *et al*., 2021). Whilst Si availability is important for diatom growth, light availability and temperature are major growth controlling factors for all algae. Increased temperature had a stimulatory impact on most algal taxa in Lake Gormire and cold periods also likely contributed to periods of reduced diatom biomass. Very low abundances of diatoms were recorded during particularly cold periods, for example towards the end of the Little Ice Age (19th century). In general, diatoms appear to be particularly sensitive to changes in these environmental variables, especially in Lake Gormire.

Despite predictions of cyanobacteria dominance in lakes subject to warming or eutrophication (e.g. Johnk *et al*., 2008; Reynolds, 2006), this was rarely experienced in any of the lakes analysed in this research. Whilst it is difficult to estimate in-lake biomass of a particular taxa from pigments alone, changes in the relative abundance can indicate if a taxa is becoming more dominant. In Sunbiggin Tarn, there were sub-decadal periods of enhanced filamentous cyanobacteria abundances as sedimentation rates declined, likely reflecting N limitation following extensive in-lake utilisation and rapid declines in nutrient loading. There was a longer period where filamentous cyanobacteria became more dominant in Lake Gormire during the 19th century. This was a period of generally low productivity, cold temperatures and probably low N availability. It was also a period of low water clarity and the gradual shift towards greater proportions of cyanobacteria likely reflects the competitive advantage of some N-fixing cyanobacteria that are well adapted for low light conditions. The increase in dominance of cyanobacteria was reversed by the start of the 20th century when chlorophytes and cryptophytes increased in relative proportions, with chlorophytes becoming more dominant during the 20th century. Increasing chlorophyte dominance was also experienced in Blea Tarn and Sunbiggin Tarn during most of the 20th century. In Blea Tarn this was likely the result of increased nutrient loading and temperature. Therefore, while a shift towards cyanobacteria dominance can occur in these lakes, it seems to preferentially take place under conditions of low nutrient availability and low water clarity.

Establishing changes in cryptophyte abundances was particularly useful as they represent a predominantly planktonic algal group. Along with being predominantly planktonic, cryptophytes are often mixotrophic which can often lead to them to responding to changes in OM and DOC concentrations, that are used as an energy source (Jansson *et al*., 2000; Jones, 2000). In general, cryptophytes represent a defined algal group which often responded differently to drivers of change than other algal groups which helped to identify the main drivers during periods of algal biomass change. For example, in Lake Gormire cryptophytes became more dominant in the algal community during the period of peak catchment erosion. Conversely cryptophytes declined in Blea Tarn following improvements in water clarity. Both likely relate to changes in OM inputs and DOC concentrations, demonstrating a more direct link between these inputs and algal biomass.

The year 1850 AD has often been suggested to represent a lake's 'baseline conditions' or its pre-anthropogenically impacted state (Bennion *et al*., 2004). However, this is unlikely to be the case for many lakes in England due to their close proximity to human populations. For Lake Gormire, there were clear impacts on algal community composition following a period of deforestation in the early 18th century and mining activity around Blea Tarn can be detected in the sediments through the entirety of the 19th century. While the sediment core of Sunbiggin Tarn extends to around the 1960s, analysis by Bennion *et al.* (2017) indicated that the lake has experienced other periods of change in the early 20th century, likely reflecting the impact of a degree of nutrient enrichment and the absence of *Chara* sp. Considering the range of impacts that are recorded in the cores at different points in time, it is likely that to confidently establish a lakes pre-impacted state then the sediment cores should ideally extend several hundred years before AD 1850.

Although anthropogenic impacts can be detected from several hundred years before the present, analysis from the 1950s often captures the period of predominant and maximum change, representing the start of the Anthropocene (Syvitski *et al*., 2020). The period of maximum change for Lake Gormire and Blea Tarn occurred during the Anthropocene, with anthropogenic impacts accelerating from the 1970s and 1950s respectively. Analysis of the relationship between algal biomass and metrological data from ca 1960 is justified due to the ^{210}Pb dating uncertainty ranges, which generally increase the older the sediments. As a result, the reliability of timings and rates of changes from sediments prior to ca 1960s are limited. Accurate chronologies are essential in being able to link the timings and the rate of change to anthropogenic and climate drivers.

7.3 Identifying changes in sedimentary OM sources using C/N, δ^{13}C and δ^{15}N

The $\delta^{13}C_{org}$, δ^{15}N and C/N values were used to indicate periods of deforestation, eutrophication from gulls, increased catchment productivity and increased algal productivity. Ultimately, all three lakes showed that OM changes were heavily controlled by changes in the catchments. However, there were some clear differences between the magnitude of the impacts. Both Lake Gormire and Blea Tarn have experienced deforestation in the catchment during the time periods captured by the sediment cores. For Lake Gormire, deforestation resulted in rapid declines in %C, driven by dilution from enhanced allochthonous inputs, with progressive increases in $\delta^{13}C_{org}$, δ^{15}N and a decline in C/N. These trends were replicated in Blea Tarn during the period of deforestation, however the impacts were markedly different between these lakes. For Blea Tarn, the change in $\delta^{13}C_{org}$ and C/N was relatively small (<0.2‰ and 0.8, respectively) and in comparison, $\delta^{13}C_{org}$ and C/N shifted by ~3‰ and 1.5‰, respectively, in Lake Gormire. The large difference in the response between the two lakes to deforestation may reflect differences in the extent of forest loss. However it is more likely to reflect their sensitivity to deforestation which is largely related to catchment size.

While the extent of deforestation in the Blea Tarn catchment in the first half of the 20th century is known (Haworth, 1969), for Lake Gormire this is not the case. The catchment of Lake Gormire is ~5 times smaller than Blea Tarn (relative to the lake surface area) and is currently >80% woodland. In comparison, the woodland extent at Blea Tarn is <10%. Whilst there would have been changes in woodland cover over time, woodland still dominates the Lake Gormire catchment while it is a relatively minor constituent in Blea Tarn. Therefore, it is likely that there was greater deforestation in the Lake Gormire catchment, relative to the total catchment size, which would result in a greater impact in changing the OM delivery to the lake. The greater impacts from deforestation in Lake Gormire were also reflected by the algae. Blea Tarn experienced some minor stimulation from enhanced nutrient loading, but in Lake Gormire there was essentially a restructuring of the algal community with diatoms rapidly losing dominance in the lake. This indicates how catchment land cover and size have a strong influence on OM delivery to these lakes. It highlights how lakes with a smaller catchment and a more homogeneous landcover are more likely to be sensitive to changes in the catchment.

Both Lake Gormire and Blea Tarn showed declines in $\delta^{13}C_{org}$ and $\delta^{15}N$ during the 20th century, reflecting greater productivity. In general, it is likely that these declines were a combination of an increase in both in-lake and catchment productivity, leading the delivery of OM with lower $\delta^{13}C$ and $\delta^{15}N$ to the sediments. However, there appears to be some clear differences in the dominant driver of the declines in $\delta^{13}C_{org}$ and $\delta^{15}N$ during the 20th century between these lakes. For Blea Tarn, $\delta^{13}C_{org}$ started to decline around 20 years before any indication of algal biomass increasing. Considering the strong correlation between lake water $\delta^{13}C_{DIC}$ and catchment productivity in the Lake District (Maberly *et al.*, 2013), this earlier shift in $\delta^{13}C_{org}$ is likely to be driven by catchment changes. For Lake Gormire, $\delta^{13}C_{org}$ and algal biomass started to increase concurrently, around 50 years before any documented increase in catchment productivity. Therefore, for the 20th century, it appears that $\delta^{13}C_{org}$ is primarily reflecting algal productivity in Lake Gormire, whereas in Blea Tarn the $\delta^{13}C_{org}$ signal is more likely a composite of catchment and algal productivity. These variations highlight the need for multiproxy analysis to add lines of supporting evidence in establishing the drivers of $\delta^{13}C$ change.

The differences in the dominant driver of $\delta^{13}C_{org}$ change again likely reflects the differences in catchment characteristics between these lakes. For Blea Tarn, the larger catchment size means that it is likely to be supplied with a high quantity of OM from a range of sources. This probably makes it more resilient to any changes in discrete parts of the catchment, but a catchment wide change will have a large impact. Conversely, relatively small changes in the Lake Gormire catchment may have a profound impact. However, when these pressures are removed, the smaller catchment size means that a greater proportion of OM may be derived from algal sources. Ultimately, the greater sensitivity of Lake Gormire means that it is more responsive to change in the catchment. This lake-catchment relationship links to climate change, as enhanced temperatures during the second half of the 20th century have likely contributed towards the simulation of productivity in the Blea Tarn catchment, along with enhanced atmospheric N deposition. Enhanced catchment productivity at both Blea Tarn and Lake Gormire would be expected to impact the lake OM due to both the lakes being heavily influenced by their catchment. Whilst an increase in catchment productivity is likely to also be contributing towards enhanced algal biomass in Lake Gormire the closed hydrological basin will amplify changes in catchment derived inputs. Therefore, while both lakes are highly controlled by their catchments, as Blea Tarn is a hydrologically open basin, it will likely make it comparatively more resilient to change.

While the trends in Blea Tarn and Lake Gormire are largely reflective of productivity increases in the 20th century, for Sunbiggin Tarn it is most likely predominantly controlled by changes in the black-headed gull populations. The concurrent changes in $\delta^{13}C_{org}$ and $\delta^{15}N$ closely follow the trends in the documented gull populations (Fig. 7.1), despite some large increases in algal productivity at the time that would be expected to lower $\delta^{13}C_{org}$. This indicates the overwhelming impact of the gull population during most of the time period and prevents the use of $\delta^{13}C$ to infer changes in productivity in this lake during periods of large gull populations. However it does further support the use of $\delta^{15}N$ to track changes in gull population, as proposed by Michelutti *et al*. (2008).

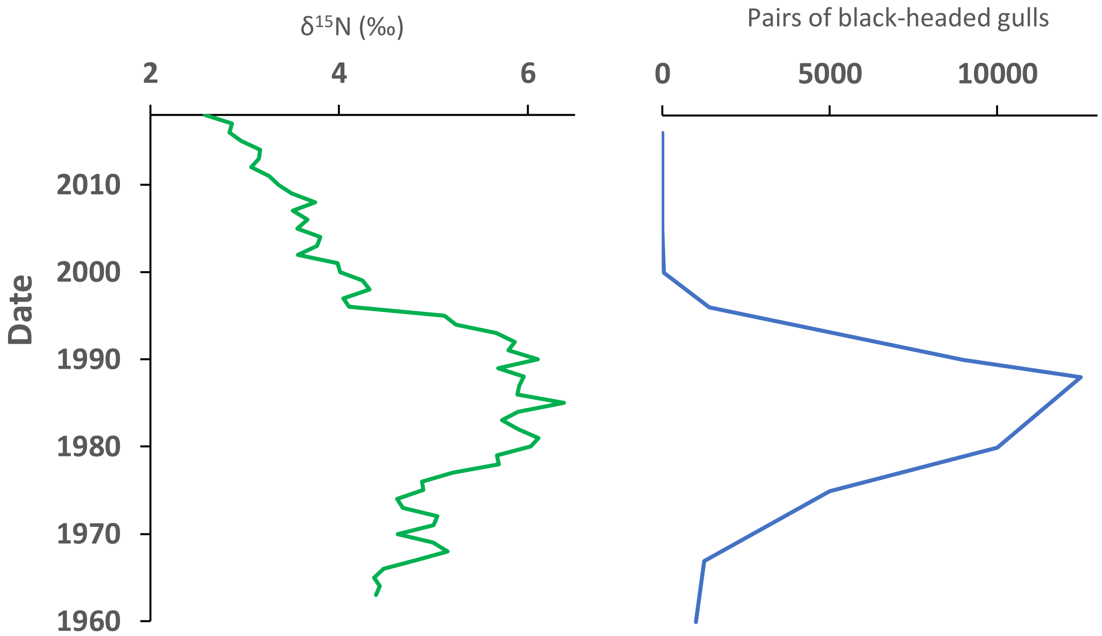

Fig. 7.1 Changes in δ^{15}N and pairs of black-headed gulls at Sunbiggin Tarn, synthesised from the observed and estimated population figures presented by Goldsmith *et al*. (2003) and Holdgate (2016).

Overall the trends in C, N and their isotopes show that lake OM is heavily impacted by changes in the catchment. This can overprint the signal of aquatic OM during periods of high catchment inputs as experienced most prominently in Lake Gormire and Sunbiggin Tarn. While the direction of change is likely to be the same, the magnitude can be different, largely controlled by catchment features and characteristics. In general, the data show a range of utilities for δ^{13}C, including recording catchment wide changes. If the dominant control of algal biomass is catchment derived nutrient inputs, then the reconstruction of δ^{13}C change is a useful tool to assess the drivers of in-lake change.

7.4 Anthropogenic pollution history and the impacts to algal communities

Both Blea Tarn and Lake Gormire showed clear signals of anthropogenic pollution from the middle of the 19th century. Typical for many lakes in the UK there were concurrent increases in most heavy metals (Cu, Cd, Zn, Pb) from around the middle of the 20th century (ROTAP, 2012; Yang and Rose, 2005a). While it is likely that atmospheric deposition was the primary delivery method, there were some clear differences in the timing of increases in heavy metal concentrations, indicating atmospheric pollution to be driven by change on a regional-local level. For Blea Tarn, there have been increases in heavy metal concentrations since the 17th century, likely reflecting a progressive expansion in anthropogenic activity in the catchment. One of the most impactful activities was mining which was extensive in the Windermere catchment during the second half of the 19th century. In comparison, there was a relatively rapid increase in heavy metal concentrations in Lake Gormire from the start of the 20th century. While the source of atmospheric pollution is unclear it may represent an industrial source from a more urbanised part of Yorkshire. The number of steam-driven textile mills in Bradford increased considerably during the second half of the 19th century (Richardson, 1986). This industry was powered primarily by coal combustion which would have emitted large quantities of smoke, ash and coal associated metals to the atmosphere. In general, the trends in atmospheric pollution between the two lakes is consistent with the observed trends across the UK, with the levelling off and some declines in sedimentary heavy metal concentrations from the second half of the 20th century.

The impacts of heavy metal pollution on lake algae are largely unclear in any of the three lakes. It would be expected that high loadings of heavy metals would have a negative impact on algal growth. Reductions in chlorophyte growth rate have been experienced in laboratory experiments subjected with elevated Cu and Cd concentrations (Visviki and Rachlin, 1994). However, the impacts are likely to be largely species specific as Cu pollution from the Greenburn Copper Mine resulted in the increase in Cu resistant diatom taxa in Little Langdale Tarn (Oswald *et al*., 2001). For Blea Tarn, there is evidence to suggest that increased mining activity resulted in the stimulation of diatoms and possibly cyanobacteria. However, for diatoms, this would likely have been due to an increase in Si input from industrial activities associated with mining rather than being related to the increasing heavy metal inputs at the time. Lake Gormire also shows little direct impact from heavy metal pollution, and although the increases in heavy metals occur around the same time algal productivity starts to increase these seem likely to be coincidental increases. At the start of the 20th century, allochthonous inputs were particularly high providing a constant source of minerals and metals to the lake. In conjunction, there was a period of enhanced algal biomass that occurred ~30 years prior to the increase in heavy metal concentrations. Therefore, it is unlikely that the algae in Lake Gormire would have been deficient of these micronutrients. For Sunbiggin Tarn, any impact from heavy metal pollution is overwhelmed by the changes in the gull populations. However, the gull populations do appear to be driving some of the change in heavy metal flux, probably reflecting changes in populations as they bioaccumulate and excrete these metals. The gull populations driving changes in heavy metal flux may represent a more indirect impact of atmospheric pollution to the lake as these metals bioaccumulate in the gulls. In general, heavy metal pollution to the lakes is identifiable in the sediment cores, but the impact on the algal communities appears largely undetectable. For the Windermere catchment, there has been documented changes in specific species in response to increased Cu loading (Miller *et al*., 2014). Therefore, it would be expected that similar impacts would be recorded in Blea Tarn considering its close proximity to mining activities. The reason that this is not identified in the sediment record likely represents more species-specific shifts in the diatom community itself, something that is not possibly to identify through pigment analysis alone.

The impacts of anthropogenic eutrophication were also largely unclear in all three lakes. While the lakes were selected to represent catchments with minimal to no agricultural use, atmospheric N deposition is widespread across the industrialised world (Holtgrieve *et al*., 2011). For Sunbiggin Tarn, any impact from atmospheric N deposition was obscured by the short time series and overwhelming impacts of the gull-driven eutrophication. For Blea Tarn and Lake Gormire, there was no evidence of the ‘hockey stick’ profile of δ^{15}N change since the 1950s, which has been experienced in many lakes subject to substantial N deposition (Holtgrieve *et al*., 2011). While it is difficult to assess the direct impacts from atmospheric N deposition on any of these lakes, it is likely that it had led to some stimulation of catchment vegetation in Blea Tarn, which ultimately contributed towards increases in algal biomass. For Lake Gormire, there is little evidence of an impact from atmospheric N deposition, with the δ^{15}N change likely reflecting a progressive increase in algal biomass in the lake from the first half of the 20th century. The differences in response may again be due to some catchment specific features, however the extremely high N deposition in the Lake District is also likely to be a big factor. Therefore, the differences in the impact of N deposition to the algal communities of these lakes may reflect regional differences in atmospheric N deposition.

7.5 Weather and climate

The impacts of weather and climate change were different between all three lakes. The strongest evidence for meteorological changes having an impact on lake algal biomass and community composition was in Lake Gormire. The strong impact of temperature on Lake Gormire indicates that the lake is a particularly sensitive to environmental change. The sensitivity of the lake to environmental change is expected in small, closed basin lakes (Bates *et al*., 2008). Therefore, it is likely that the morphological features of the lake act to amplify changes in temperature. In comparison, Blea Tarn appears to have been impacted by changes in temperature although it is a less dominant driver. While Blea Tarn is comparable in size to Lake Gormire, being a hydrologically open lake means that there is much greater transport of water to and from the lake system. While the lake may warm from direct solar heating, incoming water is often cooler and outflows can transport warmer water away from the lake. Therefore, hydrologically open lakes have a greater capacity to mitigate against temperature change and reduce the impacts of warming.

The sensitivity of Lake Gormire to meteorological variations was also indicated by the clear declines in algal biomass around the time of notable cold periods, such as towards the end of the Little Ice Age (15th – 19th centuries) and in the extreme cold winter of 1963 (Fig. 7.2). In comparison, Blea Tarn did not show any clear impacts from these widespread cold events. This likely emphasises the differences in the morphology between these lakes, with Lake Gormire more susceptible to extensive ice cover. Ice cover may be particularly quick to form and long lasting due to a greater degree of sheltering and lack of streams which would reduce ice breakup, along with reduced direct solar inputs in winter months due to the surrounding cliffs and woodlands.

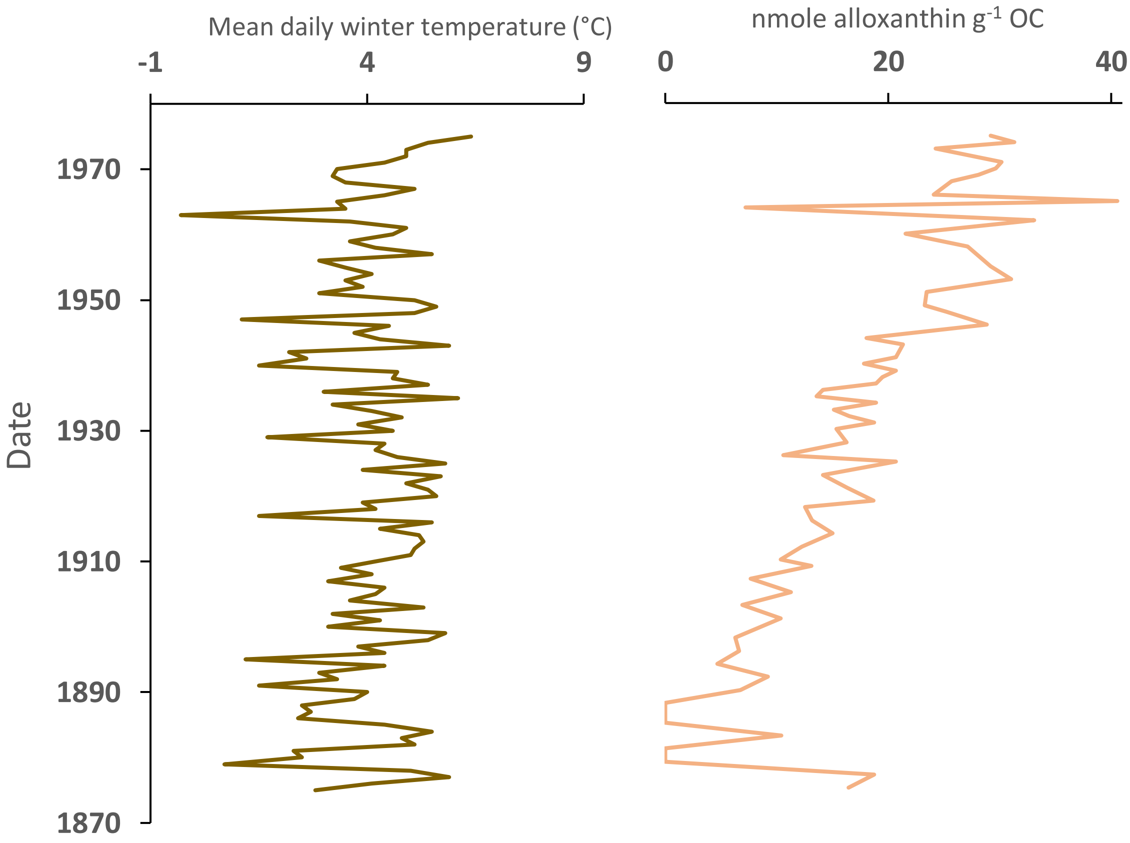

Fig. 7.2 Mean daily winter (December-February) temperature from the Central England Temperature record with alloxanthin concentrations between 1875 and 1975.

For both Lake Gormire and Blea Tarn the main period of algal biomass increase occurs from the 1970s, which represents the period when temperatures started to increase more rapidly at these sites. This is likely to be coincidental considering the change in the rest of the Windermere catchment is largely incoherent temporally (Moorhouse, 2016). Blea Tarn is likely to be more impacted by changes in catchment productivity since the 1950s.

While all algal groups were significantly stimulated by temperature in Lake Gormire, for Blea Tarn the impacts were more variable between taxa. Chlorophytes had the strongest correlation to changes in temperature, indicating climate to be a relatively strong driver of biomass change. In comparison with Lake Gormire there was no significant relationship to picocyanobacteria and cryptophytes with a negative relationship between temperature and diatoms. This shows that while there has been an increase in total lake algae there was also change in community composition. The shift in community composition in Blea Tarn indicates that there is likely to be more competition for resources, which has led to some taxa responding better to environmental changes than others. Therefore, chlorophytes have likely gained an advantage over most other algal taxa in Blea Tarn, possible reflecting their high optimum growth temperatures and nutrient uptake rates. The fact that this is not observed in Lake Gormire indicates less competition in the lake in response to rising temperatures. Potentially this represents the greater nutrient pool available to algae in Lake Gormire, with Blea Tarn subject to greater limitations on growth. Overall, while the response between total algal biomass and temperature is comparable between the two lakes, the response of the algal communities has been very different.

For Sunbiggin Tarn, the impacts from the extensive gull eutrophication probably obscured any climate impact, compromising statistical analysis to meteorological data. However, Sunbiggin Tarn shares a similarity with both Lake Gormire and Blea Tarn with increases in algal biomass during the 21st century. For Sunbiggin Tarn, this period of increase occurs as nutrient loading from the tarn decreased which has been identified through the reductions in lake water TP during the 21st century (Maberly *et al*., 2020). While the cause of the increase in chlorophytes uncertain, the timing and shift towards greater chlorophytes and picocyanobacteria is consistent with that experienced in the other two lakes, and in the Windermere catchment in response to warming (Moorhouse, 2016).

The sensitivity of Lake Gormire may also be related to a reduced degree of sediment resuspension. The more exposed environments of Blea Tarn and Sunbiggin Tarn are likely to create more water turbulence, which can disturb the sediments. Even relatively minor amounts of sediment disturbance can lead to a degree of mixing that ‘smooths out’ some of the shorter-term variations in algal pigments. For Sunbiggin Tarn, abundances of *Navicula* spp diatoms indicates that sediments were likely to be regularly disturbed (Goldsmith *et al*., 2003), reflecting high wave action and bank erosion at the lake. Therefore, the relatively sheltered Lake Gormire should be a site where change can be preserved at a higher resolution than the other sites. The sampling resolution of 0.25cm was selected to capture shorter-term variations that may have been recorded in the sediment profile. The finer scale sampling of sediment cores also allowed for a higher resolution comparison with meteorological data. In all three cores there were pigment samples that corresponded to a time period of 2 years from the 1960s which increased to at least an annual resolution from the 1990s. This allowed for greater statistical power in the regression analysis.

7.6 Using multiproxy approach to understand the drivers of algal community change

A range of techniques was used to establish the drivers of algal change in the lakes studied in the research. While algal pigments were primarily used to reconstruct changes in past biomass and community composition, they also presented a way to reconstruct past lake conditions. The use of the pigment scytonemin was particularly useful as this presented a way to reconstruct changes in water clarity. For Lake Gormire, there were concurrent declines in water clarity and %C during the period of deforestation and this change was related to an increase in minerogenic input from the catchment. The increase in minerogenic input was supported by the ICP analysis, which showed concurrent increases in typically catchment derived elements (e.g. Al, K, Li, Mg). The range of elements analysed allowed for the assessment of the influence of catchment derived inputs on in-lake changes.

The quantification of a wide range of elements allowed for a chain of cause and effect to be established where periods of deforestation enhanced catchment erosion and reduced water clarity, to the extent where they supressed diatom abundances. While the concurrent increase in minerogenic content and decline in diatoms alone may suggest that a reduction in water clarity led to their suppression, the ability to reconstruct water clarity independently allowed this interpretation to be tested.

In general, combining reconstructed water clarity with indicators of catchment erosion allowed for the assessment of the main drivers of change in water clarity. In Blea Tarn there were periods when changes in water clarity appeared unrelated to changes in catchment erosion, such as during the period of intensive mining activity. In conjunction with the changes in diatom derived pigments and heavy metal concentrations, this allowed for the mining activity to be identified as the most likely cause of change. Without these additional data it is unlikely these links would have been able to be identified, and the changes in water clarity may have appeared to remain related to changes in catchment erosion.

The elemental data allowed for the investigation of a wider range of potential drivers of change in the lakes analysed. The combination of $\delta^{13}C$, $\delta^{15}N$ and C/N with algal pigments also helped to establish changes in algal productivity. Together they can be used to establish periods of enhanced algal biomass. Changes in $\delta^{13}C_{org}$ can be driven by variations in terrestrial inputs that may have a positive or negative impact on algal communities. For instance, in Blea Tarn $\delta^{13}C_{org}$ started to decline from the 1950s which may have indicated a shift towards greater in lake production. However there was no increase in algal pigments until at least the 1970s, indicating that it was likely related to a change in catchment inputs. Conversely, algal pigments were useful at establishing changes in algal biomass during periods when $\delta^{13}C_{org}$ was dominated by catchment inputs, therefore diluting the in-lake signal. Pigments also identified periods of shorter-term change that did not appear in the $\delta^{13}C_{org}$ or %C record. This may reflect the fact that $\delta^{13}C_{org}$ analysis is unable to differentiate between aquatic groups as they use the same source of C or indicate that the pigments were recording change at a much higher resolution.

For Sunbiggin Tarn the use of $\delta^{13}C_{org}$ to indicate changes in lake algal productivity or catchment inputs was largely confounded by the changes in gull population, which were likely driving the $\delta^{13}C_{org}$ and $\delta^{15}N$ changes over time. Additionally, the rapid changes in sedimentation rate affected the use of algal pigment concentrations themselves as they had likely been heavily diluted from large inputs of catchment OM. In Sunbiggin Tarn radiometric dating became essential in being able to establish changes in algal biomass over the time period. Due to the high sedimentation rates, the core spanned a relatively short time period compared to the other lakes. This allowed for a more accurate estimation of the sediment age throughout the entire core. As sedimentation rates were also able to be accurately estimated for all parts of the sediment core this allowed the pigment concentrations data to be transformed into flux rates. The establishment of pigment flux rates for Sunbiggin Tarn dramatically altered the interpretation of the pigment data, providing a more accurate representation of the changes in algal community through the time series.

The changes in $\delta^{15}N$ largely followed the changes in $\delta^{13}C_{org}$ for all three of the lakes, although there were some differences in the timings and magnitude of change. Along with C/N, these proxies enabled a greater understanding of the shifts in OM as they are likely to respond at different timescales. In Lake Gormire during the 20th century there were concurrent declines in $\delta^{13}C_{org}$ and $\delta^{15}N$ for the majority of the century, however the start of the decline is offset by ~25 years. Whilst $\delta^{13}C_{org}$ and $\delta^{15}N$ are likely responding to the same driver the difference in timing of these shifts likely represents a difference in the sensitives of the $\delta^{13}C$ and $\delta^{15}N$ pools to change. Therefore, using $\delta^{13}C$ or $\delta^{15}N$ from OM alone may obscure the timing of change. For instance, a lake which is heavily buffered against change in $\delta^{13}C$ may require relatively large changes in the source of OM to detect a shift. The relative insensitivity of $\delta^{13}C$ compared to $\delta^{15}N$ was likely reflected in the Blea Tarn sediment core, with $\delta^{15}N$ recording a greater and more pronounced change throughout while being highly correlated.

$\delta^{15}N$ has regularly been used to identify changes in nutrient sources. However, in systems largely devoid of anthropogenic nutrient loading it is likely that change in $\delta^{15}N$ will be dominated by other drivers, such as algal productivity. Therefore, additional indicators of nutrient loading may help to establish changes in nutrient dynamics. Sedimentary P concentration established through ICP analysis was another measure of change in nutrient dynamics, which helped to support the interpretation of the isotope data. For example, the decline in sedimentary P in Blea Tarn during the second half of the 20th century indicated a reduction in nutrient loading. The concurrent decrease in P, $\delta^{13}C_{org}$ and $\delta^{15}N$ from the 1950s indicated that the P reduction was likely due to increased utilisation. However, an absence of an increase in algal biomass during this period suggests the catchment to be the driver of the increase in utilisation, reducing P loading to lake. Therefore, sedimentary P concentration were essential to support the link between the changes in the catchment and the lake during the second half of the 20th century.

7.7 Summary

This thesis has used sediment cores from three small lakes across northern England to reconstruct change in algal biomass and community composition. Stable isotopes from OM ($\delta^{13}C$, $\delta^{15}N$) and trace elemental data were used to establish the drivers of change with statistical analysis to meteorological data performed to establish the influence of temperature and precipitation change. This research utilised a multiproxy approach to provide a high-resolution record of environmental change to add to the understanding on how small lakes are responding to climate change. The reconstruction of algal community change indicated rapid increases from the second half of the 20th century in all three lakes. Temperature had a strong positive impact on all algal groups in Lake Gormire, with the increases in Blea Tarn limited to specific groups. For Sunbiggin Tarn any impacts of temperature were likely to have been obscured by the overwhelming influence of the gull populations. In general, the catchment characteristics of these lakes had a strong regulatory effect on the in-lake response to environmental change.

8. Conclusions and management recommendations

This research was undertaken to better understand the response of small English lakes to climate change from the mid-20th century to the present day. This was essential in expanding the understanding of these understudied lakes and assess their sensitivity to change.

Algal biomass in all three lakes analysed was greater in the 21st century than at the start of the Anthropocene (from 1950). The response of the lakes to meteorological change was largely variable, primarily driven by differences in catchment characteristics and pollution history. Even in lakes which have appeared ecologically stable over much of the Holocene, such as Blea Tarn, there have been relatively rapid changes in algal communities during the second half of the 20th century. With temperature being a significant driver of change, the data from the previously stable Blea Tarn may indicate that most small lakes in England have experienced a degree of impact from 20th century climate warming. For Sunbiggin Tarn, any climate signals in the sedimentary records were masked by the influence of the gull population on the lake. However, the more recent increases in algal biomass in the lake may indicate the start of a detectable climate signal. Further analysis of Sunbiggin Tarn, through monitoring of seasonal changes in the lake algal community, would be required to establish if temperature is driving the most recent increase in algal biomass.

The greater response of Lake Gormire to meteorological change is largely due to it being a closed basin lake, which naturally amplifies external drivers of change such as temperature. In comparison, the open basin of Blea Tarn will enable greater regulation of the water temperature and buffer any major changes imparted from climate warming. These findings reinforce that closed basin lakes are naturally sensitive to meteorological and environmental change and as a result will typically experience greater ecological shifts than lakes that are of a similar size, but hydrologically open. The changes in Lake Gormire indicate that the greater sensitivity of the lake has led to earlier shifts and a greater magnitude of change in the algal community. Considering most of the lake research globally is undertaken on large hydrologically open lakes, there could be greater ecological change occurring in the more numerous smaller water bodies, in particular those which have hydrologically closed basins. Therefore, future research should be undertaken which analyses a wider range of closed basin lakes to assess whether the magnitude of changes experienced in Lake Gormire is widespread. Through this, improvements to management strategies can be made to help mitigate against the impacts of future climate warming. In general, climate change is predicted to impact lakes by increasing phytoplankton biomass with a shift in community composition towards higher proportions of cyanobacteria. While climate change has likely contributed towards increases in algal biomass in at least two of the lakes studied in this research, there has not been a shift towards cyanobacteria dominance.

All three lakes have recorded periods when the lake algal communities were clearly impacted by changes in their catchments. For Sunbiggin Tarn, the impacts of the changing gull populations dominated almost the entire timeseries, driving nutrient loading and increases in algal biomass. The rapid changes caused by the gull populations indicate a threshold response to nutrient loading, that has also been recorded in other English marl lakes such as Cunswick Tarn (Wiik *et al*., 2015b) and Hawes Water (Wiik *et al*., 2015a). While marl lakes may be naturally more resilient to nutrient loading, they can still be heavily impacted by it, potentially resulting in dramatic changes. These dramatic changes can occur when the natural resilience of marl lakes to change becomes overwhelmed. Such 'tipping points' in marl lakes is likely to be heavily influenced by a combination of the extent of nutrient loading, the abundances of *Chara* and their ability to co-precipitate additional P inputs. It is uncertain as to whether climate induced increases in nutrient loading may exceed the natural buffer capacity of most marl lakes. However, this is likely to be largely site specific, driven by catchment characteristics, land use and *Chara* abundance, all which control in lake nutrient concentrations. Establishing nutrient loadings at which the regulatory capabilities of marl lakes are exceeded could provide the opportunity to produce important modelling tools for future risk assessments. Therefore, more research on a wider range of marl lakes will be essential to better understand how these thresholds are reached and the long-term impacts on the ecological communities.

For the two non-marl lakes, periods of deforestation were indicated by changes in the inputs of OM, its isotopic composition and shifts in the algal community. The magnitude of change between these lakes was very different, with deforestation around Lake Gormire leading to greater and longer lasting impacts which were probably related to its relatively small catchment size. This would support the theory that smaller catchments are more sensitive to change. Conversely, the larger catchment of Blea Tarn is likely one of the main factors in its long-term ecological stability. Therefore, the data presented in this research indicate that lakes which have a closed-basin, are small or have a relatively small catchment are likely to be more sensitive, not only to climate change but to environmental change in general. Further research is needed to cover a wider range of lakes with these features to establish the precise impacts of these characteristics. Establishing how these characteristics influence a lake's sensitivity to change will help to identify the lakes which are more at risk from climate change in the future. This will aid in developing effective mitigation measures and ensure that the sustainability of these ecosystems is maintained.

This research also demonstrates how high-resolution multiproxy analyses can be used to establish the drivers and impacts of change on algal communities in lakes. It has presented pigment and isotope data at an annual, or bi-annual, resolution (every 0.25cm of sediment core) for the entirety of the Anthropocene (ca 1950), enabling a higher number of samples to be used for statistical testing, most notably the correlation to the meteorological data. High resolution sampling also allowed for the assessment of ecological impacts from shorter term events, indicated by the rapid declines in pigment concentrations in Lake Gormire during extremely cold winters. Whilst the ability to detect these relatively short-term events are probably related to the morphological features of the lake and the surrounding catchment, a lower resolution of sampling would probably have missed or smoothed out this change. For Blea Tarn, the more exposed nature of the site likely prevented the preservation of some of the more subtle changes but the timings of key periods of change were clearly recorded in the pigment and isotope records. Key events were also reflected in the data for Sunbiggin Tarn, with $\delta^{15}N$ tracking the changes in the black-headed gull populations. Therefore, this study supports the use of $\delta^{15}N$ to track historic changes in water bird populations around a lake. This technique could be used in lakes where accessibility is poor, such as in the arctic.

In conclusion, the data presented in this thesis contributes knowledge on how ecological communities in small English lakes are responding to climate change. The research has demonstrated that small closed-basin lakes are particularly sensitive to environmental change but also highlights their potential for indicating changes that may occur in other lakes, both regionally and nationally. The establishment of how small closed-basin lakes can be used as a sensitive indicator of the impacts of climate change has applicability not just for the UK but in other temperate parts of the world. While more research is needed to further test this hypothesis, for regions where the ecological changes in small closed-basin lakes is representative of other waterbodies in the region they could act as sentinels for wider change. Therefore, small closed-basin lakes may be utilised as ‘early warning systems’ to indicate the potential future response of the more numerous open-basin lakes. Through this, regions and nations may be able to focus resources to help protect these sensitive ecosystems from future environmental changes.

8.1 Future impacts, mitigation and management recommendations

8.1.1 Lake Gormire

For Lake Gormire, algal biomass was shown to have the strongest relationship to temperature out of the three lakes studied. Along with impacting the lake directly, warming will also impact the catchment through increasing terrestrial growth and OM mineralisation rates. Enhancements of the C and N cycles would provide greater nutrient loading to the lake. Therefore, under future climate warming, the observed changes during the 20th century would be expected to progress in Lake Gormire, with further dominance of chlorophytes and fast-growing cyanobacteria.

As a closed-basin lake, Lake Gormire is expected to be particularly impacted by climate change as additional nutrients naturally accumulate in the lake with little loss. Woodlands are often N limited and as a result, lakes with predominantly woodland catchments can also become N limited (Hayes *et al.*, 2015). Under such conditions it would be expected that N-fixing cyanobacteria would start to dominate and result in a loss of chlorophytes, which have high N demands. However, the long-term storage of nutrients in closed basin lakes may mean that N limitation in Lake Gormire is unlikely. As a result, it would be expected that the algal biomass in Lake Gormire will continue to increase under most climate change scenarios. Due to the high storage of P in the sediment and enhanced internal nutrient loading in summer months, algal biomass may become particularly high, especially in years with enhanced water loss.

The progression towards a highly productive algal-dominated lake may have been a natural one, with indications that C/N has gradually declined over the last ~3,500 years (Fisher *et al.*, 2003). However, it is likely that human activity in the catchment, along with climate change, has accelerated this process. The recovery of the woodland may help to slow this change, by increasing nutrient uptake in the catchment and reducing the quantities transported to the lake. The closed basin and steep sided catchment results in nutrients being readily delivered and easily retained in Lake Gormire. Therefore, it is essential that the lake catchment remains protected and tree cover is increased to enhance nutrient uptake and soil stability. Increases in soil stability will also help to increase water clarity, which has been improving during the 20th century. Ultimately Lake Gormire would benefit from the reestablishment of high abundances of submerged macrophytes. The pigment data indicated that the lake was a relatively clear water benthic system at the start of the 18th century, however this is not a state the lake has returned to. Therefore, increasing macrophyte abundance with the aim of reducing in-lake nutrient concentrations, and algal biomass, would be recommended. The extent of intervention largely depends on the desired endpoint, however it may be largely futile if the lake continues to progress towards a more productive system as this would be expected to restrict light availability to the benthic zone.

8.1.2 Blea Tarn

As with Lake Gormire, there has been an increase in total algal biomass at Blea Tarn partially driven by temperature since ~1970. As the climate warms the increase in algal biomass would be likely to continue. The community shift towards a greater chlorophyte dominance in Blea Tarn, largely at the expense of diatoms, would also be expected to continue. The response of other algal groups is less clear, but in the longer term they would probably be outcompeted by faster growing taxa, such as cyanobacteria. As increasing temperatures have likely contributed towards enhanced catchment productivity around Blea Tarn this would also be expected to continue in the future along with the associated decline in P loading. While the lake was likely N-limited in the past, it may become P-limited in the future if P loading continues to decline. However, while P utilisation in the catchment will likely increase with temperature, it may become more available through greater internal loading and OM degradation rates. While the net balance in change is difficult to estimate, the consistent decline in P concentrations since the 1950s indicates a net loss of P to the lake despite increases in temperature. If external P loading continues to decline there may be a point where in-lake productivity becomes limited by the catchment. Previous work by Haworth (1969) and Grosvenor *et al*. (2017) indicated that Blea Tarn has remained remarkably stable for over 6000 years, with $\delta^{13}C_{org}$ values today only slightly higher than the lows recorded between 5810 and 6232 BP. These findings may indicate that the features of the lake and the catchment results in a natural regulation system that has maintained the ecological conditions of the lake within relatively narrow and well-defined boundaries during large parts of the Holocene. While it is largely uncertain, it may be that the algal community in Blea Tarn is already close to the upper end of change that the lake can naturally exhibit. However, considering the rate and potential magnitude of temperature change by the end of the 21st century, there may still be a particular temperature/nutrient threshold that has not previously been reached in the lake. Such climate induced ‘tipping points’ could be reached if increases in nutrient availability, such as through enhanced OM degradation and internal loading, exceed the uptake rates of catchment vegetation. It is possible that under future climate warming catchment vegetation will reach their own thresholds for growth and potentially become limited by factors other than nutrient supply. Under such conditions, nutrient exports to Blea Tarn could increase and the regulatory ability of the catchment weakened. Therefore, it should be anticipated that climate change could alter these ecological boundaries and increase the potential for a shift to a new ecological state. However, the lake has not shown signs of a major shift until relatively recently, despite evidence for periods of deforestation, heavy metal pollution and atmospheric N deposition.

It is evident that the catchment of Blea Tarn has an overwhelming control on the lake's ecological community. Therefore, ensuring that the catchment is not subject to any extensive alteration is essential in mitigating against the changes already occurring in the lake. While it is possible that the lake will self-regulate in the future and buffer any impacts of climate change, this is uncertain. If it does, the point at which self-regulation occurs maybe one of a much higher algal and chlorophyte biomass than has been experienced in the lake for much of the Holocene. If the algal biomass increases enough it may start impacting on the ecological conditions of the lake, recreational or leisure services and downstream water courses. To help ensure that the lake can return to a relatively stable state, as it has done for much of the Holocene, some degree of reforestation would be beneficial to the lake. Increases in tree cover around the catchment would help to enhance nutrient uptake, reduce nutrient export and erosion rates. However, considering the relatively small impact that the previous period of deforestation had on the lake, any reforestation may need to be extensive to have any notable impact.

8.1.3 Sunbiggin Tarn

The overwhelming influence on Sunbiggin Tarn has been the changes in the black-headed gull population. However, with numbers currently negligible and no indication of their return the lake is likely to enter a period of relative stability as eutrophication continues to decline and submerged macrophytes recover. The effects from the gull eutrophication show that despite being relatively resilience to nutrient loading, it can still result in dramatic changes in marl lakes. Therefore, this research provides an example of the impacts to marl lakes from environmental disturbance which can be applied to anthropogenic drivers of change.

Marl lakes are typically quick to recover from eutrophication, however the catchment itself appears to be recovering at a slower rate. As a result, nutrient loading from the catchment may continue to decline in future years, in the absence of any further gull pressures. Improvements in the catchment, with associated improvements in water clarity and macrophytes abundances, will further reduce in-lake nutrient concentrations through enhanced utilisation and co-precipitation of P from *Chara*.

Whilst the current impact of temperature on the algal communities of Sunbiggin Tarn is largely unknown, it would be expected to be less impacted than Blea Tarn considering the natural resilience of marl lakes. Additionally, Sunbiggin Tarn is fed through springs which emerge relatively close to the lake. Being spring-fed means that the lake is resupplied by relatively cold water as there is less time to be warmed by the atmosphere before the water enters the lake. Therefore, it may be the case that there have not been any temperature-driven changes to the algal communities of Sunbiggin Tarn to date. However, the most recent increase in chlorophytes indicate a driver of change unlikely to be related to the previous gull pressures. Whilst this may represent a temperature-driven impact, the recent increase in chlorophytes may be directly related to the increase in water clarity stimulating benthic taxa. In general, it would be expected that Sunbiggin Tarn will be less impacted by climate changes in the future, in comparison to non-marl lakes such as Blea Tarn. Sunbiggin Tarn and Blea Tarn are roughly the same size (in both lake and catchment surface area), of similar altitude and there is only 30 miles distance between them. While there are some clear differences in terms of catchment geography and land cover, Sunbiggin Tarn would also be expected to be resilient to change.

Mitigation measures should be focussed on maintaining the relatively clear water and macrophyte dominated state that marl lakes are defined by. The current management strategies should be preserved or strengthened, including the current fencing surrounding the lake which excludes livestock from the parts of the catchment closest to the lake. In general, the low densities of livestock around the catchment are unlikely to have a big impact on nutrient loading to the lake (Bennion *et al.*, 2003). However, preventing livestock from degrading the surrounding fenland may be more beneficial considering the impacts previously experienced by the gull populations.

9. References

Adrian, R., O'Reilly, C., Zagarese, H., Baines, S., Hessen, D., Keller, W., Livingstone, D., Sommaruga, R., Straile, D., Van Donk, E., Weyhenmeyer, G. and Winder, M. (2009). *Lakes as sentinels of climate change*. *Limnology and Oceanography*, 54(6part2), 2283-2297.

Adrian, R., Walz, N., Hintze, T., Hoeg, S. and Rusche, R. (1999). Effects of ice duration on plankton succession during spring in a shallow polymictic lake. *Freshwater Biology*, 41(3), 621-634.

Adrian, R., Wilhelm, S. and Gerten, D. (2006). Life-history traits of lake plankton species may govern their phenological response to climate warming. *Global Change Biology*, 12(4), 652-661.

Airs, R., Jie, C. and Keely, B. (2000). A novel sedimentary chlorin: structural evidence for a chlorophyll origin for aetioporphyrins. *Organic Geochemistry*, 31(11), 1253-1256.

Airs, R., Atkinson, J. and Keely, B. (2001). Development and application of a high resolution liquid chromatographic method for the analysis of complex pigment distributions. *Journal of Chromatography* A, 917(1-2), 167-177.

Akselsson, C., Westling, O., Alveteg, M., Thelin, G., Fransson, A. and Hellsten, S., 2008. The influence of N load and harvest intensity on the risk of P limitation in Swedish forest soils. *Science of The Total Environment*, 404(2-3), 284-289.

Alexander, L.V., Tett, S.F.B. and Jonsson, T. (2005). Recent observed changes in severe storms over the United Kingdom and Iceland. *Geophysical Research Letters*, 32, L13704.

Algül, F. and Beyhan, M., 2020. Concentrations and sources of heavy metals in shallow sediments in Lake Bafa, Turkey. *Scientific Reports*, 10(1), 11782.

Allan, R. (2011). Climate change: Human influence on rainfall. *Nature*, 470(7334), 344-345.

Anderson, N., Curtis, C., Whiteford, E., Jones, V., McGowan, S., Simpson, G. and Kaiser, J. (2018). Regional variability in the atmospheric nitrogen deposition signal and its transfer to the sediment record in Greenland lakes. *Limnology and Oceanography*, 63(5), 2250-2265.

Apolinarska, K., Woszczyk, M. and Obremska, M. (2011). Late Weichselian and Holocene palaeoenvironmental changes in northern Poland based on the Lake Skrzynka record. *Boreas*, 41(2), 292-307.

Appleby, P.G. and Oldfield, F. (1978). The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported 210Pb to the sediment. *Catena*, 5, 1-8.

Appleby, P. G., Nolan, P. J., Gifford, D. W., Godfrey, M. J., Oldfield, F., Anderson, N. J. and Battarbee, R. W. (1986). ^{210}Pb dating by low background gamma counting. *Hydrobiologia*, 141, 21-27.

Appleby, P., Richardson, N. and Nolan, P. (1991). ^{241}Am dating of lake sediments. *Hydrobiologia*, 214(1), 35-42.

Appleby, P. G., Richardson, N. and Nolan, P.J. (1992). Self-absorption corrections for well-type germanium detectors. *Nuclear Instruments and Methods in Physics Research* Section B, 71, 228-233.

Appleby, P. G. (2001). Chronostratigraphic techniques in recent sediments. In: Last, W. M. and Smol, J. P. (eds.) *Tracking Environmental Change in Lake Sediments*. Kluwer, 171-203.

Appleby, P. (2004). Environmental change and atmospheric contamination on Svalbard: sediment chronology. *Journal of Paleolimnology*, 31, 433-443.

Appleby, P. (2008). Three decades of dating recent sediments by fallout radionuclides: a review. *The Holocene*, 18(1), 83-93.

Appleby, P. (2013). 210Pb dating: thirty-five years on. *Journal of Paleolimnology*, 49(4), 697-702.

Arenas, C., Vázquez-Urbez, M., Auqué, L., Sancho, C., Osácar, C. and Pardo, G. (2013). Intrinsic and extrinsic controls of spatial and temporal variations in modern fluvial tufa sedimentation: A thirteen-year record from a semi-arid environment. *Sedimentology*, 61(1), 90-132.

Arias-Ortiz, A., Masqué, P., Garcia-Orellana, J., Serrano, O., Mazarrasa, I., Marbà, N., Lovelock, C., Lavery, P. and Duarte, C. (2018). Reviews and syntheses: ^{210}Pb-derived sediment and carbon accumulation rates in vegetated coastal ecosystems – setting the record straight. *Biogeosciences*, 15(22), 6791-6818.

Arnell, N., Halliday, S., Battarbee, R., Skeffington, R. and Wade, A. (2015). The implications of climate change for the water environment in England. *Progress in Physical Geography*, 39(1), 93-120.

Arvola, L., George, G., Livingstone, D. M., Järvinen, M., Blenckner, T., Dokulil, M. T., Jennings, E., Aonghusa, C. N., Nõges, P., Nõges, T. and Weyhenmeyer, G. A. (2010). ‘The Impact of the Changing Climate on the Thermal Characteristics of Lakes’ in D.G. George (ed.), *The Impact of Climate Change on European Lakes*, 85 Aquatic Ecology Series 4.

ASC. (2016). UK Climate Change Risk Assessment 2017 Synthesis Report: priorities for the next five years. *Adaptation Sub-Committee of the Committee on Climate Change*, London.

Bakker, E. and Hilt, S. (2015). Impact of water-level fluctuations on cyanobacterial blooms: options for management. *Aquatic Ecology*, 50(3), 485-498.

Bancroft, B. A., Baker, N. J. and Blaustein, A. R. (2007). Effects of UVB radiation on marine and freshwater organisms: a synthesis through meta-analysis. *Ecology Letters*, 10, 332-345.

Bard, E. (2001). Comparison of alkenone estimates with other paleotemperature proxies. *Geochemistry, Geophysics, Geosystems*, 2(1), 2000GC000050.

Barlow, D., Harris, E., and McFarlane, A. (2009). Windermere Fluvial Audit. Report A: Catchment Scale Geomorphology - Technical Report. *Report to Environment Agency North West Region prepared by JACOBS Engineering UK Ltd*. Tech. rep.

Barica, J., Kling, H. and Gibson, J. (1980). Experimental Manipulation of Algal Bloom Composition by Nitrogen Addition. *Canadian Journal of Fisheries and Aquatic Sciences*, 37(7), 1175-1183.

Barker, P., Pates, J., Payne, R. and Healey, R. (2005). Changing nutrient levels in Grasmere, English Lake District, during recent centuries. *Freshwater Biology*, 50(12), 1971-1981.

Barker, P.A., Wilby, R.L. and Borrows J. (2004). A 200 year precipitation index for the Central English Lake District. *Hydrological Sciences Journal*, 49, 769-785.

Bates, B., Kundzewicz, Z., Wu, S. and Palutikof, J. Eds. (2008). Climate Change and Water. *Technical Paper of the Intergovernmental Panel on Climate Change*. IPCC Secretariat, Geneva, 210 pp.

Battarbee, R. W. (1984). Diatom analysis and the acidification of lakes. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 305, 451-477.

Battarbee, R. (2000). Palaeolimnological approaches to climate change, with special regard to the biological record. *Quaternary Science Reviews*, 19(1-5), 107-124.

Battarbee, R., Anderson, N., Bennion, H. and Simpson, G. (2012). Combining limnological and palaeolimnological data to disentangle the effects of nutrient pollution and climate change on lake ecosystems: problems and potential. *Freshwater Biology*, 57(10), 2091-2106.

Battarbee, R. W., Charles, D. F., Dixit, S. S. and Renberg, I. (1999). Diatoms as indicators of surface water acidity. In Stoermer E. F. and Smol J. P. (eds.) *The Diatoms: Applications for the Environmental and Earth Sciences*, Cambridge University Press, Cambridge, 85-127.

Battarbee, R., Shilland, E., Kernan, M., Monteith, D. and Curtis, C. (2014). Recovery of acidified surface waters from acidification in the United Kingdom after twenty years of chemical and biological monitoring (1988–2008). *Ecological Indicators*, 37, 267-273.

Battarbee, R., Simpson, G., Bennion, H. and Curtis, C. (2010). A reference typology of low alkalinity lakes in the UK based on pre-acidification diatom assemblages from lake sediment cores. *Journal of Paleolimnology*, 45(4), 489-505.

Bennion, H., Appleby, P. G. and Phillips, G. L. (2001). Reconstructing nutrient histories in the Norfolk Broads, UK: implications for the role of diatom-total phosphorus transfer functions in shallow lake management. *Journal of Paleolimnology*, 26(2), 181-204.

Bennion, H., Battarbee, R. W., Sayer, C. D., Simpson, G. L. and Davidson, T. A. (2011). Defining reference conditions and restoration targets for lake ecosystems using paleolimnology: a synthesis. *Journal of Paleolimnology*, 45, 533-544.

Bennion, H., Clarke, G., Davidson, T., Rose, C., Rose, N., Turner, S., Sayer, C. (2008). Using novel palaeolimnological techniques to define lake conservation objectives (Phase 1). *Final Report to Natural England*. (ECRC Research Report 126). ECRC, UCL.

Bennion, H., Fluin, J. and Simpson, G. L. (2004). Assessing eutrophication and reference conditions for Scottish freshwater lochs using subfossil diatoms. *Journal of Applied Ecology*, 41, 124-138.

Bennion, H., Hilton, J. Hughes, M. Clark, J. Hornby, D. Kernan, M and Simpson, G. (2003). Development of a risk based prioritisation protocol for standing waters in Great Britain based on a georeferenced inventory – Phase 2. *R&D Technical Report*, P2-260/2/TR1.

Bennion, H., Kelly, M., Juggins, S., Yallop, M., Burgess, A., Jamieson, J. and Krokowski, J. (2014). Assessment of ecological status in UK lakes using benthic diatoms. *Freshwater Science*, 33(2), 639-654.

Bennion, H., Rawcliffe, R., Burgess, A., Clarke, G., Clarke, S., Davidson, T., Rose, C., Rose, N., Sayer, C. and Turner, S. (2009). Using novel palaeolimnological techniques to define lake conservation objectives. *Final Report to Natural England*, ISSN: 1366-7300.

Bennion, H., Rose, N. L., Burgess, A., Yang, H. and Bowers, J. (2006). Palaeolimnological investigation of English Lake SSSIs. *English Nature Research Reports*, No 694.

Bennion, H., Sayer, C., Clarke, S., Davidson, T., Rose, N., Goldsmith, B., Rawcliffe, R., Burgess, A., Clarke, G., Turner, S. and Wiik, E. (2017). Sedimentary macrofossil records reveal ecological change in English lakes: implications for conservation. *Journal of Paleolimnology*, 60(2), 329-348.

Bianchi, T., Engelhaupt, E., McKee, B., Miles, S., Elmgren, R., Hajdu, S., Savage, C. and Baskaran, M. (2002). Do sediments from coastal sites accurately reflect time trends in water column phytoplankton? A test from Himmerfjärden Bay (Baltic Sea proper). *Limnology and Oceanography*, 47(5), 1537-1544.

Bianchi, T. S., Johansson, B. and Elmgren, R. (2000). Breakdown of phytoplankton pigments in Baltic sediments: effects of anoxia and loss of deposit-feeding macrofauna. *Journal of Experimental Marine Biology and Ecology*, 251, 161-183.

Billen, G., Garnier, J., Ficht, A. and Cun, C. (2001). Modeling the response of water quality in the Seine River estuary to human activity in its watershed over the last 50 years. *Estuaries,* 24, 977-993.

Birks, H., Heiri, O., Seppa, H. and Bjune, A. (2010). Strengths and Weaknesses of Quantitative Climate Reconstructions Based on Late-Quaternary Biological Proxies. *The Open Ecology Journal*, 3, 68-110.

Birks, H. J., Line, J. M., Juggins, S., Stevenson, A. C. and Braak, C. J. (1990). Diatoms and pH Reconstruction. *Philosophical Transactions of the Royal Society of London. B, Biological Sciences*, 327, 263-278.

Blais, J., Macdonald, R., Mackay, D., Webster, E., Harvey, C. and Smol, J. (2007). Biologically Mediated Transport of Contaminants to Aquatic Systems. *Environmental Science and Technology*, 41(4), 1075-1084.

Boës X, Rydberg, J. Martinez-Cortizas, A., Bindler, R., Renberg, I. (2011) Evaluation of conservative lithogenic elements (Ti, Zr, Al, and Rb) to study anthropogenic element enrichments in lake sediments. *Journal of Paleolimnology*, 46, 75-87

Bogard, M., Vogt, R., Hayes, N. and Leavitt, P. (2020). Unabated Nitrogen Pollution Favors Growth of Toxic Cyanobacteria over Chlorophytes in Most Hypereutrophic Lakes. *Environmental Science and Technology*, 54(6), 3219-3227.

Bonk, A., Kinder, M., Enters, D., Grosjean, M., Meyer-Jacob, C. and Tylmann, W. (2016). Sedimentological and geochemical responses of Lake Żabińskie (north-eastern Poland) to erosion changes during the last millennium. *Journal of Paleolimnology*, 56(2-3), 239-252.

Borgå, K., Campbell, L., Gabrielsen, G. W., Norstrom, R. J., Muir, D. C. G., Fisk, A. T. (2006). Regional and species specific bioaccumulation of major and trace elements in Arctic seabirds. *Environmental Toxicology*, 25, 2927-2936.

Botter, G., Basu, N., Zanardo, S., Rao, P. and Rinaldo, A. (2010). Stochastic modeling of nutrient losses in streams: Interactions of climatic, hydrologic, and biogeochemical controls. *Water Resources Research*, 46(8), W08509.

Boyle, J., Chiverrell, R., Davies, H. and Alderson, D. (2014). An approach to modelling the impact of prehistoric farming on Holocene landscape phosphorus dynamics. *The Holocene*, 25(1), 203-214.

Brahney, J., Ballantyne, A., Turner, B., Spaulding, S., Otu, M. and Neff, J. (2014). Separating the influences of diagenesis, productivity and anthropogenic nitrogen deposition on sedimentary δ15N variations. *Organic Geochemistry*, 75, 140-150.

Brenner, M., Whitmore, T. J., Curtis, J. H., Hodell, D. A. and Schelske, C. L. (1999). Stable isotope (d13C and d15N) signatures of sedimented organic matter as indicators of historic lake trophic state. *Journel of Paleolimnology*, 22, 205-221.

Brenowitz, S. and Castenholz, R. W. (1997). Long-term effects of UV and visible irradiance on natural populations of a scytonemin-containing cyanobacterium (Calothrix sp.). *FEMS Microbiology Ecology*, 24, 343-352.

Brimble, S., Foster, K., Mallory, M., Macdonald, R., Smol, J. and Blais, J. (2009). High arctic ponds receiving biotransported nutrients from a nearby seabird colony are also subject to potentially toxic loadings of arsenic, cadmium and zinc. *Environmental Toxicology and Chemistry*, 28(11), 2426-2433.

Britton, G., Liaaen-Jensen, S. and Pfander, H. (2004). *Carotenoids handbook* (1st ed), Birkhäuser Verlag, Basel.

Brooks, S. J., Bennion, H. and Birks, J. B. (2001). Tracing lake trophic history with a chironomid – total phosphorus inference model. *Freshwater Biology*, 46, 513-533.

Brown, M.R. and Jeffrey, S. W. (1992). Biochemical composition of microalgae from the green algal classes Chlorophyceae and Prasinophyceae. 1. Amino acids, sugars and pigments. *Journal of Experimental Marine Biology and Ecology*, 161, 91-113.

Brunet, C., Brylinski, J. and Lemoine, Y. (1993). In situ variations of the xanthophylls diatoxanthin and diadinoxanthin: photoadaptation and relationships with a hydrodynamical system in the eastern English Channel. *Marine Ecology Progress Series*, 102, 69-77.

Buchaca, T. and Catalan, J. (2007). Factors influencing the variability of pigments in the surface sediments of mountain lakes. *Freshwater Biology*, 52(7), 1365-1379.

Bunting, L., Leavitt, P. R., Gibson, C. E., Mcgee, E. J. and Hall, V. A. (2007). Degradation of water quality in Lough Neagh, Northern Ireland, by diffuse nitrogen flux from a phosphorus-rich catchment. *Limnology and Oceanography*, 52, 354-369.

Bunting, L., Leavitt, P. R., Weidman, R. P. and Vinebrooke, R. D. (2010). Regulation of the nitrogen biogeochemistry of mountain lakes by subsidies of terrestrial dissolved organic matter and the implications for climate studies. *Limnology and Oceanography*, 55, 333-345.

Burkholder, J. M., Glibert, P. M. and Skelton, H. M. (2008). Mixotrophy, a major mode of nutrition for harmful algal species in eutrophic waters. *Harmful Algae*, 8, 77-93.

Burt, T. and Ferranti, E. (2012). Changing patterns of heavy rainfall in upland areas: a case study from northern England. *International Journal of Climatology*, 32(4), 518-532.

Cael, B., Heathcote, A. and Seekell, D., 2017. The volume and mean depth of Earth's lakes. *Geophysical Research Letters*, 44(1), 209-218.

Callieri, C., Bertoni, R., Contesini, M. and Bertoni, F. (2014). Lake Level Fluctuations Boost Toxic Cyanobacterial “Oligotrophic Blooms”. *PLoS ONE*, 9(10), 109526.

Campbell, L.M., Norstrom, R.J., Hobson, K.A., Muir, D.C.G., Backus, S., Fish, A.T. (2005). Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). *Science of the Total Environment*. 351, 247-263.

Cantonati, M., Guella, G., Spitale, D., Angeli, N., Borsato, A., Lencioni, V. and Filippi, M. (2014). The contribution of lake benthic algae to the sediment record in a carbonate mountain lake influenced by marked natural water-level fluctuations. *Freshwater Science*, 33(2), 499-512.

Carpenter, S. R. (2003). Regime shifts in lake ecosystems: pattern, and variation. *International Ecology Institute*, Oldendorf, Germany.

Carpenter, S. and Bergquist, A. M. (1985). Experimental tests of grazing indicators based on chlorophyll a degradation products. *Arch Hydrobiol*, 102: 303-317.

Carpenter, S., Elser, M. and Elser, J. (1986). Chlorophyll production, degradation, and sedimentation: Implications for paleolimnology1. *Limnology and Oceanography*, 31(1), 112-124.

Carvalho, L., Beklioglu, M. and Moss, B. (1995). Changes in a deep lake following sewage diversion - a challenge to the orthodoxy of external phosphorus control as a restoration strategy?. *Freshwater Biology*, 34(2), 399-410.

Carvalho, L., Miller, C., Spears, B., Gunn, I., Bennion, H., Kirika, A. and May, L. (2011). Water quality of Loch Leven: responses to enrichment, restoration and climate change. *Hydrobiologia*, 681(1), 35-47.

Castañeda, I. and Schouten, S. (2011). A review of molecular organic proxies for examining modern and ancient lacustrine environments. *Quaternary Science Reviews*, 30(21-22), 2851-2891.

Chan, S., Kendon, E., Fowler, H., Blenkinsop, S. and Roberts, N. (2014). Projected increases in summer and winter UK sub-daily precipitation extremes from high-resolution regional climate models. *Environmental Research Letters*, 9(8), 084019.

Charlton, M., Bowes, M., Hutchins, M., Orr, H., Soley, R. and Davison, P. (2018). Mapping eutrophication risk from climate change: Future phosphorus concentrations in English rivers. *Science of The Total Environment*, 613, 1510-1526.

Chen, N., Bianchi, T. S., McKee, B. A., Bland, J. M. (2001). Historical trends of hypoxia on the Louisiana shelf: application of pigments as biomarkers. *Organic Geochemistry*, 32, 543-561.

Chen, Q., Nie, Y., Liu, X., Xu, L. and Emslie, S. (2015). An 800-year ultraviolet radiation record inferred from sedimentary pigments in the Ross Sea area, East Antarctica. *Boreas*, 44(4), 693-705.

Cheng, F. and Basu, N. (2017). Biogeochemical hotspots: Role of small water bodies in landscape nutrient processing. *Water Resources Research*, 53(6), 5038-5056.

Chiverrell, R., Oldfield, F., Appleby, P., Barlow, D., Fisher, E., Thompson, R. and Wolff, G. (2008). Evidence for changes in Holocene sediment flux in Semer Water and Raydale, North Yorkshire, UK. *Geomorphology*, 100(1-2), 70-82.

Choi, W. J., Lee, S. M. and Ro, H. M. (2003). Evaluation of contamination sources of groundwater NO_3 - using nitrogen isotope data: a review. *Geosciences Journal*, 7, 81-87.

Choi, W. J. and Ro, H. M. (2003). Difference in isotopic fractionation of nitrogen in water- saturated and unsaturated soils. *Soil Biology and Biochemistry*, 35, 483-486.

Choi, W., Kwak, J., Lim, S., Park, H., Chang, S., Lee, S., Arshad, M., Yun, S. and Kim, H. (2017). Synthetic fertilizer and livestock manure differently affect δ15N in the agricultural landscape: A review. *Agriculture, Ecosystems and Environment*, 237, 1-15.

Cohen, A. S. (2003). Paleolimnology. *The History and Evolution of Lake Systems*, University Press Oxford, Oxford.

Connell, J. H. and Sousa, W. P. (1983). On the evidence needed to judge ecological stability or persistence. *American Naturalist*, 121, 789-824.

Costanzo, S. D., O'Donohue, M. J., Dennison, W. C., Loneragan, N. R. and Thomas, M. (2001). A new approach for detecting and mapping sewage impacts. *Marine Pollution Bulletin*, 42, 149-156.

Coulson, J. C. (1988). Black-headed gulls at Sunbiggin Tarn, Cumbria. *Report to the Nature Conservancy Council*. NCC.

Covington, W. W. (1981). Changes in forest floor organic matter and nutrient content following clear cutting in Northern Hardwoods. *Ecology*, 62, 41-48.

Cox, B. and Whitehead, P. (2009). Impacts of climate change scenarios on dissolved oxygen in the River Thames, UK. *Hydrology Research*, 40(2-3), 138-152.

Crossman, J., Eimers, M., Watmough, S., Futter, M., Kerr, J., Baker, S. and Dillon, P. (2016). Can recovery from disturbance explain observed declines in total phosphorus in Precambrian Shield catchments?. *Canadian Journal of Fisheries and Aquatic Sciences*, 73(8), 1202-1212.

Crossman, J., Futter, M., Whitehead, P., Stainsby, E., Baulch, H., Jin, L., Oni, S., Wilby, R. and Dillon, P. (2014). Flow pathways and nutrient transport mechanisms drive hydrochemical sensitivity to climate change across catchments with different geology and topography. *Hydrology and Earth System Sciences*, 18(12), 5125-5148.

Curtis, C., Battarbee, R., Monteith, D. and Shilland, E. (2014). The future of upland water ecosystems of the UK in the 21st century: A synthesis. *Ecological Indicators*, 37, 412-430.

Curtis, C., Evans, C., Helliwell, R. and Monteith, D. (2005). Nitrate leaching as a confounding factor in chemical recovery from acidification in UK upland waters. *Environmental Pollution*, 137(1), 73-82.

Curtis, C. J., Flower, R., Rose, N., Shilland, J., Simpson, G. L., Turner, S., Yang, H. and Pla, S. (2010). Palaeolimnological assessment of lake acidification and environmental change in the Athabasca Oil Sands Region, Alberta. *Journal of Limnology*, 69, 92-104.

Danen-Louwerse, H.J., Lijklema, L. and Coenraats, M. (1995). Coprecipitation of phosphate with calcium carbonate in Lake Veluwe. *Water Research,* 29(7), 1781-1785.

Daufresne M., Roger M. C., Capra H. and Lamouroux N. (2004). Long-term changes within the invertebrate and fish communities of the Upper Rhone River: effects of climatic factors. *Global Change Biology*, 10, 124-140.

Davis, P. A., Dent, M., Parker, J., Reynolds, C. S. and Walsby, A. E. (2003). The annual cycle of growth rate and biomass change in Planktothrix spp. In Blelham Tarn, English Lake District. *Freshwater Biology*, 48, 852-867.

Davies, J., Jenkins, A., Monteith, D., Evans, C. and Cooper, D. (2005). Trends in surface water chemistry of acidified UK Freshwaters, 1988–2002. *Environmental Pollution*, 137(1), 27-39.

Davies, S. J., Lamb, H. F. and Roberts, S. (2015). Micro-XRF core scanning in palaeolimnology: recent developments. In : Croudace, I.W. and Rothwell, R.G (eds) *Micro-XRF Studies of Sediment Cores*. Dordrecht, Springer Netherlands, 189-226.

Davison, W. (1993). Iron and manganese in lakes. *Earth-Science Reviews*, 34, 119-163.

Davidson, T., Bennion, H., Yang, H., Appleby, P. and Luckes, S. (2002). Investigation of recent environmental change at the Bosherston Lakes, Pembrokeshire. CCW Contract Science Report No. *Environmental Change Research Centre*, University College London, Research Report No. 496.

Davidson, T. A., Clarke, G. H., Morley, D., Rose, N., Turner, S. and Sayer, C.D. (2008). Palaeoecological investigation of the past biological structure and function of the Trinity Broads. *Environmental Change Research Centre*, University College London, Research Report No. 122. Report to the Trinity Broads Partnership.

de Leeuw, J., Methven, J. and Blackburn, M. (2015). Variability and trends in England and Wales precipitation. *International Journal of Climatology*, 36(8), 2823-2836.

de Wit, H., Mulder, J., Hindar, A. and Hole, L. (2007). Long-Term Increase in Dissolved Organic Carbon in Streamwaters in Norway Is Response to Reduced Acid Deposition. *Environmental Science* and *Technology*, 41(22), 7706-7713.

Delian, F., Tiebing, L. and Jie, Y., 1992. The process of formation of manganese carbonate deposits hosted in black shale series. *Economic Geology*, 87(5), 1419-1429.

DeNicola, D. M. (1996). Periphyton responses to temperature at different ecological levels. In Stevenson et al. (eds) *Algal Ecology: Freshwater Benthic Ecosystem*. United Kingdom, Elsevier Science, 149-181.

Deshpande, B., Tremblay, R., Pienitz, R. and Vincent, W. (2014). Sedimentary pigments as indicators of cyanobacterial dynamics in a hypereutrophic lake. *Journal of Paleolimnology*, 52(3), 171-184.

Devlin, M., Bricker, S. and Painting, S. (2011). Comparison of five methods for assessing impacts of nutrient enrichment using estuarine case studies. *Biogeochemistry*, 106, 177-205.

Dillon, J.G., Tatsumi, C.M., Tandingan, P.G., Castenholz, R.W. (2002). Effect of environmental factors on the synthesis of scytonemin, a UV-screening pigment, in a cyanobacterium (Chroococcidiopsis sp.). *Archives of Microbiology*, 177, 322-331.

Doi, H., Kikuchi, E., Shikano, S., Takagi, S. (2009). Differences in nitrogen and carbon stable isotopes between planktonic and benthic microalgae. *Limnology*, 11, 185-192.

Dolman, A., Rücker, J., Pick, F., Fastner, J., Rohrlack, T., Mischke, U. and Wiedner, C. (2012). Cyanobacteria and Cyanotoxins: The Influence of Nitrogen versus Phosphorus. *PLoS ONE*, 7(6), p.e38757.

Donald, D., Bogard, M., Finlay, K. and Leavitt, P. (2011). Comparative effects of urea, ammonium, and nitrate on phytoplankton abundance, community composition, and toxicity in hypereutrophic freshwaters. *Limnology and Oceanography*, 56(6), 2161-2175.

Dong, X., Bennion, H., Battarbee, R. W. and Sayer, C. D. (2011). A multiproxy palaeolimnological study of climate and nutrient impacts on Esthwaite Water, England over the past 1200 years. *The Holocene*, 22(1), 107-118.

Dong, X., Bennion, H., Maberly, S., Sayer, C., Simpson, G. and Battarbee, R. (2012). Nutrients exert a stronger control than climate on recent diatom communities in Esthwaite Water: evidence from monitoring and palaeolimnological records. *Freshwater Biology*, 57(10), 2044-2056.

Dodson, S., Arnott, S. and Cottingham, K. (2000). The relationship in lake communities between primary productivity and species richness. *Ecology*, 81(10), 2662-2679.

Douglass, M. S., Hamilton, P. B. Peinitz, R. and Smol, J. P. (2004). Algal indicators of environmental change in arctic and antarctic lakes and pond. In: Peinitz, R., Douglass, M. S. and Smol, J. P. (eds). *Long-Term Environmental Change in Arctic and Antarctic Lakes*. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Downing, J. A. (2010). Emerging global role of small lakes and ponds: little things mean a lot. *Limnetica*, 1, 9-24.

Downing, J., Prairie, Y., Cole, J., Duarte, C., Tranvik, L., Striegl, R., McDowell, W., Kortelainen, P., Caraco, N., Melack, J. and Middelburg, J. (2006). The global abundance and size distribution of lakes, ponds, and impoundments. *Limnology and Oceanography*, 51(5), 2388-2397.

Du, E., Terrer, C., Pellegrini, A., Ahlström, A., van Lissa, C., Zhao, X., Xia, N., Wu, X. and Jackson, R. (2020). Global patterns of terrestrial nitrogen and phosphorus limitation. *Nature Geoscience*, 13(3), 221-226.

Duarte, C. M. and Prairie, Y. T. (2005). Prevalence of heterotrophy and atmospheric CO2 emissions from aquatic ecosystems. *Ecosystems*, 8, 862-870.

Dupuis, A. and Hann, B. (2009). Warm spring and summer water temperatures in small eutrophic lakes of the Canadian prairies: potential implications for phytoplankton and zooplankton. *Journal of Plankton Research*, 31(5), 489-502.

Elliott, A. (2012). Is the future blue-green? A review of the current model predictions of how climate change could affect pelagic freshwater cyanobacteria. *Water Research*, 46(5), 1364-1371.

Elliott, J. A., Jones, I. D. and Thackeray, S. J. (2006). Testing the sensitivity of phytoplankton communities to changes in water temperature and nutrient load, in a temperate lake. *Hydrobiologia,* 559, 401-411.

Elliott, A., McElarney, Y. and Allen, M. (2016). The past and future of phytoplankton in the UK's largest lake, Lough Neagh. *Ecological Indicators*, 68, 142-149.

Elliott, J., Thackeray, S., Huntingford, C. and Jones, R. (2005). Combining a regional climate model with a phytoplankton community model to predict future changes in phytoplankton in lakes. *Freshwater Biology*, 50(8), 1404-1411.

Elmslie, B., Gushulak, C., Boreux, M., Lamoureux, S., Leavitt, P. and Cumming, B. (2020). Complex responses of phototrophic communities to climate warming during the Holocene of northeastern Ontario, Canada. *The Holocene*, 30(2), 272-288.

Elser, J. J. (2011). A world awash with nitrogen. *Science*, 334, 1504-1505.

Enders, S., Pagani, M., Pantoja, S., Baron, J., Wolfe, A., Pedentchouk, N. and Nuñez, L. (2008). Compound-specific stable isotopes of organic compounds from lake sediments track recent environmental changes in an alpine ecosystem, Rocky Mountain National Park, Colorado. *Limnology and Oceanography*, 53(4), 1468-1478.

English Nature. (1994). Site of Special Scientific Interest (SSSI) notification sheet under section 28 of the Wildlife and Countryside Act 1981. *File Ref. NY60/5 Sunbiggin Tarn and Little Asby Scar*. English Nature.

Engstrom, D. and Rose, N. (2013). A whole-basin, mass-balance approach to paleolimnology. *Journal of Paleolimnology*, 49(3), 333-347.

Environment Agency. (2008). Water quality data archive. Available at: https://environment.data.gov.uk/water-quality/view/landing [Accessed 09/06/2020].

Evans, C. and Monteith, D. (2001). Chemical trends at lakes and streams in the UK Acid Waters Monitoring Network, 1988-2000: Evidence for recent recovery at a national scale. *Hydrology and Earth System Sciences*, 5, 351-366.

Evans, C., Chapman, P., Clark, J., Monteith, D. and Cresser, M. (2006). Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology*, 12(11), 2044-2053.

Evans, C., Monteith, D. and Cooper, D. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, 137(1), 55-71.

Fedotov, A., Phedorin, M., Enushchenko, I., Vershinin, K., Krapivina, S., Vologina, E., Petrovskii, S., Melgunov, M. and Sklyarova, O. (2012). Drastic desalination of small lakes in East Siberia (Russia) in the early twentieth century: inferred from sedimentological, geochemical and palynological composition of small lakes. *Environmental Earth Sciences*, 68(6), 1733-1744.

Feller, M. C. (2009). Deforestation and Nutrient Loading to Fresh Waters. In Liken, G (ed.) *Encyclopedia of Inland Waters*, Academic Press, 29-44.

Fenn, M., Poth, M., Aber, J., Baron, J., Bormann, B., Johnson, D., Lemly, A., McNulty, S., Ryan, D. and Stottlemyer, R. (1998). Nitrogen Excess in North American Ecosystems: Predisposing Factors, Ecosystem Responses, and Management Strategies. *Ecological Applications*, 8(3), 706-733.

Fernandez, E. and Galvan, A. (2007). Inorganic nitrogen assimilation in Chlamydomonas. *Journal of Experimental Botany*, 58(9), 2279-2287.

Feuchtmayr, H., Thackeray, S. J., Jones, I. D., De Ville, M., Fletcher, J., James, B. and Kelly, J. (2012). Spring phytoplankton phenology - are patterns and drivers of change consistent among lakes in the same climatological region? *Freshwater Biology*, 57, 331-344.

Fielding, J., Croudace, I., Kemp, A., Pearce, R., Cotterill, C., Langdon, P. and Avery, R. (2020). Tracing lake pollution, eutrophication and partial recovery from the sediments of Windermere, UK, using geochemistry and sediment microfabrics. *Science of The Total Environment*, 722, 137745.

Findlay, D. L., Kasian, S. E. M., Stainton, M. P., Beaty, K. and Lyng, M. (2001). Climatic influences on algal populations of boreal forest lakes in the Experimental Lakes Area. *Limnology and Oceanography*, 46, 1784-1793.

Finlay, K., Patoine, A., Donald, D., Bogard, M. and Leavitt, P. (2010). Experimental evidence that pollution with urea can degrade water quality in phosphorus-rich lakes of the Northern Great Plains. *Limnology and Oceanography*, 55(3), 1213-1230.

Finstad, A., Andersen, T., Larsen, S., Tominaga, K., Blumentrath, S., de Wit, H., Tømmervik, H. and Hessen, D., 2016. From greening to browning: Catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes. *Scientific Reports*, 6(1), 31944.

Fisher, J., Barker, T., James, C. and Clarke, S. (2009). Water Quality in Chronically Nutrient-Rich Lakes: The Example of the Shropshire-Cheshire Meres. *Freshwater Reviews*, 2(1), 79-99.

Fisher, E., Oldfield, F., Wake, R., Boyle, J., Appleby, P. and Wolff, G. (2003). Molecular marker records of land use change. *Organic Geochemistry*, 34(1), 105-119.

Florian, C., Miller, G., Fogel, M., Wolfe, A., Vinebrooke, R. and Geirsdóttir, Á. (2015). Algal pigments in Arctic lake sediments record biogeochemical changes due to Holocene climate variability and anthropogenic global change. *Journal of Paleolimnology*, 54(1), 53-69.

Flower, R. J. (1993). Diatom preservation: experiments and observations on dissolution and breakage in modern and fossil material. *Hydrobiologica*, 269/270, 473-484.

Foerster, V., Junginger, A., Langkamp, O., Gebru, T., Asrat, A., Umer, M., Lamb, H., Wennrich, V., Rethemeyer, J., Nowaczyk, N., Trauth, M. and Schaebitz, F., 2012. Climatic change recorded in the sediments of the Chew Bahir basin, southern Ethiopia, during the last 45,000 years. *Quaternary International*, 274, 25-37.

Fogel, M. L. and Cifuentes, L. A. (1993). Isotope fractionation during primary production. In: Engel, M. H. and Macko, S. A. (eds.) *Organic Geochemistry: Principles and Applications*. New York. Plenum Press.

Foley, B., Jones, I., Maberly, S. and Rippey, B. (2012). Long-term changes in oxygen depletion in a small temperate lake: effects of climate change and eutrophication. *Freshwater Biology*, 57(2), 278-289.

Forstner, U. and Wittmann, G. (1979). Metal Pollution in The Aquatic Environment. Springer-Verlag, Berlin-Heidelberg, 486 pp.

Fortin, M. and Gajewski, K. (2009). Assessing the use of sediment organic, carbonate and biogenic silica content as indicators of environmental conditions in Arctic lakes. *Polar Biology*, 32(7), 985-998.

Foster, I., Chapman, A., Hodgkinson, R., Jones, A., Lees, J., Turner, S. and Scott, M. (2003). Changing suspended sediment and particulate phosphorus loads and pathways in underdrained lowland agricultural catchments; Herefordshire and Worcestershire, U.K. *Hydrobiologia*, 494(1-3), 119-126.

Foster, I. D., Mighall, T., Proffitt, H., Walling, D. and Owens, P. (2006). Postdepositional ^{137}Cs mobility in the sediments of three shallow coastal lagoons, SW England. *Journal of Paleolimnology*, 35, 881-895.

Foulds, S., Brewer, P., Macklin, M., Haresign, W., Betson, R. and Rassner, S. (2014). Flood-related contamination in catchments affected by historical metal mining: An unexpected and emerging hazard of climate change. *Science of The Total Environment*, 476, 165-180.

Fowler, D., Smith, R., Muller, J., Hayman, G. and Vincent, K. (2005). Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. *Environmental Pollution*, 137(1), 15-25.

France, R.L. (1995). Carbon-13 enrichment in benthic compared to planktonic algae: foodweb implications. *Marine Ecology Progress Series*, 124, 307-312.

Freeman C., Evans C. D., Monteith D. T., Reynolds B. and Fenner N. (2001). Export of organic carbon from peat soils. *Nature*, 412, 785.

Friedrich, J., Janssen, F., Aleynik, D., Bange, H., Boltacheva, N., Çagatay, M., Dale, A., Etiope, G., Erdem, Z., Geraga, M., Gilli, A., Gomoiu, M., Hall, P., Hansson, D., He, Y., Holtappels, M., Kirf, M., Kononets, M., Konovalov, S., Lichtschlag, A., Livingstone, D., Marinaro, G., Mazlumyan, S., Naeher, S., North, R., Papatheodorou, G., Pfannkuche, O., Prien, R., Rehder, G., Schubert, C., Soltwedel, T., Sommer, S., Stahl, H., Stanev, E., Teaca, A., Tengberg, A., Waldmann, C., Wehrli, B. and Wenzhöfer, F. (2014). Investigating hypoxia in aquatic environments: diverse approaches to addressing a complex phenomenon. *Biogeosciences*, 11(4), 1215-1259.

Freiberg, R., Nõmm, M., Tõnno, I., Alliksaar, T., Nõges, T. and Kisand, A. (2011). Dynamics of phytoplankton pigments in water and surface sediments of a large shallow lake. *Estonian Journal of Earth Sciences*, 60(2), 91-101.

Fry, B. and Wainright, S. (1991). Diatom sources of 13C-rich carbon in marine food webs. *Marine Ecology Progress Series*, 76, 149-157.

Gaiser, E., Trexler, J., Richards, J., Childers, D., Lee, D., Edwards, A., Scinto, L., Jayachandran, K., Noe, G. and Jones, R. (2005). Cascading Ecological Effects of Low-Level Phosphorus Enrichment in the Florida Everglades. *Journal of Environmental Quality*, 34(2), 717-723.

Gälman, V., Rydberg, J. and Bigler, C. (2009). Decadal diagenetic effects on δ13C and δ15N studied in varved lake sediment. *Limnology and Oceanography*, 54(3), 917-924.

Gälman, V., Rydberg, J., de-Luna, S., Bindler, R. and Renberg, I. (2008). Carbon and nitrogen loss rates during aging of lake sediment: Changes over 27 years studied in varved lake sediment. *Limnology and Oceanography*, 53(3), 1076-1082.

Gan, F. and Bryant, D. (2015). Adaptive and acclimative responses of cyanobacteria to far-red light. *Environmental Microbiology*, 17(10), 3450-3465.

Gao, K. S. and Xu, J. T. (2008). Effects of solar UV radiation on diurnal photosynthetic performance and growth of Gracilaria lemaneiformis (Rhodophyta). *European Journal of Phycology*, 3, 297-307.

Garcia-Pichel, F. and Castenholz, R.W. (1991). Characterization and biological implications of scytonemin a cyanobacterial sheath pigment. *Journal of Phycology*, 27, 395-409.

Garner, G., Hannah, D. and Watts, G. (2017). Climate change and water in the UK: Recent scientific evidence for past and future change. *Progress in Physical Geography*, 41(2), 154-170

Garnett, M., Ineson, P. and Stevenson, A. (2000). Effects of burning and grazing on carbon sequestration in a Pennine blanket bog, UK. *The Holocene*, 10(6), 729-736.

Gąsiorowski, M. and Sienkiewicz, E. (2013). The Sources of Carbon and Nitrogen in Mountain Lakes and the Role of Human Activity in Their Modification Determined by Tracking Stable Isotope Composition. *Water, Air, and Soil Pollution*, 224(4), 1498.

Gburek, W. J., Drungil, C. C., Srinivasan, M. S., Needelman, B. A. and Woodward, D. E. (2002). Variable-source-area controls on phosphorus transport: bridging the gap between research and design. *Journal of Soil Water Conservation*, 57 (6), 534-543.

Geider, R. J, Maclntyre, H. L. and Kana, T. M. (1997). Dynamic model of phytoplankton growth and acclimation: responses of the balanced growth rate and the chlorophyll a: carbon ratio to light, nutrient-limitation and temperature. *Marine Ecology Progress Series*, 148, 187-200.

George, G., Hurley, M. and Hewitt, D. (2007a). The impact of climate change on the physical characteristics of the larger lakes in the English Lake District. *Freshwater Biology*, 52, 1647-1666.

George. D. G., Hewitt, D. P., Jennings, E., Allott, N. and McGinnity, P. (2007b). The impact of changes in the weather on the surface temperatures of Windermere (UK) and Lough Feeagh (Ireland). In: *Water in Celtic countries: quantity, quality and climatic variability*. Proceedings of the Fourth Inter-Celtic Colloquium on Hydrology and Management of Water Resources, Guimaraes, Portugal, July 2005, IAHS Publications. 310, 86-93.

George, D. G., Maberly, S. C. and Hewitt, D. P. (2004). The influence of the North Atlantic Oscillation on the physical, chemical and biological characteristics of four lakes in the English Lake District. *Freshwater Biology*, 49, 760-774.

Gerhardt, S., Boos, K. and Schink, B. (2010). Uptake and release of phosphate by littoral sediment of a freshwater lake under the influence of light or mechanical perturbation. *Journal of Limnology* 69(1), 54-63.

Gervais, F. (1997). Diel vertical migration of *Cryptomonas* and *Chromatium* in the deep chlorophyll maximum of a eutrophic lake. *Journal of Plankton Research,* 19, 553-550.

Ghannoum, O., Evans, J. and von Caemmerer, S. (2011). Chapter 8 Nitrogen and Water Use Efficiency of C4 Plants. *C4 Photosynthesis and Related CO2 Concentrating Mechanisms*, 129-146.

Gibbons, K. and Bridgeman, T. (2020). Effect of temperature on phosphorus flux from anoxic western Lake Erie sediments. *Water Research*, 182, 116022.

Giovannetti, R., Alibabaei, L., Zannotti, M., Ferraro, S. and Petetta, L. (2013). HPLC-DAD-ESI/MS Identification of Light Harvesting and Light Screening Pigments in the Lake Sediments at Edmonson Point. *The Scientific World Journal*, 1-9.

Gisriel, C., Shen, G., Kurashov, V., Ho, M., Zhang, S., Williams, D., Golbeck, J., Fromme, P. and Bryant, D. (2020). The structure of Photosystem I acclimated to far-red light illuminates an ecologically important acclimation process in photosynthesis. *Science Advances*, 6(6).

Gleick, P. H. (1989). Climate change, hydrology, and water resources. *Reviews of Geophysics*, 27, 329-344.

Godfray, H., Beddington, J., Crute, I., Haddad, L., Lawrence, D., Muir, J., Pretty, J., Robinson, S., Thomas, S. and Toulmin, C. (2010). Food Security: The Challenge of Feeding 9 Billion People. *Science*, 327(5967), 812-818.

Gohar L., Bernie D., Good P. and Lowe J. A. (2018) UKCP18 Derived Projections of Future Climate over the UK. Available at [https://www.metoffice.gov.uk/pub/data/weather/uk/ukcp18/science-reports/UKCP18-Derived-Projections-ofFuture-Climate-over-the-UK.pdf].

Gökçe, D. (2016). Algae as an Indicator of Water Quality. *Algae - Organisms for Imminent Biotechnology*. Nooruddin Thajuddin and Dharumadurai Dhanasekaran.

Goldsmith, B. J., Luckes, S. J., Bennion, H., Carvalho, L., Hughes, M., Appleby, P. G. and Sayer, C. D. (2003). Feasibility Studies on the Restoration Needs of Four Lake SSSI's: Final Report to English Nature. Contract No. EIT 30-05-005. *Environmental Change Research Centre*, University College London.

Gorham, E., Lund, J. W. G., Sanger, J. E. and Dean, J. W. E. (1974). Some relationships between algal standing crop, water chemistry, and sediment chemistry in the English Lakes. *Limnology and Oceanography*, 19, 601-617.

Graham M. C., Vinogradoff S. I., Chipchase A. J., Dunn S. M., Bacon J. R. and Farmer J. G. (2006). Using size fractionation and Pb isotopes to study Pb transport in the waters of an organic rich upland catchment. *Environmental Science and Technology*, 40, 1250-1256.

Grant, C. S. and Louda, J. W. (2010). Microphytoplankton pigment ratios in relation to light intensity: implications for chemotaxonomy. *Aquatic Biology*, 11, 127-138.

Graven, H., Allison, C., Etheridge, D., Hammer, S., Keeling, R., Levin, I., Meijer, H., Rubino, M., Tans, P., Trudinger, C., Vaughn, B. and White, J. (2017). Compiled records of carbon isotopes in atmospheric CO_2 for historical simulations in CMIP6. *Geoscientific Model Development*, 10(12), 4405-4417.

Grayson, R. and Plater, A. (2008). A lake sediment record of Pb mining from Ullswater, English Lake District, UK. *Journal of Paleolimnology*, 42(2), 183-197.

Gregory, B., Reinhardt, E., Macumber, A., Nasser, N., Patterson, R., Kovacs, S. and Galloway, J. (2017). Sequential sample reservoirs for Itrax-XRF analysis of discrete samples. *Journal of Paleolimnology*, 57(3), 287-293.

Grosjean, M., von Gunten, L., Trachsel, M. and Kamenik, C. (2009). Calibration-in-time: Transforming biogeochemical lake sediment proxies into quantitative climate variables. *PAGES news*, 17(3), 108-110.

Grosvenor, M., Jones, R., Turney, C., Charman, D., Hogg, A., Coward, D. and Wilson, R. (2017). Human activity was a major driver of the mid-Holocene vegetation change in southern Cumbria: implications for the elm decline in the British Isles. *Journal of Quaternary Science*, 32(7), 934-945.

Gu, B., Schelske, C. and Brenner, M. (1996). Relationship between sediment and plankton isotope ratios (δ13C and δ15N) and primary productivity in Florida lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 53(4), 875-883.

Gudasz, C., Bastviken, D., Steger, K., Premke, K., Sobek, S. and Tranvik, L. J. (2010). Temperature controlled organic carbon mineralization in lake sediments. *Nature*, 466, 478-481.

Guertin, J. (2005). Chromium(VI) handbook. *Boca Raton*, FL: CRC Press.

Hadley, K. R., Paterson, A. M., Hall, R. I. and Smol, J. P. (2013). Effects of multiple stressors on lakes in south-central Ontario: 15 years of change in lakewater chemistry and sedimentary diatom assemblages. *Aquatic Sciences*, 75, 349-360.

Hall, R.I., Leavitt, P.R., Smol, J.P. and Zirnhelt, N. (1997). Comparison of diatoms, fossil pigments and historical records as measures of lake eutrophication. *Freshwater Biology*, 38 (2), 401-417.

Hammarlund, D. (1993). A distinct 13C decline in organic lake sediments at the Pleistocene-holocene transition in southern Sweden. *Boreas*, 22, 236-243.

Hannaford, J. (2015). Climate-driven changes in UK river flows. Progress in *Physical Geography*, 39(1), 29-48.

Hannah, D. and Garner, G. (2015). River water temperature in the United Kingdom. *Progress in Physical Geography*, 39(1), 68-92.

Hansen, J. and Sato, M. (2004). Greenhouse gas growth rates. *Proceedings of the National Academy of Sciences*, 101(46), 16109-16114.

Hansson, L. A. (1992). Factors regulating periphytic algal biomass. *Limnology and Oceanography*, 37, 322-328.

Hargeby, A., Andersson, G., Blindow, I. and Johansson, S. (1994). Trophic web structure in a shallow eutrophic lake during a dominance shift from phytoplankton to submerged macrophytes. *Hydrobiologia,* 279/280, 83-90.

Hargan, K., Michelutti, N., Coleman, K., Grooms, C., Blais, J., Kimpe, L., Gilchrist, G., Mallory, M. and Smol, J. (2017). Cliff-nesting seabirds influence production and sediment chemistry of lakes situated above their colony. *Science of The Total Environment*, 576, 85-98.

Hargan, K., Stewart, E., Michelutti, N., Grooms, C., Kimpe, L., Mallory, M., Smol, J. and Blais, J. (2018). Sterols and stanols as novel tracers of waterbird population dynamics in freshwater ponds. *Proceedings of the Royal Society B: Biological Sciences*, 285(1877), p20180631.

Harle, K. and Heijinis, H. (2014). Radioisotope dating. OzCoasts, Australian Online Coastal Information.

Harrison, J., Maranger, R., Alexander, R., Giblin, A., Jacinthe, P., Mayorga, E., Seitzinger, S., Sobota, D. and Wollheim, W. (2008). The regional and global significance of nitrogen removal in lakes and reservoirs. *Biogeochemistry*, 93(1-2), 143-157.

Hassett, J. and Anderson, M. (1982). Effects of dissolved organic matter on adsorption of hydrophobic organic compounds by river- and sewage-borne particles. *Water Research*, 16(5), 681-686.

Hastings, M., Jarvis, J. and Steig, E. (2009). Anthropogenic Impacts on Nitrogen Isotopes of Ice-Core Nitrate. *Science*, 324(5932), 1288-1288.

Hatfield, R. G., Maher, B. A., Pates, J. M., and Barker, P. A. (2008). Sediment dynamics in an upland temperate catchment: changing sediment sources, rates and deposition. *Journal of Paleolimnology*, 40(4), 1143-1158.

Haworth, E. Y. (1969). The diatoms of a sediment core from Blea Tarn, Langdale. *Journal of Ecology*, 57, 429-439.

Haworth, E. Y., De Boer, G., Evans, I., Osmaston, H., Pennington, W., Smith, A., Storey, P. and Ware, B. (2003). Tarns of the Central Lake District. Brathay Exploration Group Trust Ltd.

Hayes, N., Vanni, M., Horgan, M. and Renwick, W. (2015). Climate and land use interactively affect lake phytoplankton nutrient limitation status. *Ecology*, 96(2), 392-402.

Heaton, T., Wynn, P. and Tye, A. (2004). Low 15N/14N ratios for nitrate in snow in the High Arctic (79°N). *Atmospheric Environment*, 38(33), 5611-5621.

Heiri, O., Lotter A. F. and Lemcke, G. (2001): Loss-on-ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology*, 25, 101-110.

Heisler, J., Glibert, P., Burkholder, J., Anderson, D., Cochlan, W., Dennison, W., Dortch, Q., Gobler, C., Heil, C., Humphries, E., Lewitus, A., Magnien, R., Marshall, H., Sellner, K., Stockwell, D., Stoecker, D. and Suddleson, M. (2008). Eutrophication and harmful algal blooms: A scientific consensus. *Harmful Algae*, 8(1), 3-13.

Helliwell R. C., Lilly A. and Bell J. S. (2007). The development, distribution and properties of soils in the Lochnagar catchment and their influence on soil water chemistry. In Rose, N. L. (ed) *Lochnagar: the natural history of a mountain lake*, Springer, Dordrecht, 93-120.

Hense, I. (2007). Regulative feedback mechanisms in cyanobacteria-driven systems: a model study. *Marine Ecology Progress Series*, 339, 41-47.

Herrero, A., Muro-Pastor, A., Valladares, A. and Flores, E. (2004). Cellular differentiation and the NtcA transcription factor in filamentous cyanobacteria. *FEMS Microbiology Reviews*, 28(4), 469-487.

Hickman, M. (1974). The seasonal succession and vertical distribution of the phytoplankton in Abbot's Pond, North Somerset, U.K. *Hydrobiologia*, 44: 127-147.

Hilt, S., I, H., Rücker, J. and Nixdorf, B. (2010). Can submerged macrophytes influence turbidity and trophic state in deep lakes? Suggestions from a case study. *Journal of Environmental Quality,* 39, 725-733.

Hobbie, S., Schimel, J., Trumbore, S. and Randerson, J. (2000). Controls over carbon storage and turnover in high-latitude soils. *Global Change Biology*, 6(S1), 196-210.

Hobbs, W., Dreher, T., Davis, E., Vinebrooke, R., Wong, S., Weissman, T. and Dawson, M. (2021). Using a lake sediment record to infer the long-term history of cyanobacteria and the recent rise of an anatoxin producing Dolichospermum sp. *Harmful Algae*, 101, 101971.

Hodell, D. and Schelske, C. (1998). Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. *Limnology and Oceanography*, 43(2), 200-214.

Hodgson, D. A., Vyverman, W., Verleyen, E., Sabbe, K., Leavitt, P. R., Taton, A., Squier, A. H. and Keely, B. J. (2004). Environmental factors influencing the pigment composition of in situ benthic microbial communities in east Antarctic lakes. *Aquatic Microbial Ecology*, 37, 247-263.

Hodgson, D. A., Vyverman,W. and Verleyen, E. (2005). Late Pleistocene record of elevated UV radiation in an Antarctic lake. *Earth and Planetary Science Letters*, 236, 765-772.

Hodgson, D. A., Wright, S. W., Tyler, P. A. and Davies, N. (1998). Analysis of fossil pigments from algae and bacteria in meromictic Lake Fidler, Tasmania, and its application to lake management. *Journal of Paleolimnology*, 19, 1-22.

Holdgate, M. (2016). Sunbiggin Tarn – Notes of changes between 1950 and 2016. Personal communication.

Hollis, D., McCarthy, M., Kendon, M., Legg, T. and Simpson, I. (2019). HadUK-Grid—A new UK dataset of gridded climate observations. *Geoscience Data Journal*, 6(2), 151-159.

Holt, N. E., Zigmantas, D., Valkunas, L., Li, X. P., Niyogi, K. K. and Fleming, G. R. (2005). Carotenoid cation formation and the regulation of photosynthetic light harvesting. *Science*, 307, 433-436.

Holtgrieve, G. W., Schindler, D. E., Hobbs, W. O., Leavitt, P. R., Ward, E. J., Bunting, L., Chen, G., Finney, B. P., Gregory-Eaves, I., Holmgren, S., Lisac, M. J., Lisi, P. J., Nydick, K., Rogers, L. A., Saros, J. E., Selbie, D. T., Shapley, M. D., Walsh, P. B. and Wolfe, A. P. (2011). A coherent signature of anthropogenic nitrogen deposition to remote watersheds of the Northern Hemisphere. *Science,* 334, 1545-1548.

Holzinger, A., Roleda, M. and Lütz, C. (2009). The vegetative arctic freshwater green alga Zygnema is insensitive to experimental UV exposure. *Micron*, 40(8), 831-838.

Hope, D., Billett, M. F. and Cresser, M. S. (1994). A review of the export of carbon in river water: fluxes and processes. *Environmental Pollution*, 84, 301-324

House, W. A. (1990). The prediction of phosphate coprecipitation with calcite in freshwaters. *Water Research*, 24, 1017-1023.

Howarth, R., Chan, F., Conley, D., Garnier, J., Doney, S., Marino, R. and Billen, G. (2011). Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. *Frontiers in Ecology and the Environment*, 9(1), 18-26.

Hu, Z., Anderson, N., Yang, X. and McGowan, S. (2014). Catchment-mediated atmospheric nitrogen deposition drives ecological change in two alpine lakes in SE Tibet. *Global Change Biology*, 20(5), 1614-1628.

Huber, V., Wagner, C., Gerten, D. and Adrian, R. (2011). To bloom or not to bloom: contrasting responses of cyanobacteria to recent heat waves explained by critical thresholds of abiotic drivers. *Oecologia*, 169(1), 245-256.

Hughes, N. (2002). Factors Affecting Benthic Diatom Assemblages in Shallow, Lowland Lakes. Unpublished PhD, University College London.

Hughes, M., Hornby, D. D., Bennion, H., Kernan, M., Hilton, J., Phillips, G. and Thomas, R. (2004). The development of a GIS-based inventory of standing waters in Great Britain together with a risk-based prioritisation protocol. *Water, Air and Soil Pollution: Focus*, 4, 73-84.

Huisman, J., Jonker, R., Zonneveld, C. and Weissing, F. (1999). Competition for light between phytoplankton species: experimental tests of mechanistic theory. *Ecology*, 80(1), 211-222.

Hürrig, L. (1999). Sedimentological investigation of recent environmental change of two upland tarns in the UK. Project Report, Albert Ludwigs University.

Huser, B., Futter, M., Wang, R. and Fölster, J. (2018). Persistent and widespread long-term phosphorus declines in Boreal lakes in Sweden. *Science of The Total Environment*, 613-614, 240-249.

Hyenstrand P., Blomqvist P. and Pettersson A. (1998). Factors determining cyanobacterial success in aquatic systems – a literature review. *Archiv fur Hydrobiologie Special Issues Advances in Limnology*, 51, 41-62.

Ibelings, B.W., Vonk, M., Los, H.F.J., Van der Molen, D.T., and Mooij, W.M. (2003). Fuzzy modeling of cyanobacterial surface waterblooms: validation with NOAA-AVHRR satellite images. *Ecological Application*. 13(5), 1456-1472.

Ingalls, A. E., Aller, R. C., Lee, C. and Sun, M. Y. (2000). The influence of deposit-feeding on chlorophyll-a degradation in coastal marine sediments. *Journal of Marine Research*, 58, 631-651.

Ingri, J., Widerlund, A., Suteerasak, T., Bauer, S. and Elming, S. (2014). Changes in trace metal sedimentation during freshening of a coastal basin. *Marine Chemistry*, 167, 2-12.

IPCC. (2014). Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, 151.

IPCC. (2021). Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Masson-Delmotte, V., P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J. B. Matthews, T. K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, and B. Zhou (eds.)]. Cambridge University Press. In Press.

Irick, D., Gu, B., Li, Y., Inglett, P., Frederick, P., Ross, M., Wright, A. and Ewe, S., 2015. Wading bird guano enrichment of soil nutrients in tree islands of the Florida Everglades. *Science of The Total Environment*, 532, 40-47.

James, C., Fisher, L. J. and Moss, B. (2003). Nitrogen driven lakes: The Shropshire and Cheshire meres? *Arch Hydrobiol*. 158, 249-266.

James C., Fisher J., Russell V., Collings S. and Moss B. (2005). Nitrate availability and plant species richness: implications for management of freshwater lakes. *Freshwater Biology*, 50, 1049-1063.

Jansson, M., Bergstrom, A-K., Blomqvist, P. and Drakare, S. (2000). Allochthonous organic carbon and phytoplankton/bacterioplankton production relationships in lakes. *Ecology*, 81, 3250-3255.

Jeffrey, S. W., Mantoura, R. F. C. and Wright, S. W. (1997). Phytoplankton pigments in oceanography. SCOR-UNESCO Publ., Paris, 661 pp.

Jenkins, G. J., Perry, M. C. and Prior, M. J. (2009). The climate of the United Kingdom and recent trends. Met Office Hadley Centre, Exeter, UK. Available at: https://www.ukcip.org.uk/wp-content/PDFs/UKCP09_Trends.pdf [Accessed 09/11/2021].

Jensen J. P., Jeppesen E., Olrik K. and Kristensen P. (1994). Impact of nutrients and physical factors on the shift from cyanobacterial to chlorophyte dominance in shallow Danish lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 51, 1692-1699.

Jensen, H. S., Kristensen, P., Jeppesen, E. and Skytthe, A. (1992). Iron:phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. *Hydrobiologia*, 235- 236, 731-743.

Jeppesen, E., Kronvang, B., Meerhoff, M., Søndergaard, M., Hansen, K., Andersen, H., Lauridsen, T., Liboriussen, L., Beklioglu, M., Özen, A. and Olesen, J. (2009). Climate Change Effects on Runoff, Catchment Phosphorus Loading and Lake Ecological State, and Potential Adaptations. *Journal of Environmental Quality*, 38(5), 1930-1941.

Jeppesen, E., Meerhoff, M., Davidson, T., Trolle, D., Søndergaard, M., Lauridsen, T., Beklioglu, M., Brucet, S., Volta, P., González-Bergonzoni, I. and Nielsen, A. (2014). Climate change impacts on lakes: an integrated ecological perspective based on a multi-faceted approach, with special focus on shallow lakes. *Journal of Limnology*, 73(s1), 84-107.

Jeppesen, E., Mehner, T., Winfield, I., Kangur, K., Sarvala, J., Gerdeaux, D., Rask, M., Malmquist, H., Holmgren, K., Volta, P., Romo, S., Eckmann, R., Sandström, A., Blanco, S., Kangur, A., Ragnarsson Stabo, H., Tarvainen, M., Ventelä, A., Søndergaard, M., Lauridsen, T. and Meerhoff, M. (2012). Impacts of climate warming on the long-term dynamics of key fish species in 24 European lakes. *Hydrobiologia*, 694(1), 1-39.

Jeppesen, E., Sondergaard, M., Jensen, J., Havens, K., Anneville, O., Caralho, L., Coveney, M., Deneke, R., Dokulil, M., Foy, B., Gerdeaux, D., Hampton, S., Hilt, S., Kangur, K., Kohler, J., Lammens, E., Lauridsen, T., Manca, M., Miracle, M., Moss, B., Noges, P., Persson, G., Phillips, G., Portielje, R., Romo, S., Schelske, C., Striale, D., Tatrai, I., Wilen, E. and Winder, M. (2005). Lake responses to reduced nutrient loading - an analysis of contemporary long-term data from 35 case studies. *Freshwater Biology*, 50(10), 1747-1771.

Jin, L., Whitehead, P., Futter, M. and Lu, Z. (2012). Modelling the impacts of climate change on flow and nitrate in the River Thames: assessing potential adaptation strategies. *Hydrology Research*, 43(6), 902-916.

Jöhnk, K. D., Huisman, J. E., Sharples, J., Sommeijer, B. E., Visser, P. M. and Stroom, J. M. (2008). Summer heatwaves promote blooms of harmful cyanobacteria. *Global Change Biology*, 14, 495-512.

Johnson, A., Acreman, M., Dunbar, M., Feist, S., Giacomello, A., Gozlan, R., Hinsley, S., Ibbotson, A., Jarvie, H., Jones, J., Longshaw, M., Maberly, S., Marsh, T., Neal, C., Newman, J., Nunn, M., Pickup, R., Reynard, N., Sullivan, C., Sumpter, J. and Williams, R. (2009). The British river of the future: How climate change and human activity might affect two contrasting river ecosystems in England. *Science of the Total Environment*, 407(17), 4787-4798.

Jones, R. I. (1992) The influence of humic substances on lacustrine planktonic food-chains. *Hydrobiologia*, 229, 73-91.

Jones, R. I. (2000). Mixotrophy in planktonic protists: an overview. *Freshwater Biology*, 45, 219-226.

Jones, I. D. and Elliott, J. A. (2007). Modelling the effects of changing retention time on abundance and composition of phytoplankton species in a small lake. *Freshwater Biology,* 52, 988-997.

Jones, R. I., King, L., Dent, M. M., Maberly, S. C. and Gibson, C. E. (2004). Nitrogen stable isotope ratios in surface sediments, epilithon and macrophytes from upland lakes with differing nutrient status. *Freshwater Biology*, 49, 382-391.

Jones, I., Sahlberg, J. and Persson, I. (2010). Modelling the impact of climate change on the thermal characteristics of lakes. In: George, G, (ed.) *The Impact of Climate Change on European Lakes*. Springer, Aquatic Ecology Series, 103-120.

Juggins, S., Flower, R. and Battarbee, R. (1996). Palaeolimnological evidence for recent chemical and biological changes in U.K. Acid Waters Monitoring Network sites. *Freshwater Biology*, 36(1), 203-219.

Juggins, S. (2013). Quantitative reconstructions in palaeolimnology: new paradigm or sick science? *Quaternary Science Reviews*, 64, 20-32.

Junlong, L., Zheng, B., Hu, X., Wang, Y., Ding, Y. and Liu, F. (2015). Terrestrial input and nutrient change reflected by sediment records of the Changjiang River Estuary in recent 80 years. *Acta Oceanologica Sinica*, 34(2), 27-35.

Kagami, M., Bruin, A., Ibelings, B. W. and Van Donk, E. (2007) Parasitic chytrids: their effects on phytoplankton communities and food-web dynamics. *Hydrobiologia*, 578, 113-129.

Karlsson, J., Byström, P., Ask, J., Ask, P., Persson, L. and Jansson, M. (2009). Light limitation of nutrient-poor lake ecosystems. *Nature*, 460(7254), 506-509.

Katechakis, A., Haseneder, T., Kling, R. and Stibor, H. (2005). Mixotrophic versus photoautotrophic specialist algae as food for zooplankton: The light : nutrient hypothesis might not hold for mixotrophs. *Limnology and Oceanography*, 50(4), 1290-1299.

Kaushal, S. and Binford, M. (1999). Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA. *Journal of Paleolimnology*, 22(4), 439-442.

Keeling, R., Graven, H., Welp, L., Resplandy, L., Bi, J., Piper, S., Sun, Y., Bollenbacher, A. and Meijer, H. (2017). Atmospheric evidence for a global secular increase in carbon isotopic discrimination of land photosynthesis. *Proceedings of the National Academy of Sciences*, 114(39), 10361-10366.

Keely, B. J. (2006). Geochemistry of Chlorophyll. *Advances in Photosynthesis and Respiration*, 25, 535-561.

Kendon, E., Roberts, N., Fowler, H., Roberts, M., Chan, S. and Senior, C. (2014). Heavier summer downpours with climate change revealed by weather forecast resolution model. *Nature Climate Change*, 4(7), 570-576.

Kendon, M., McCarthy, M., Jevrejeva, S. and Legg, T. (2017). State of the UK Climate 2016, Met Office, Exeter, UK.

Kendon, M., McCarthy, M., Jevrejeva, S., Matthews, A. and Legg, T. (2019). State of the UK climate 2018. *International Journal of Climatology*, 39(S1), 1-55.

Kenworthy, J. M. (2014). Regional weather and climates of the British Isles – Part 7: North West England and the Isle of Man. *Weather*, 69, 87-93.

Kernan, M., Battarbee, R. W., Curtis, C. J., Monteith, D. T., Shilland, E. M. (2010). UK Acid Waters Monitoring Network 20 Year Interpretative Report. ENSIS Ltd, *Environmental Change Research Centre*, University College London, London.

Kilinc, S. and Moss, B. (2002). Whitemere, a lake that defies some conventions about nutrients. *Freshwater Biology*, 47(2), 207-218.

Kim, Y. J., Choi, W. J., Lim, S. S., Kwak, J. H., Chang, S. X., Kim, H. Y., Yoon, K. S., Ro, H. M. (2008). Changes in nitrogen isotopic compositions during composting of cattle feedlot manure: effects of bedding material type. *Bioresourse Technology*, 99, 5452-5458.

Kohn, M. J. (2010). Carbon isotope compositions of terrestrial C3 plants as indicators of (paleo)ecology and (paleo)climate. *Proceedings of the National Academy of Sciences of the United States of America*, 107, 19691-19695.

Komárek, M., Ettler, V., Chrastný, V. and Mihaljevic, M. (2008). Lead isotopes in environmental sciences: A review. *Environment International*, 34(4), 562-577.

Kong, X., Seewald, M., Dadi, T., Friese, K., Mi, C., Boehrer, B., Schultze, M., Rinke, K. and Shatwell, T. (2021). Unravelling winter diatom blooms in temperate lakes using high frequency data and ecological modeling. *Water Research*, 190, 116681.

Kosten, S., Huszar, V. L. M., Bécares, E., Costa, L. S., Van Donk, E., Hansson, L.-A., Jeppesen, E., Kruk, C., Lacerot, G., Mazzeo, N., De Meester, L., Moss, B., Lürling, M., Nõges, T., Romo, S. and Scheffer, M. (2012). Warmer climates boost cyanobacterial dominance in shallow lakes. *Global Change Biology*, 18, 118-126.

Krajewska, M., Szymczak-Żyła, M., Kobos, J., Witak, M. and Kowalewska, G. (2019). Canthaxanthin in recent sediments as an indicator of heterocystous cyanobacteria in coastal waters. *Oceanologia*, 61(1), 78-88.

Krauze, K. and Wagner, I. (2007). An ecohydrological approach for the protection and enhancement of ecosystem services. In: Petrosillo, I., Müller, F., Jones, K. B., Zurlini, G., Krauze, K., Victorov, S., Li, B.-L. and Kepner, W. G. (eds.) *Use of landscape sciences for the assessment of environmental security*. Springer Netherlands.

Krienitz, L., Kasprzak, P. and Koschel, R. (1996). Long term study on the influence of eutrophication, restoration and biomanipulation on the structure and development of phytoplankton communities in Feldberger Haussee (Baltic Lake District, Germany). *Hydrobiologia,* 330, 89-110.

Kritzberg, E. (2017). Centennial-long trends of lake browning show major effect of afforestation. *Limnology and Oceanography Letters*, 2(4), 105-112.

Krolikowska, J. (1997). Eutrophication processes in a shallow, macrophyte-dominated lake –species differentiation, biomass and the distribution of submerged macrophytes in Lake Łuknajno (Poland). *Hydrobiologia*, 342/343, 411-416.

Kryzevicius, Z., Janusiene, L., Karcauskiene, D., Slepetiene, A., Vilkiene, M. and Zukauskaite, A., 2019. Aluminium leaching response to acid precipitation in a lime-affected soil. *Zemdirbyste-Agriculture*, 106(4), 315-320.

Kuczynska, P., Jemiola-Rzeminska, M. and Strzalka, K. (2017). Characterisation of Carotenoids Involved in the Xanthophyll Cycle. *Carotenoids*.

Kufel, L., and Kufel, I. (2002). Chara beds acting as nutrient sinks in shallow lakes - a review. *Aquatic Botony*, 72, 249-260.

Lacey, J., Leng, M., Vane, C., Radbourne, A., Yang, H. and Ryves, D. (2018). Assessing human impact on Rostherne Mere, UK, using the geochemistry of organic matter. *Anthropocene*, 21, 52-65.

Lafrancois, B., Nydick, K., Johnson, B. and Baron, J. (2004). Cumulative effects of nutrients and pH on the plankton of two mountain lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 61(7), 1153-1165.

Lake, B., Coolidge, K., Norton, S. and Amirbahman, A. (2007). Factors contributing to the internal loading of phosphorus from anoxic sediments in six Maine, USA, lakes. *Science of The Total Environment*, 373(2-3), 534-541.

Lake, J., McKinney, R., Osterman, F., Pruell, R., Kiddon, J., Ryba, S. and Libby, A. (2001). Stable nitrogen isotopes as indicators of anthropogenic activities in small freshwater systems. *Canadian Journal of Fisheries and Aquatic Sciences*, 58(5), 870-878.

Lamb, H. (1965). The early medieval warm epoch and its sequel. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 1, 13-37.

Lambert, S. and Davy, A. (2011). Water quality as a threat to aquatic plants: discriminating between the effects of nitrate, phosphate, boron and heavy metals on charophytes. *New Phytologist*, 189(4), 1051-1059.

Lami, A., P., Guilizzoni, A. and Marchetto, R. (2000). High resolution analysis of fossil pigments, carbon, nitrogen and sulphur in the sediment of eight European Alpine lakes: the MOLAR project. *Journal of Limnology*, 59 (Suppl. 1), 15-28.

Larsen, S., Andersen, T. and Hessen, D. (2011). Climate change predicted to cause severe increase of organic carbon in lakes. *Global Change Biology*, 17(2), 1186-1192.

Latowski, D., Grzyb, J. and Strzalka, K. (2004). The xanthophyll cycle – Molecular mechanism and physiological significance. *Acta Physiologiae Plantarium*, 26, 197-212.

Laudon, H., Buttle, J., Carey, S., McDonnell, J., McGuire, K., Seibert, J., Shanley, J., Soulsby, C. and Tetzlaff, D. (2012). Cross-regional prediction of long-term trajectory of stream water DOC response to climate change. *Geophysical Research Letters*, 39(18).

Lauterbach, S., Brauer, A., Andersen, N., Danielopol, D., Dulski, P., Hüls, M., Milecka, K., Namiotko, T., Obremska, M. and Von Grafenstein, U. (2011). Environmental responses to Lateglacial climatic fluctuations recorded in the sediments of pre-Alpine Lake Mondsee (northeastern Alps). *Journal of Quaternary Science*, 26(3), 253-267.

Law, R. J. (2011). A review of the function and uses of, and factors affecting, stream phytobenthos. *Freshwater Reviews*, 4(2), 135-166.

Leavitt, P. R. (1993). A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. *Journal of Paleolimnology*, 9, 109-127.

Leavitt, P. R., and Carpenter, S. R. (1990). Regulation of pigment sedimentation by photo-oxidation and herbivore grazing. *Canadian Journal of Fisheries and Aquatic Sciences*, 47: 1166-1176.

Leavitt, P. and Findlay, D. (1994). Comparison of Fossil Pigments with 20 Years of Phytoplankton Data from Eutrophic Lake 227, Experimental Lakes Area, Ontario. *Canadian Journal of Fisheries and Aquatic Sciences*, 51(10), 2286-2299.

Leavitt, P. R. and Hodgson, D. A. (2001). Sedimentary Pigments. In: Smol, J. P., Birks, H. J. B. and Last, W. M. (eds.) *Tracking environmental change using lake sediments*. Dordrecht. Kluwer Academic Press.

Leavitt, P. R., Brock, C. S., Ebel, C. and Patoine, A. (2006). Landscape-scale effects of urban nitrogen on a chain of freshwater lakes in central North America. *Limnology and Oceanography*, 51, 2262-2277.

Leavitt, P., Findlay, D., Hall, R. and Smol, J. (1999). Phytoplankton responses to dissolved organic carbon loss and pH decline during whole-lake acidification: Evidence from paleolimnology. *Limnology and Oceanography*, 44(3part2), 757-773.

Leavitt, P., Fritz, S., Anderson, N., Baker, P., Blenckner, T., Bunting, L., Catalan, J., Conley, D., Hobbs, W., Jeppesen, E., Korhola, A., McGowan, S., RÜhland, K., Rusak, J., Simpson, G., Solovieva, N. and Werne, J. (2009). Paleolimnological evidence of the effects on lakes of energy and mass transfer from climate and humans. *Limnology and Oceanography*, 54, 2330-2348.

Leavitt, P. R., Vinebrooke, R. D., Donald, D. B., Smol, J. P. and Schindler, D. W. (1997). Past ultraviolet radiation environments in lakes derived from fossil pigments. *Nature*, 388, 457-459.

Lehmann, M., Bernasconi, S., Barbieri, A. and McKenzie, J. (2002). Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. *Geochimica et Cosmochimica Acta*, 66(20), 3573-3584.

Lehmann, M. F., Bernasconi, S. M., Mckenzie, J. A., Barbieri, A., Simona, M. and Veronesi, M. (2004). Seasonal variation of the δ13C and δ15N of particulate and dissolved carbon and nitrogen in Lake Lugano: Constraints on biogeochemical cycling in a eutrophic lake. *Limnology and Oceanography*, 49, 415-429.

Lemarchand, E., Chabaux, F., Vigier, N., Millot, R. and Pierret, M. (2010). Lithium isotope systematics in a forested granitic catchment (Strengbach, Vosges Mountains, France). *Geochimica et Cosmochimica Acta*, 74(16), 4612-4628.

Leng, M. and Barker, P. (2006). A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. *Earth-Science Reviews*, 75(1-4), 5-27.

Leng, M. and Marshall, J. (2004). Palaeoclimate interpretation of stable isotope data from lake sediment archives. Quaternary Science Reviews, 23(7-8), 811-831.

Lepistö, L. and Rosenström, U. (1998). The most typical phytoplankton taxa in four types of boreal lakes. *Hydrobiologia*, 369, 89-97.

Lepori, F. and Robin, J. (2014). Nitrogen limitation of the phytobenthos in Alpine lakes: results from nutrient-diffusing substrata. *Freshwater Biology*, 59(8), 1633-1645.

Liao, M., Herzschuh, U., Wang, Y., Liu, X., Ni, J. and Li, K. (2020). Lake diatom response to climate change and sedimentary events on the southeastern Tibetan Plateau during the last millennium. *Quaternary Science Reviews*, 241, 106409.

Liboriussen, L. and Jeppesen, E. (2003). Temporal dynamics in epipelic, pelagic, and epiphytic algal production in a clear, and a turbid shallow lake. *Freshwater Biology*, 48, 418-431.

Lim, S. S., Kwak, J. H., Lee, K. S., Chang, S. X., Yoon, K. S., Kim, H. Y., Choi, W. J. (2015). Soil and plant nitrogen pools in paddy and upland ecosystems have contrasting d15N. *Biology and Fertility of Soils*, 51, 231-239.

Lin, Y. P. and Singer, P.C. (2006). Inhibition of calcite precipitation by orthophosphate: Speciation and thermodynamic considerations. *Geochimica et Cosmochimica Acta,* 70(10), 2530-2539.

Litchman, E., Klausmeier, C., Schofield, O. and Falkowski, P. (2007). The role of functional traits and trade-offs in structuring phytoplankton communities: scaling from cellular to ecosystem level. *Ecology Letters*, 10(12), 1170-1181.

Liu, Q., Ding, S., Chen, X., Sun, Q., Chen, M. and Zhang, C. (2018). Effects of temperature on phosphorus mobilization in sediments in microcosm experiment and in the field. *Applied Geochemistry*, 88, 158-166.

Liu, W., Ma, L. and Abuduwaili, J. (2020). Anthropogenic Influences on Environmental Changes of Lake Bosten, the Largest Inland Freshwater Lake in China. *Sustainability*, 12(2), p.711.

Liu, X., Colman, S., Brown, E., Minor, E. and Li, H. (2013). Estimation of carbonate, total organic carbon, and biogenic silica content by FTIR and XRF techniques in lacustrine sediments. *Journal of Paleolimnology*, 50(3), 387-398.

Lizumi, Y. (2007). Studies of lake environments using stable isotope ratios of nitrogen (δ15N) and Carbon (δ13C). *Journal of Japanese Association of Hydrological Sciences*, 37(4), 209-220.

Lodenius, M., Raukola, T., Soltanpour-Gargari, A., Tulisalo, E. and Voigt, H. R. (2008). Diatom and Metal Stratigraphy of a Small and Shallow Lake in Southern Finland. *Universitas Carolinae*, 22.

Lotter, A.F. and Bigler, C. (2000). Do diatom in the Swiss Alps reflect the length of ice-cover? *Aquatic Science*, 62, 125-141.

Louda, J., Li, J., Liu, L., Winfree, M. and Baker, E. (1998). Chlorophyll-a degradation during cellular senescence and death. *Organic Geochemistry*, 29(5-7), 1233-1251.

Louda, J. W. (2008). Pigment-based chemotaxonomy of Florida Bay phytoplankton; development and difficulties. *Journal of Liquid Chromatography and Related Technologies*, 31, 295-323.

Lurling, M., Eshetu, F., Faassen, E., Kosten, S. and Huszar, V, (2013). Comparison of cyanobacterial and green algal growth rates at different temperatures. *Freshwater Biology*, 58(3), 552-559.

Ma, L., Wu, J., Abuduwaili, J. and Liu, W. (2016). Geochemical Responses to Anthropogenic and Natural Influences in Ebinur Lake Sediments of Arid Northwest China. *PLOS ONE*, 11(5), p.e0155819.

Maberly, S. C., Barker, P. A., Stott, A. W. and De Ville, M. M. (2013). Catchment productivity controls CO2 emissions from lakes. *Nature Climate Change*, 3, 391-394.

Maberly, S. C., DeVille, M. M., James, J. B., Keenan, P. O. and Thackeray, S. J. (2020). Sunbiggin Tarn & Moors & Little Asby Common SSSI water quality monitoring survey. Report to Friends of the Lake District and Natural England.

Maberly, S., Hurley, M., Butterwick, C., Corry, J., Heany, S., Irish, A., Jaworski, G., Lund, J., Reynolds, C. and Roscoe, J. (1994). The rise and fall of Asterionella formosa in the South Basin of Windermere: analysis of a 45-year series of data. *Freshwater Biology*, 31(1), 19-34.

Maberly, S. C., King, L., Gibson, C. E., May, L., Jones, R., Dent, M. M. and Jordan, C. (2003). Linking nutrient limitation and water chemistry in upland lakes to catchment characteristics. *Hydrobiologia*, 506-509, 83-91.

MacDonald, D. D., Ingersoll, C. G., Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, 39, 20-31.

Mackey, A. and Berrie, A. (1991). The prediction of water temperatures in chalk streams from air temperatures. *Hydrobiologia*, 210(3), 183-189.

Mackay, A., Battarbee, R., Flower, R., Jewson, D., Lees, J., Ryves, D. and Sturm, M. (2000). The deposition and accumulation of endemic planktonic diatoms in the sediments of Lake Baikal and an evaluation of their potential role in climate reconstruction during the Holocene. *Terra Nostra*, 9, 34-48.

Malby, A., Whyatt, J. D., Timmis, R., Wilby, R. and Orr, H. (2007). Long-term variations in orographic rainfall: analysis and implications for upland catchments. *Hydrological Sciences Journal*, 52, 276-291.

Mallory, M.L., Braune, B.M., Wayland,M., Gilchrist, H.G., Dickson, D.L. (2004). Contaminants in common eiders (Somateria mollissima) of the Canadian Arctic. *Environmental Reviews*. 12, 197-218.

Maraun, D., Osborn, T. and Gillett, N. (2008). United Kingdom daily precipitation intensity: improved early data, error estimates and an update from 2000 to 2006. *International Journal of Climatology*, 28(6), 833-842.

May, L., Spears, B. and O'Malley, M. (2010). An assessment of nutrient sources and water quality improvement measures in Hornsea Mere. NERC/Centre for Ecology and Hydrology, 68pp.

McCormick, P. and Cairns, J. (1994). Algae as indicators of environmental change. *Journal of Applied Phycology*, 6(5), 509-526.

McCrackin, M. L., Jones, H. P., Jones, P. C. and Moreno- Mateos, D. (2017). Recovery of lakes and coastal marine ecosystems from eutrophication: A global meta-analysis. *Limnology and Oceanography*, 62, 507-518.

McDonough, L., Santos, I., Andersen, M., O'Carroll, D., Rutlidge, H., Meredith, K., Oudone, P., Bridgeman, J., Gooddy, D., Sorensen, J., Lapworth, D., MacDonald, A., Ward, J. and Baker, A. (2020). Changes in global groundwater organic carbon driven by climate change and urbanization. *Nature Communications*, 11(1), 1279.

McGowan, S. (2013). Pigment Studies. In: Elias, S. (ed.) *The Encyclopedia of Quaternary Science*. 2nd ed. Amsterdam. Elsevier.

McGowan, S., Anderson, N., Edwards, M., Hopla, E., Jones, V., Langdon, P., Law, A., Solovieva, N., Turner, S., van Hardenbroek, M., Whiteford, E. and Wiik, E. (2018). Vegetation transitions drive the autotrophy-heterotrophy balance in Arctic lakes. *Limnology and Oceanography Letters*, 3(3), 246-255.

McGowan, S., Britton, G., Haworth, E. and Moss, B. (1999). Ancient blue-green blooms. *Limnology and Oceanography*, 44(2), 436-439.

McGowan, S. Barker, P., Haworth, E., Leavitt, P., Maberly, S. and Pates, J. (2012). Humans and climate as drivers of algal community change in Windermere since 1850. *Freshwater Biology*, 57(2), 260-277.

McGowan, S., Leavitt, P. R., Hall, R. I, Anderson, N. J, Jeppesen, E. and Odgaard, B. V. (2005). Controls of algal abundance and community composition during ecosystem state change. *Ecology*, 86, 2200-2211.

McKee, D., Atkinson, D., Collings, S., Eaton, J., Gill, A., Harvey, I., Hatton, K., Heyes, T., Wilson, D. and Moss, B., 2003. Response of freshwater microcosm communities to nutrients, fish, and elevated temperature during winter and summer. *Limnology and Oceanography*, 48(2), 707-722.

McLauchlan, K., Williams, J. and Engstrom, D. (2013). Nutrient cycling in the palaeorecord: Fluxes from terrestrial to aquatic ecosystems. *The Holocene*, 23(11), 1635-1643.

Met Office. (2021a). Historic station data – Whitby. Available at: https://www.metoffice.gov.uk/pub/data/weather/uk/climate/stationdata/whitbydata.txt [Accessed: 11 May 2021].

Met Office. (2021b). Historic station data –Newton Rigg. Available at: https://www.metoffice.gov.uk/pub/data/weather/uk/climate/stationdata/newtonriggdata.txt [Accessed: 11 May 2021].

Meyer, K. M., Macalady, J. M., Fulton, J. M., Kump, L. R., Schaperdoth, I. and Freeman, K. H. (2011). Carotenoid biomarkers as an imperfect reflection of the anoxygenic phototrophic community in meromictic Fayettevile Grren Lake. *Geobiology*, 9 (4) 321-329.

Meyers, P. A. (1994). Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, 114, 289-302.

Meyers, P.A. (1997). Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic Geochemistry*, 27, 213-250.

Meyers, P. (2003). Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic Geochemistry*, 34(2), 261-289.

Meyers, P. and Ishiwatari, R. (1993). Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry*, 20(7), 867-900.

Meyers, P. A. and Lallier-Verges, E. (1999). Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. *Journal of Paleolimnology*, 21, 345-372.

Meyers, P. A. and Teranes, J. L. (2001). Sediment organic matter. In: Last, W. M. and Smol, J. P. (eds.) *Tracking environmental change using lake sediments.* Kluwer.

Michelutti, N., Blais, J., Mallory, M., Brash, J., Thienpont, J., Kimpe, L., Douglas, M. and Smol, J. (2010). Trophic position influences the efficacy of seabirds as metal biovectors. *Proceedings of the National Academy of Sciences*, 107(23), 10543-10548.

Michelutti, N., Keatley, B., Brimble, S., Blais, J., Liu, H., Douglas, M., Mallory, M., Macdonald, R. and Smol, J. (2008). Seabird-driven shifts in Arctic pond ecosystems. *Proceedings of the Royal Society B: Biological Sciences*, 276(1656), 591-596.

Millie, D.F., Paerl, H.W, Hurley, J. P. (1993). Microphytoplankton pigment assessments using high-performance liquid chromatograhpy: a synopsis of organismal and ecological applications. *Canadian Journal of Fisheries and Aquatic Sciences*, 50, 2513-2527.

Miller, H., Croudace, I. W., Bull, J. M., Cotterill, C. J., Dix, J. K. and Taylor, R. N. (2014). A 500 year sediment lake record of anthropogenic and natural inputs to Windermere (English Lake District) using double-spike lead isotopes, radiochronology, and sediment microanalysis. *Environmental Science* and *Technology,* 48, 7254-7263.

Miller, H., Croudace, I. W., Bull, J. M., Cotterill, C. J., Dix, J. K. and Taylor, R. N. (2015). Modern pollution signals in sediments from Windermere, NW England, determined by micro-XRF and lead isotope analysis. In Croudace, I,W. and Rothwell, R.G. (eds.) *Micro-XRF Studies of Sediment Cores: Applications of a Non-destructive Tool for the Environmental Sciences: Part III*, Dordrecht, NL. Developments in Paleoenvironmental Research, 17: 423-442.

Mills, K., Schillereff, D., Saulnier-Talbot, É., Gell, P., Anderson, N., Arnaud, F., Dong, X., Jones, M., McGowan, S., Massaferro, J., Moorhouse, H., Perez, L. and Ryves, D. (2016). Deciphering long-term records of natural variability and human impact as recorded in lake sediments: a palaeolimnological puzzle. *Wiley Interdisciplinary Reviews: Water*, 4(2), p.e1195.

Milne, J. (1996). Environmental effects of low intensity systems of animal production in the hills and uplands of the UK. *Animal Science*, 63(03), 363-371.

Monteith, D., Stoddard, J., Evans, C., de Wit, H., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B., Jeffries, D., Vuorenmaa, J., Keller, B., Kopácek, J. and Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, 450, 537-541.

Monteith, D. and Evans, C. (2005). The United Kingdom Acid Waters Monitoring Network: a review of the first 15 years and introduction to the special issue. *Environmental Pollution*, 137(1), 3-13.

Monteith, D., Evans, C., Henrys, P., Simpson, G. and Malcolm, I. (2014). Trends in the hydrochemistry of acid-sensitive surface waters in the UK 1988–2008. *Ecological Indicators*, 37, 287-303.

Monteith, D., Stoddard, J., Evans, C., de Wit, H., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B., Jeffries, D., Vuorenmaa, J., Keller, B., Kopácek, J. and Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, 450(7169), 537-540.

Mooij, W., Janse, J., De Senerpont Domis, L., Hülsmann, S. and Ibelings, B. (2007). Predicting the effect of climate change on temperate shallow lakes with the ecosystem model PCLake. *Hydrobiologia*, 584(1), 443-454.

Moorhouse, H. (2016). Regional synthesis of algal community change in the lakes and tarns of the Windermere catchment, Lake District, UK, since the 19th century. PhD thesis, University of Nottingham.

Moorhouse, H., McGowan, S., Jones, M., Barker, P., Leavitt, P., Brayshaw, S. and Haworth, E. (2014). Contrasting effects of nutrients and climate on algal communities in two lakes in the Windermere catchment since the late 19th century. *Freshwater Biology*, 59(12), 2605-2620.

Moorhouse, H., McGowan, S., Taranu, Z., Gregory-Eaves, I., Leavitt, P., Jones, M., Barker, P. and Brayshaw, S. (2018). Regional versus local drivers of water quality in the Windermere catchment, Lake District, United Kingdom: The dominant influence of wastewater pollution over the past 200 years. *Global Change Biology*, 24(9), 4009-4022.

Morad, S. (2013). Feldspars in sedimentary rocks. *Encyclopaedia of Earth Science*, 452-457.

Morton, D., Rowland, C., Wood, C., Meek, L., Marston, C., Smith, G., Wadsworth, R. and Simpson, I. C. (2011). Final Report for LCM2007 – the new UK Land Cover Map. *Centre for Ecology and Hydrology*, CS Technical Report No 11/07.

Moss, B. (2010). Climate change, nutrient pollution and the bargain of Dr Faustus. *Freshwater Biology*, 55, 175-187.

Moss, B. (2014). Fresh Waters, Climate Change and UK Nature Conservation. *Freshwater Reviews*, 7(1), 25-75.

Moss, B. and Leah, R.T. (1982). Changes in the ecosystem of a guanotrophic and brackish shallow lake in eastern England: potential problems in its restoration. *Internationale Revue der gesamten Hydrobiologie*, 67, 635-659.

Moss, B., Barker, T. O. M., Stephen, D., Williams, A. E., Balayla, D. J., Beklioglu, M., Carvalho, L. (2005). Consequences of reduced nutrient loading on a lake system in a lowland catchment: deviations from the norm? *Freshwater Biology*, 50, 1687-1705.

Moss, B., Kosten, S., Meerhoff, M., Battarbee, R. W., Jeppesen, E., Mazzeo, N., Havens, K., Lacerot, G., Liu, Z., Meester, L. D., Paerl, H. and Scheffer, M. (2011). Allied attack: climate change and eutrophication*. Inland Waters*, 1(2), 101-105.

Muir, M., Spray, C. and Rowan, J. (2012). Climate change and standing freshwaters: informing adaptation strategies for conservation at multiple scales. *Area*, 44(4), 411-422.

Mur, L. R., Skulberg, O. M. and Utkilen, H. (1999). Cyanobacteria and the Environment in Chorus, I. and Bartram, J (eds.) *Toxic Cyanobacteria in Water: A guide to their public health consequences, monitoring and management*. WHO. ISBN 0-419-23930-8.

Naeher, S., Gilli, A., North, R., Hamann, Y. and Schubert, C. (2013). Tracing bottom water oxygenation with sedimentary Mn/Fe ratios in Lake Zurich, Switzerland. *Chemical Geology*, 352, 125-133.

National Atmospheric Emissions Inventory. (2014). UK emissions data selector - NAEI, UK. [online] Available at: http://naei.defra.gov.uk/data/data-selector-results?q=601 [Accessed 15 Jan. 2019].

Natural England. (2010). Gormire SSSI. Available at: https://designatedsites.naturalengland.org.uk/PDFsForWeb/Citation/1002548.pdf [Accessed 15 Aug. 2019].

Natural England (2015). Lake theme plan, ‘Improvement Programme for England’s Natura 2000 Sites – Planning for the Future’, ISBN 978-1-84754-195-9.

Natural England. (2008). Sunbiggin Tarn and Moors and Little Asby Scar SSSI. Available at: https://designatedsites.naturalengland.org.uk/PDFsForWeb/Citation/1007193.pdf [Accessed 15 Aug. 2019].

Naylor, C. and Keely, B. (1998). Sedimentary purpurins: oxidative transformation products of chlorophylls. *Organic Geochemistry*, 28(7-8), 417-422.

Neal, C., Lofts, S., Evans, C., Reynolds, B., Tipping, E. and Neal, M. (2008). Increasing Iron Concentrations in UK Upland Waters. *Aquatic Geochemistry*, 14(3), 263-288.

Neal, C., Reynolds, B., Wilkinson, J., Hill, T., Neal, M., Hill, S. and Harrow, M. (1998). The impacts of conifer harvesting on runoff water quality: a regional survey for Wales. *Hydrology and Earth System Sciences*, 2(2/3), 323-344.

Ng, S. and King, R. (2004). Geochemistry of Lake Sediments as a Record of Environmental Change in a High Arctic Watershed. *Chemie der Erde - Geochemistry*, 64(3), 257-275.

Noller, J. S. (2000). Lead-210 Geochronology. In: Noller, J. S., Sowers, J. M. and Lettis, W. R. (eds.) *Quaternary Geochronology Methods and Applications*. Washington. American Geophysical Union.

Norton, S. A., Bienert, R. W., Binford, M. W. and Kahl, J. S. (1992). Stratigraphy of total metals in PIRLA sediment cores. *Journal of Paleolimnology*, 7, 191-214.

Nydick, K., Lafrancois, B., Baron, J. and Johnson, B. (2004). Nitrogen regulation of algal biomass, productivity, and composition in shallow mountain lakes, Snowy Range, Wyoming, USA. *Canadian Journal of Fisheries and Aquatic Sciences*, 61(7), 1256-1268.

O’Neil, J. M., Davis, T. W., Burford, M. A. and Gobler, C. J. (2012). The rise of harmful cyanobacteria blooms: the potential roles of eutrophication and climate change. *Harmful Algae*, 14, 313-334.

O’Reilly, C., Dettman, D. and Cohen, A. (2005). Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: VI. Geochemical indicators. *Journal of Paleolimnology*, 34(1), 85-91.

O’Reilly, C. M., S. Sharma, D. K., Gray, S. E. Hampton, J. S., Read, R. J., Rowley, P., Schneider, J. D., Lenters, P. B., McIntyre, B. M., Kraemer, G. A., Weyhenmeyer, D., Straile, B., Dong, R., Adrian, M. G., Allan, O., Anneville, L., Arvola, J., Austin, J. L., Bailey, J. S., Baron, J. D., Brookes, E., de Eyto, M. T., Dokulil, D. P., Hamilton, K., Havens, A. L., Hetherington, S. N., Higgins, S., Hook, L. R., Izmest’eva, K.

D., Joehnk, K., Kangur, P., Kasprzak, M., Kumagai, E., Kuusisto, G., Leshkevich, D. M., Livingstone, S., MacIntyre, L., May, J. M., Melack, D. C., Mueller-Navarra, M., Naumenko, P., Noges, T., Noges, R. P., North, P.-D., Plisnier, A., Rigosi, A., Rimmer, M., Rogora, L. G., Rudstam, J. A., Rusak, N., Salmaso, N. R., Samal, D. E., Schindler, S. G., Schladow, M., Schmid, S. R., Schmidt, E., Silow, M. E., Soylu, K., Teubner, P., Verburg, A., Voutilainen, A., Watkinson, C. E., Williamson, and G. Zhang. (2015). Rapid and highly variable warming of lake surface waters around the globe. *Geophysical Research Letters*, 42(24), 10773-10781.

O'Sullivan, E. and Reynolds, E. (2005). The Lakes Handbook: 2 Volume Set. John Wiley and Sons.

Ochiai, S., Nagao, S., Yonebayashi, K., Fukuyama, T., Suzuki, T., Yamamoto, M., Kashiwaya, K. and Nakamura, K. (2015). Effect of deforestation on the transport of particulate organic matter inferred from the geochemical properties of reservoir sediments in the Noto Peninsula, Japan. *Geochemical Journal*, 49(5), 513-522.

OECD. (1982). Eutrophication of Waters, Monitoring Assessment and Control, Organisation for Economic Co-operation and Development, Paris.

Ohtsuki, H., Awano, T., Tsugeki, N., Ishida, S., Oda, H., Makino, W. and Urabe, J. (2015). Historical Changes in the Ecosystem Condition of a Small Mountain Lake over the Past 60 Years as Revealed by Plankton Remains and Daphnia Ephippial Carapaces Stored in Lake Sediments. *PLOS ONE*, 10(3), p.e0119767.

Officer, C. B. and Ryther, J. H. (1980). The possible importance of silicon in marine eutrophication. *Marine Ecology Progress Series,* 3, 83-91.

Ogden, J. (2019). Condition of SSSI Units for Site Blea Tarn SSSI. Available at: https://designatedsites.naturalengland.org.uk/ReportUnitCondition.aspx?SiteCode=S1000814&ReportTitle=Blea%20Tarn%20SSSI [Accessed 09/06/2020].

Olaizola, M., Roche, J., Kolber, Z. and Falkowski, P. G. (1994). Nonphotochemical fluorescence quenching and the diadinoxanthin cycle in a marine diatom. *Photosynthesis Research*, 41, 357-370.

Oldfield, F., Gedye, S., Hunt, A., Jones, J., Jones, M. and Richardson, N. (2014). The magnetic record of inorganic fly ash deposition in lake sediments and ombrotrophic peats. *The Holocene*, 25(1), 215-225.

Oldfield, F., Wake, R., Boyle, J., Jones, R., Nolan, S., Gibbs, Z., Appleby, P., Fisher, E. and Wolff, G. (2003). The late-Holocene history of Gormire Lake (NE England) and its catchment: a multiproxy reconstruction of past human impact. *The Holocene*, 13(5), 677-690.

Oleksy, I. A., Baron, J. S, Leavitt, P. R. and Spaulding, S. A. (2020). Nutrients and warming interact to force mountain lakes into unprecedented ecological states. *Proceedings of the Royal Society B*, 28, 20200304.

Oleksy, I., Baron, J. and Beck, W. (2021). Nutrients and warming alter mountain lake benthic algal structure and function. *Freshwater Science*, 40(1), 88-102.

Omar, W. M. W. (2010). Perspectives on the use of algae as biological indicators for monitoring and protecting aquatic environments, with special reference to Malaysian freshwater ecosystems. *Tropical Life Sciences Research*, 21(2), 51-67.

Ong, M. and Happey-Wood, C. (1979). The seasonal distribution of micro-green algae in two linked but contrasting Welsh lakes. *British Phycological Journal*, 14(4), 361-375.

OpenStreetMap. (2020). Map data. Available at: https://www.openstreetmap.org/ [Accessed 05/11/2020].

Orr, H., Davies, G., Quinton, J. N. and Newson, M. (2004). Bassenthwaite Lake Geomorphological Assessment, phase 2. *Environment Agency*, Bristol.

Oswald, A., Mcomish, D. and Ainsworth, S. (2001). Greenburn Copper Mine, Cumbria. Survey Report. *Archaeological Investigation Report Series.* A1/6/2001.

Ouyang, X., Guo, F. and Bu, H. (2015). Lipid biomarkers and pertinent indices from aquatic environment record paleoclimate and paleoenvironment changes. *Quaternary Science Reviews*, 123, 180-192.

Padilla-Gamiño, J. and Carpenter, R. (2007). Seasonal acclimatization of Asparagopsis taxiformis (Rhodophyta) from different biogeographic regions. *Limnology and Oceanography*, 52(2), 833-842.

Paerl, H. and Huisman, J. (2008). Climate: Blooms Like It Hot. *Science*, 320(5872), 57-58.

Paerl, H. and Huisman, J. (2009). Climate change: a catalyst for global expansion of harmful cyanobacterial blooms. *Environmental Microbiology Reports*, 1(1), 27-37.

Paerl, H. W. and Otten, T.G. (2013). Harmful cyanobacterial blooms: causes, consequences, and controls. *Microbial Ecology*, 65, 995-1010.

Paerl, H. W., Fulton, R. S., Moisander, P. H. and Dyble, J. (2001). Harmful freshwater algal blooms, with an emphasis on cyanobacteria. *The Scientific World Journal*, 1, 76-113.

Paerl, H. W., Valdes, L. M., Pinckney, J. L., Piehler, M. F., Dyble, J. and Moisander, P. H. (2003). Phytoplankton photopigments as indicators of estuarine and coastal eutrophication. *BioScience*, 53, 953-964.

Pal, S., Gregory-Eaves, I. and Pick, F. (2015). Temporal trends in cyanobacteria revealed through DNA and pigment analyses of temperate lake sediment cores. *Journal of Paleolimnology*, 54(1), 87-101.

Parker, J. E. and Maberly, S. C. (2001). Biological response to lake remediation by phosphate stripping: control of Cladophora. *Freshwater Biology*, 44(2), 303-309.

Parker, D. E., Legg, T. P. and Folland, C. K. (1992). A new daily central England temperature series, 1772–1991. *International Journal of Climatology,* 12, 317-342.

Patoine, A. and Leavitt, P. R. (2006). Century-long synchrony of fossil algae in a chain of canadian prairie lakes. *Ecology*, 87, 1710-1721.

Patoine, A., M. D., Graham, and Leavitt, P. R. (2006). Spatial variation of nitrogen fixation in lakes of the northern Great Plains. *Limnology and Oceanography*, 51, 1665-1677.

Paul, E., (2016). The nature and dynamics of soil organic matter: Plant inputs, microbial transformations, and organic matter stabilization. *Soil Biology and Biochemistry*, 98, 109-126.

Pędziszewska, A., Tylmann, W., Witak, M., Piotrowska, N., Maciejewska, E. and Latałowa, M. (2015). Holocene environmental changes reflected by pollen, diatoms, and geochemistry of annually laminated sediments of Lake Suminko in the Kashubian Lake District (N Poland). *Review of Palaeobotany and Palynology*, 216, 55-75.

Peña-Icart, M., Villanueva Tagle, M., Alonso-Hernández, C., Rodríguez Hernández, J., Behar, M. and Pomares Alfonso, M. (2011). Comparative study of digestion methods EPA 3050B (HNO3–H2O2–HCl) and ISO 11466.3 (aqua regia) for Cu, Ni and Pb contamination assessment in marine sediments. *Marine Environmental Research*, 72(1-2), 60-66.

Pennington, W. (1964). Pollen analyses from the deposits of six upland tarns in the Lake District. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, 248(746), 205-244.

Pennington, W. (1991). Palaeolimnology in the English Lakes ? some questions and answers over fifty years. *Hydrobiologia*, 214(1), 9-24.

Pennington, W., Cambray, R. S., Eakins, J. D. and Harkness D . D. (1976). Radionuclide dating of the recent sediments of Blelham Tarn. *Freshwater Biology*, 6, 317-331.

Pennington, F. C., Haxo, F. T., Borch, G. and Liaaen-Jensen, S. (1985). Carotenoids of cryptophyceae. *Biochemical Systematics and Ecology*, 13, 215-219.

Pentecost, A. (1998). Phosphorus fractionation in the sediments of Malham Tarn, North Yorkshire. *Environmental Science*. 9, 337-342.

Pentecost, A. (2009). The marl lakes of the British Isles. *Freshwater Reviews*, 2, 167-197.

Pentecost, A. (2013). A report on the current status of Sunbiggin Tarn, Cumbria with reference to the epiphytic algal flora, surface sediment chemistry and nutrient concentrations in the tarn and its feeder springs. Report to Natural England.

Pickering, A.D. (2001). Windermere: Restoring the health of England's largest lake. *Freshwater Biological Association*, Ambleside.

Pitcairn, C. E. R. and Fowler, D. (1995). Deposition of fixed atmospheric nitrogen and foliar nitrogen content of bryophytes and Calluna vulgaris (L.) Hull. *Environmental Pollution*, 88, 193-205.

Porra, R. J., Pfündel, E. E. and Engel, N. (1997). Metabolism and function of photosynthetic pigments. In: Jeffrey S. W., Mantoura. R. F. C. and Wright, S. W. (eds) *Phytoplankton pigments in oceanography*, UNESCO, Paris, 85-126.

Postlethwaite, J. (1975). Postlethwaite's Mines and mining in the English Lake District. Michael Moon: Beckermet, Cumbria.

Preston, C.D., Pearman D.A. and Dines, T.D. (2002). New Atlas of the British and Irish Flora. *Oxford University Press*, Oxford.

Pretty, J., Mason, C., Nedwell, D., Hine, R., Leaf, S. and Dils, R. (2003). Environmental Costs of Freshwater Eutrophication in England and Wales. *Environmental Science and Technology*, 37(2), 201-208.

Prosdocimi, I., Kjeldsen, T. R. and Svensson, C. (2014). Nonstationarity in annual and seasonal series of peak flow and precipitation in the UK. *Natural Hazards and Earth System Sciences*, 14(5), 1125-1144.

Pukacz, A., Pełechaty, M. and Frankowski, M. (2014). Carbon dynamics in a hardwater lake: effect of charophyte biomass on carbonate deposition. *Polish Journal of Ecology*, 62, 695-705.

Quan, Q., Wang, C., He, N., Zhang, Z., Wen, X., Su, H., Wang, Q. and Xue, J. (2014). Forest type affects the coupled relationships of soil C and N mineralization in the temperate forests of northern China. *Scientific Reports*, 4(1), 6584.

Rau, G. H., Takahashi, T. and Des Marais, D. (1989). Latitudinal variation in plankton δ13C: Implications for CO2 and productivity in past oceans. *Nature*, 341, 516-518.

Raven, J. and Geider, R. (1988). Temperature and algal growth. *New Phytologist*, 110(4), 441-461.

Rawcliffe, R., Sayer, C., Woodward, G., Grey, J., Davidson, T. and Iwan Jones, J. (2010). Back to the future: using palaeolimnology to infer long-term changes in shallow lake food webs. *Freshwater Biology*, 55(3), 600-613.

Reavie, E., Cai, M., Twiss, M., Carrick, H., Davis, T., Johengen, T., Gossiaux, D., Smith, D., Palladino, D., Burtner, A. and Sgro, G., 2016. Winter–spring diatom production in Lake Erie is an important driver of summer hypoxia. *Journal of Great Lakes Research*, 42(3), 608-618.

Redfield, A. C. (1958). The biological control of chemical factors in the environment. *American Scientist*, 46, 205-221.

Reuss, N. (2005). Sediment pigments as biomarkers of environmental change. PhD thesis. *National Environmental Research Institute*, Copenhagan.

Reuss, N., Conley, D. and Bianchi, T. (2005). Preservation conditions and the use of sediment pigments as a tool for recent ecological reconstruction in four Northern European estuaries. *Marine Chemistry*, 95(3-4), 283-302.

Reuss, N., Leavitt, P., Hall, R., Bigler, C. and Hammarlund, D. (2010). Development and application of sedimentary pigments for assessing effects of climatic and environmental changes on subarctic lakes in northern Sweden. *Journal of Paleolimnology,* 43(1), 149-169.

Reynolds, C. (2006). The Ecology of Phytoplankton. *Cambridge University Press,* Cambridge, Massachusetts, 436 pp.

Reynolds, C. S. and Irish, A. E. (2000). The Phytoplankton of Windermere. *Freshwater Biological Association*, Ambleside.

Reynolds, C., Maberley, S., Parker, J. and De Ville, M. (2012). Forty years of monitoring water quality in Grasmere (English Lake District): separating the effects of enrichment by treated sewage and hydraulic flushing on phytoplankton ecology. *Freshwater Biology*, 57(2), 384-399.

Ricciardi, A. and Rasmussen, J. B. (1999). Extinction rates of north American freshwater fauna. *Conservation Biology*, 13, 1220-1222.

Richardson, C. (1986). Clearing the air. *The Bradford Antiquary, the journal of the Bradford Historical and Antiquarian Society*, volume 2, 28-34.

Rigosi, A., Carey, C. C., Ibelings, B. W. and Brookes, J. D. (2014). The interaction between climate warming and eutrophication to promote cyanobacteria is dependent on trophic state and varies among taxa. *Limnology and Oceanography*, 59, 99-114.

Rippey, B. (2010). A model for the concentration of lead and polychlorinated biphenyls in lake sediment. *Journal of Paleolimnology*, 43, 565-576.

Robbins, J. A. (1978). Geochemical and geophysical applications of radioactive lead. In Nriagu, J.O., editor, Biogeochemistry of lead in the environment. *Elsevier Scientific*, 285-393.

Robertson, D. M., Garn, H. S. and Rose, W. J. (2007). Response of calcareous Nagawicka Lake, Wisconsin, to changes in phosphorus loading. *Lake and Reservoir Management*, 23, 298-312.

Robinson, D. (2001). d15N as an indicator of the nitrogen cycle. *Trends in Ecology and Evolution*, 16, 153-162.

Rollinson, W. (1967). A History of Man in the Lake District, London, J. M. Dent.

Romero-Viana, L., Keely, B., Camacho, A., Vicente, E. and Miracle, M. (2010). Primary production in Lake La Cruz (Spain) over the last four centuries: reconstruction based on sedimentary signal of photosynthetic pigments. *Journal of Paleolimnology*, 43(4), 771-786.

Rose, N. L. (2001). Fly-ash particles. In: Last, W. M. and Smol, J. P. (eds) *Tracking Environmental Change Using Lake Sediments*, vol. 2: Physical and Geochemical Methods. Dordrecht: Kluwer Academic Publishers, 319-350.

Rose, N., Yang, H., Turner, S. and Simpson, G. (2012). An assessment of the mechanisms for the transfer of lead and mercury from atmospherically contaminated organic soils to lake sediments with particular reference to Scotland, UK. *Geochimica et Cosmochimica Acta*, 82, 113-135.

RoTAP. (2012). Review of Transboundary Air Pollution: Acidification, Eutrophication, Ground Level Ozone and Heavy Metals in the UK. *Contract Report to the Department for Environment, Food and Rural Affairs.* Centre for Ecology and Hydrology.

Rowan, K. S. (1989). Photosynthetic pigments of algae, *Cambridge University Press*, UK.

Rumpel, C. and Kögel-Knabner, I. (2011). Deep soil organic matter-a key but poorly understood component of terrestrial C cycle. *Plant and Soil*, 338, 143-158.

Ryan, C., Thomas, M. and Litchman, E. (2017). The effects of phosphorus and temperature on the competitive success of an invasive cyanobacterium. *Aquatic Ecology*, 51(3), 463-472.

Ryves, D., Battarbee, R., Juggins, S., Fritz, S. and Anderson, N. (2006). Physical and chemical predictors of diatom dissolution in freshwater and saline lake sediments in North America and West Greenland. *Limnology and Oceanography*, 51(3), 1355-1368.

Sabater, S. and Haworth, E. (1995). An assessment of recent trophic changes in Windermere South Basin (England) based on diatom remains and fossil pigments. *Journal of Paleolimnology*, 14(2), 151-163.

Sachs J. P. and Repeta D. J. (1999). Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. *Science*, 286, 2485-2488.

Sachs J. P., Repeta D. J., Goericke R. (1999). Nitrogen and carbon isotopic ratios of chlorophyll from marine phytoplankton. *Geochim. Cosmochim. Acta*, 63 1431-1441.

Salmaso, N., Buzzi, F., Garibaldi, L., Morabito, G. and Simona, M. (2012). Effects of nutrient availability and temperature on phytoplankton development: a case study from large lakes south of the Alps. *Aquatic Sciences*, 74(3), 555-570.

Salomons, W. and Forstner, U. (1984). Metals in The Hydrocycle. *Springer-Verlag*, Berlin-Heidelberg, 349 pp.

Sarkar, S., Ahmed, T., Swami, K., Judd, C., Bari, A., Dutkiewicz, V. and Husain, L. (2015). History of atmospheric deposition of trace elements in lake sediments, ~1880 to 2007. *Journal of Geophysical Research: Atmospheres*, 120(11), 5658-5669.

Scheffer, M. and van Nes, E. H. (2007). Shallow lakes theory revisited: various alternative regimes driven by climate, nutrients, depth and lake size. *Hydrobiologia*, 584, 455-466.

Scheffer, M., Rinaldi, S., Gragnani, A., Mur, L. and van Nes, E. (1997). On the dominance of filamentous cyanobacteria in shallow, turbid lakes. *Ecology*, 78(1), 272-282.

Scheffer, M., van Geest, G., Zimmer, K., Jeppesen, E., Søndergaard, M., Butler, M., Hanson, M., Declerck, S. and De Meester, L. (2006). Small habitat size and isolation can promote species richness: second-order effects on biodiversity in shallow lakes and ponds. *Oikos*, 112(1), 227-231.

Schillereff, D., Chiverrell, R., Macdonald, N., Hooke, J. and Welsh, K. (2016). Quantifying system disturbance and recovery from historical mining-derived metal contamination at Brotherswater, northwest England. *Journal of Paleolimnology*, 56(2-3), 205-221.

Schindler, D. W. (1998). Sustaining aquatic ecosystems in boreal regions. *Ecology and Society*, 2, 18.

Schindler, D. (2009). Lakes as sentinels and integrators for the effects of climate change on watersheds, airsheds, and landscapes. *Limnology and Oceanography*, 54(6part2), 2349-2358.

Schindler, D. and Scheuerell, M. (2002). Habitat coupling in lake ecosystems. *Oikos*, 98, 177-189.

Schindler, D. W., Bayley, S. E., Parker, B. R., Beaty, K. G., Cruikshank, D. R., Fee, E. J., Schindler, E. U., and Stainton, M. P. (1997). The effects of climate warming on the properties of boreal lakes and streams at the Experimental Lakes Area, northwestern Ontario. *Limnology and Oceanography*, 41, 1004-1017.

Schindler, D., Hecky, R., Findlay, D., Stainton, M., Parker, B., Paterson, M., Beaty, K., Lyng, M. and Kasian, S. (2008). Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences*, 105(32), 11254-11258.

Schlüter, L., Garde, K., Kaas, H. (2004). Detection of the toxic cyanobacteria Nodularia spumigena by means of a 4-keto-myxoxanthophyll-like pigment in the Baltic Sea. *Marine Ecology Progress Seies*, 275, 69-78.

Schoeninger, M. and DeNiro, M. (1984). Nitrogen and carbon isotopic composition of bone collagen from marine and terrestrial animals. *Geochimica et Cosmochimica Acta*, 48(4), 625-639.

Scott, L. I. (1948). Algae. In: Yorkshire Naturalists' Union excursions in 1948 – Thirsk. *Naturalist*, 159-161.

Seekell, D., Lapierre, J., Ask, J., Bergström, A., Deininger, A., Rodríguez, P. and Karlsson, J. (2015). The influence of dissolved organic carbon on primary production in northern lakes. *Limnology and Oceanography*, 60(4), 1276-1285.

Seitzinger, S., Harrison, J., Böhlke, J., Bouwman, A., Lowrance, R., Peterson, B., Tobias, C. and Drecht, G. (2006). Denitrification across landscapes and waterscapes: A synthesis. *Ecological Applications*, 16(6), 2064-2090.

Shatwell, T. and Köhler, J. (2019). Decreased nitrogen loading controls summer cyanobacterial blooms without promoting nitrogen-fixing taxa: Long-term response of a shallow lake. *Limnology and Oceanography*, 64(S1).

Shatwell, T. and Köhler, J. (2019). Decreased nitrogen loading controls summer cyanobacterial blooms without promoting nitrogen-fixing taxa: long-term response of a shallow lake. *Limnology and Oceanography*, 64 (S1), S166-S178.

Shatwell, T., Köhler, J. and Nicklisch, A. (2008). Warming promotes cold-adapted phytoplankton in temperate lakes and opens a loophole for *Oscillatoriales* in spring. *Global Change Biology*, 14 (9), 2194-2200.

Shearer, G. and Kohl, D.H. (1989). Estimates of N2 fixation in Ecosystems: the need for and basis of the 15N natural abundance method. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.) *Stable Isotopes in Ecological Research*. Ecological Studies 68. Springer-Verlag, Berlin, 342-374.

Sheng, W., Yu, G., Fang, H., Liu, Y., Wang, Q., Chen, Z. and Zhang, L. (2014). Regional patterns of 15N natural abundance in forest ecosystems along a large transect in eastern China. *Scientific Reports*, 4(1), 4249.

Shuter B. J., Schlesinger D. A. and Zimmerman A. P. (1983), Empirical predictors of annual surface water temperature cycles in North American Lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 40, 1838-1845.

Simons, J., Ohm, M., Daalder, R., Boers, P. and Rip, W. (1994). Restoration of Botshol (The Netherlands) by reduction of external nutrient load: recovery of a characean community, dominated by *Chara connivens*. *Hydrobiologia,* 275/276, 243-253.

Sinha, R. P. and Hader, D. P. (2002). UV-induced DNA damage and repair: a review. *Photochemical and Photobiological Sciences*, 1, 225-236.

Sinha. R. P., Klisch, M., Gröniger, A. and Häder, D. P. (1998). Ultraviolet-absorbing/screening substances in cyanobacteria, phytoplankton and macroalgae. *Journal of Photochemistry and Photobiology B: Biology*, 47, 83-94.

Sivarajah, B., Rühland, K., Labaj, A., Paterson, A. and Smol, J. (2016). Why is the relative abundance of Asterionella formosa increasing in a Boreal Shield lake as nutrient levels decline?. *Journal of Paleolimnology*, 55(4), 357-367.

Smith, A. (2010). Condition of SSSI Units for Site Gormire SSSI. Available at: https://designatedsites.naturalengland.org.uk/ReportUnitCondition.aspx?SiteCode=S1002548&ReportTitle=Gormire%20SSSI [Accessed 15 Aug. 2019].

Smol, J. (2008). Pollution of Lakes and Rivers: A Paleoenvironmental Perspective. 2nd ed. Oxford Univ. Press.

Smol, J., Wolfe, A., Birks, H., Douglas, M., Jones, V., Korhola, A., Pienitz, R., Ruhland, K., Sorvari, S., Antoniades, D., Brooks, S., Fallu, M., Hughes, M., Keatley, B., Laing, T., Michelutti, N., Nazarova, L., Nyman, M., Paterson, A., Perren, B., Quinlan, R., Rautio, M., Saulnier-Talbot, E., Siitonen, S., Solovieva, N. and Weckstrom, J. (2005). Climate-driven regime shifts in the biological communities of arctic lakes. *Proceedings of the National Academy of Sciences*, 102(12), 4397-4402.

Sneddon, J., Hardaway, C., Bobbadi, K. and Reddy, A. (2006). Sample preparation of solid samples for metal determination by atomic spectroscopydan overview and selected recent applications. *Applied Spectroscopy Reviews* 41, 1-14.

Snucins, E. and John, G. (2000). Interannual variation in the thermal structure of clear and colored lakes. *Limnology and Oceanography*, 45, 1639-1646.

Sobek, S., Anderson, N., Bernasconi, S. and Del Sontro, T. (2014). Low organic carbon burial efficiency in arctic lake sediments. Journal of Geophysical Research: *Biogeosciences*, 119(6), 1231-1243.

Sobek, S., Durisch-Kaiser, E., Zurbrügg, R., Wongfun, N., Wessels, M., Pasche, N. and Wehrli, B. (2009). Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnology and Oceanography*, 54(6), 2243-2254.

Sobek, S., Tranvik, L., Prairie, Y., Kortelainen, P. and Cole, J. (2007). Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnology and Oceanography*, 52(3), 1208-1219.

Sollins, P., Spycher, G. and Glassman, C. A. (1984). Net nitrogen mineralization from light-fraction and heavy fraction forest soil organic matter. *Soil Biology and Biochemistry*, 16, 31-37.

Sommer, U., Gliwicz, Z. M., Lampert, W. and Duncan, A. (1986). The PEG-model of seasonal succession of planktonic events in fresh waters. *Arch Hydrobiol*, 106 (4), 433-471.

Søndergaard, M. (2007). Nutrient dynamics in lakes – with emphasis on phosphorus, sediment and lake restoration. Doctor’s dissertation (DSc), University of Aarhus, Denmark.

Søndergaard, M., Jensen, J. and Jeppesen, E. (2003). Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia*, 506-509(1-3), 135-145.

Søndergaard, M., Kristensen, P. and Jeppesen, E. (1992). Phosphorus release from resuspended sediment in the shallow and wind-exposed Lake Arresø, Denmark. *Hydrobiologia* 228, 91-99.

Sparber, K., Dalton, C., de Eyto, E., Jennings, E., Lenihan, D. and Cassina, F. (2015). Contrasting pelagic plankton in temperate Irish lakes: the relative contribution of heterotrophic, mixotrophic, and autotrophic components, and the effects of extreme rainfall events. *Inland Waters*, 5(3), 295-310.

Squier, A. H., Hodgson, D. A. and Keely, B. (2004). A critical assessment of the analysis and distributions of scytonemin and related UV screening pigments in sediments. *Organic Geochemistry*, 35, 1221-1228.

Squier, A., Hodgson, D. and Keely, B. (2005). Evidence of late Quaternary environmental change in a continental east Antarctic lake from lacustrine sedimentary pigment distributions. *Antarctic Science*, 17(3), 361-376.

Stal, L., Albertano, P., Bergman, B., Bröckel, K., Gallon, J., Hayes, P., Sivonen, K. and Walsby, A. (2003). BASIC: Baltic Sea cyanobacteria. An investigation of the structure and dynamics of water blooms of cyanobacteria in the Baltic Sea—responses to a changing environment. *Continental Shelf Research*, 23(17-19), 1695-1714.

Stevens, L. R., Ito, E. and Olson, D. (2000). Relationship of Mn-carbonates in varved lake-sediments to catchment vegetation in Big Watab Lake, MN, USA. *Journal of Paleolimnology*, 24**,** 199-211.

Stevenson, M., McGowan, S., Anderson, N., Foy, R., Leavitt, P., McElarney, Y., Engstrom, D. and Pla-Rabés, S. (2016). Impacts of forestry planting on primary production in upland lakes from north-west Ireland. *Global Change Biology*, 22(4), 1490-1504.

Stumm, W. and Morgan, J. (2013). Aquatic chemistry: chemical equilibria and rates in natural waters. Environmental science and technology: a Wiley-Interscience series of texts and monographs. Wiley.

Sutcliffe, D. W. and Carrick, T. R. (1988). Alkalinity and pH of tarns and streams in the English Lake District (Cumbria). *Freshwater Biology*, 19, 179-189.

Szpak, P., Longstaffe, F., Millaire, J. and White, C. (2012). Stable Isotope Biogeochemistry of Seabird Guano Fertilization: Results from Growth Chamber Studies with Maize (Zea Mays). *PLoS ONE*, 7(3), 33741.

Szymczak-Żyła, M., Krajewska, M., Winogradow, A., Zaborska, A., Breedveld, G. and Kowalewska, G. (2017). Tracking trends in eutrophication based on pigments in recent coastal sediments. *Oceanologia*, 59(1), 1-17.

Syvitski, J., Waters, C., Day, J., Milliman, J., Summerhayes, C., Steffen, W., Zalasiewicz, J., Cearreta, A., Gałuszka, A., Hajdas, I., Head, M., Leinfelder, R., McNeill, J., Poirier, C., Rose, N., Shotyk, W., Wagreich, M. and Williams, M. (2020). Extraordinary human energy consumption and resultant geological impacts beginning around 1950 CE initiated the proposed Anthropocene Epoch. *Communications Earth & Environment*, 1(1).

Takaichi, S. (2011). Carotenoids in Algae: Distributions, Biosyntheses and Functions. *Marine Drugs*, 9(6), 1101-1118.

Talbot, M. R. (2001). Nitrogen isotopes in palaeolimnology. In Eds W.M. Last and J.P. Smol (eds) *Tracking Environmental Change Using Lake Sediments*. Volume 2: Physical and Geochemical Methods , 401-439. Kluwer Academic Publications, Dordrecht.

Talbot, H., Head, R., Harris, R. and Maxwell, J. (1999). Distribution and stability of steryl chlorin esters in copepod faecal pellets from diatom grazing. *Organic Geochemistry*, 30(9), 1163-1174.

Talling J. F. and Heaney S. I. (1988). Long-term changes in some English (Cumbrian) lakes subject to increased nutrient inputs. *Algae and the Aquatic Environment* (Ed. F.E. Round), 1-29. Biopress, Bristol.

Taranu, Z., Gregory-Eaves, I., Leavitt, P., Bunting, L., Buchaca, T., Catalan, J., Domaizon, I., Guilizzoni, P., Lami, A., McGowan, S., Moorhouse, H., Morabito, G., Pick, F., Stevenson, M., Thompson, P. and Vinebrooke, R. (2015). Acceleration of cyanobacterial dominance in north temperate-subarctic lakes during the Anthropocene. *Ecology Letters*, 18(4), 375-384.

Taranu, Z. E., Zurawell, R. W., Pick, F. and Gregory-Eaves, I. (2012). Predicting cyanobacterial dynamics in the face of global change: the importance of scale and environmental context. *Global Change Biology*, 18, 3477-3490.

Taylor, H.A. (1985). Dimension Stone. *Mineral Facts and Problems,* U.S. Bureau of Mines Bulletin No. 675, U.S. Government Print Off, 769-776.

Teranes, J. L. and Bernasconi, S. M. (2000). The record of nitrate utilisation and productivity limitation provided by δ15N values in lake organic matter-A study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnology and Oceanography*, 45, 801-813.

Thackeray, S. J., Henrys, P. A., Feuchtmayr, H., Jones, I. D., Maberly, S. C. and Winfield, I. J. (2013). Food web de-synchronization in England's largest lake: an assessment based on multiple phenological metrics. *Global Change Biology*, 19, 3568-3580.

Thackeray, S., Jones, I. and Maberly, S. (2008). Long-term change in the phenology of spring phytoplankton: species-specific responses to nutrient enrichment and climatic change. *Journal of Ecology*, 96(3), 523-535.

Thrane, J. E., Hessen, D. O. and Andersen, T. (2017). Plasticity in algal stoichiometry: Experimental evidence of a temperature induced shift in optimal supply N:P ratio. *Limnology and Oceanography*, 62, 1346-1354.

Tipping, E. and Chaplow, J. (2011). Atmospheric pollution histories of three Cumbrian surface waters. *Freshwater Biology*, 57(2), 244-259.

Tipping, E., Bass, J. a. B., Hardie, D., Haworth, E. Y., Hurley, M. A. and Wills, G. (2002). Biological responses to the reversal of acidification in surface waters of the English Lake District. *Environmental Pollution*, 116, 137-146.

Tipping, E., Bettney, R., Hurley, M., Isgren, F., James, J., Lawlor, A., Lofts, S., Rigg, E., Simon, B., Smith, E. and Woof, C. (2000). Reversal of acidification in tributaries of the River Duddon (English Lake District) between 1970 and 1998. *Environmental Pollution*, 109(2), 183-191.

Tipping, E., Lofts, S., Lawlor, A., Ashmore, M., Shotbolt, L., Rose, N. (2005). Heavy metals in British upland waters. In: Battarbee, R.W.; Curtis, C.J.; Binney, H.A., (eds.) *The future of Britain's upland waters*. London, Ensis Publishing, 36-39.

Tipping, E., Thacker, S., Wilson, D. and Hall, J. (2008). Long-term nitrate increases in two oligotrophic lakes, due to the leaching of atmospherically-deposited N from moorland ranker soils. *Environmental Pollution*, 152(1), 41-49.

Toming, K., Kotta, J., Uuemaa, E., Sobek, S., Kutser, T. and Tranvik, L. (2020). Predicting lake dissolved organic carbon at a global scale. *Scientific Reports*, 10(1).

Townsend, D. W., Keller, M. D., Sieracki, M. E. Ackleson, S. G. (1992). Spring phytoplankton blooms in the absence of vertical water column stratification. *Nature*, 360, 59-62.

Tranvik, L. J. and Jansson, M. (2002). Climate change—terrestrial export of organic carbon. *Nature*, 415, 861-862.

Trochine, C., Guerrieri, M., Liboruissen, L., Meerhoff, M., Lauridsen, T., Sindergaard, M. and Jeppesen, E. (2011). Filamentous green algae inhibit phytoplankton with enhanced effects when lakes get warmer. *Freshwater Biology*, 56(3), 541-553.

Tylmann, W., Szpakowska, K., Ohlendorf, C., Woszczyk, M. and Zolitschka, B. (2012). Conditions for deposition of annually laminated sediments in small meromictic lakes: a case study of Lake Suminko (northern Poland). *Journal of Paleolimnology*, 47(1), 55-70.

Vadeboncoeur, Y., Jeppesen, E., Zanden, M., Schierup, H., Christoffersen, K. and Lodge, D. (2003). From Greenland to green lakes: Cultural eutrophication and the loss of benthic pathways in lakes. *Limnology and Oceanography*, 48(4), 1408-1418.

Vadeboncoeur, Y., Peterson, G., Vander Zanden, M. J. and Kalff, J. (2008). Benthic algal production across lake size gradients: interactions among morphometry, nutrients, and light. *Ecology*, 89, 2542-2552.

Verburg, P. (2007). The need to correct for the Suess effect in the application of δ13C in sediment of autotrophic Lake Tanganyika, as a productivity proxy in the Anthropocene. *Journal of Paleolimnology*, 37, 591-602.

Verleyen, E., Hodgson, D. A., Sabbe, K. and Vyverman, W. (2005). Late Holocene changes in ultraviolet radiation penetration recorded in an East Antarctic lake. *Journal of Paleolimnology*, 34, 191-202.

Vermeer, C. P., Escher, M., Portielje, R. and de Klein, J. J. M. (2003). Nitrogen uptake and translocation by *Chara*. *Aquatic Botany*, 76, 245-258.

Vílchez, C., Forján, E., Cuaresma, M., Bédmar, F., Garbayo, I. and Vega, J. M. (2011). Marine carotenoids: Biological functions and commercial applications. *Marine Drugs*, 9, 319-33.

Vincent, W. F., Downes, M. T., Castenholz, R. W., Howard-Williams, C. (1993). Community structure and pigment organization of cyanobacteria-dominated microbial mats in Antarctica. *European Journal of Phycology*, 28, 213-221.

Vinebrooke, R. D. and Leavitt, P. R. (1999). Differential responses of littoral communities to Ultraviolet Radiation in an alpine lake. *Ecology*, 80, 223-237.

Vinebrooke, R. D., Dixit, S. S., Graham, M. D., Gunn, J. M., Chen, Y.-W. and Belzile, N. (2002). Whole-lake algal responses to a century of acidic industrial deposition on the Canadian Shield. *Canadian Journal of Fisheries and Aquatic Sciences*, 59, 483-493.

Visviki, I. and Rachlin, J. (1994). Acute and chronic exposure of Dunaliella salina and Chlamydomonas bullosa to copper and cadmium: Effects on growth. *Archives of Environmental Contamination and Toxicology*, 26(2), 149-153.

Von Wachenfeldt, E. (2008). Flocculation of allochthonous dissolved organic matter. Uppsala: Acta Universitatis Upsaliensis.

Waghorne, R., Hancock, J. and Candy, I. (2012). Environmental controls on the δ18O composition of freshwater calcite and aragonite in a temperate, lowland river system: significance for palaeoclimatic studies. *Proceedings of the Geologists' Association*, 123(4), 576-583.

Wagner, C. and Adrian, R. (2009). Cyanobacteria dominance: quantifying the effects of climate change. *Limnology and Oceanography*, 54, 2460-2468.

Walker, S. J., Squier, A., Hodgson, D. and Keely, B. (2002). Origin and significance of 13 2 -hydroxychlorophyll derivatives in sediments. *Organic Geochemistry*, 33(12), 1667-1674.

Wang, Q., Liao, Z., Yao, D., Yang, Z., Wu, Y. and Tang, C. (2021). Phosphorus immobilization in water and sediment using iron-based materials: A review. *Science of The Total Environment*, 767, 144246.

Wang, L., Mackay, A., Leng, M., Rioual, P., Panizzo, V., Lu, H., Gu, Z., Chu, G., Han, J. and Kendrick, C. (2013). Influence of the ratio of planktonic to benthic diatoms on lacustrine organic matter δ13C from Erlongwan maar lake, northeast China. *Organic Geochemistry*, 54, 62-68.

Waters, M., Smoak, J. and Saunders, C. (2012). Historic primary producer communities linked to water quality and hydrologic changes in the northern Everglades. *Journal of Paleolimnology*, 49(1), 67-81.

Watts, G., Battarbee, R., Bloomfield, J., Crossman, J., Daccache, A., Durance, I., Elliott, J., Garner, G., Hannaford, J., Hannah, D., Hess, T., Jackson, C., Kay, A., Kernan, M., Knox, J., Mackay, J., Monteith, D., Ormerod, S., Rance, J., Stuart, M., Wade, A., Wade, S., Weatherhead, K., Whitehead, P. and Wilby, R. (2015). Climate change and water in the UK – past changes and future prospects. *Progress in Physical Geography*, 39(1), 6-28.

Weber, P., Bol, R., Dixon, L. and Bardgett, R. (2008). Large old trees influence patterns of δ^{13}C and δ^{15}N in forests. *Rapid Communications in Mass Spectrometry*, 22(11), 1627-1630.

Werritty, A. (2002). Living with uncertainty: climate change, river flows and water resource management in Scotland. *Science of The Total Environment*, 294(1-3), 29-40.

West, H., Quinn, N. and Horswell, M. (2019). Regional rainfall response to the North Atlantic Oscillation (NAO) across Great Britain. *Hydrology Research*, 50(6), 1549-1563.

Wetzel, R. G. (1983). Limnology. Second Edition. Saunders College Publishing, New York.

Wetzel, R. G. (2001). Limnology, 3rd ed. Academic Press.

Weyhenmeyer, G., Blenckner, T. and Pettersson, K. (1999). Changes of the plankton spring outburst related to the North Atlantic Oscillation. *Limnology and Oceanography*, 44(7), 1788-1792.

White, L. (2013). Gormire and Butterdale Lake Bathymetry and Water Quality Survey. Xylem, Report Number: 476903062013.

Whitehead, P., Wilby, R., Butterfield, D. and Wade, A. (2006). Impacts of climate change on in-stream nitrogen in a lowland chalk stream: An appraisal of adaptation strategies. *Science of The Total Environment*, 365(1-3), 260-273.

Whiteside, M. C. (1983). The mythical concept of eutrophication. In: Meriläinen, J., Huttunen, P. and Battarbee, R. W. (eds.) *Paleolimnology*. Springer Netherlands.

WHO. (2017). Water quality and heath – review of turbidity: Information for regulators and water suppliers. World Health Organization. Available at: https://www.who.int/water_sanitation_health/publications/turbidity-information-200217.pdf [Accessed 01/09/2021].

Wigley, T. M. L., Lough, J. M. and Jones, P. D. (1984). Spatial patterns of precipitation in England and Wales and a revised, homogeneous England and Wales precipitation series. *Journal of Climatology*, 4, 1-25.

Wiik, E., Bennion, H., Sayer, C. and Clarke, S. (2014). Assessing the status of marl lakes under the European Union Water Framework Directive – insights from contemporary and palaeolimnological studies of three English lakes. *Fundamental and Applied Limnology*, 185(2), 121-138.

Wiik, E., Bennion, H., Sayer, C., Davidson, T., McGowan, S., Patmore, I. and Clarke, S. (2015a). Ecological sensitivity of marl lakes to nutrient enrichment: evidence from Hawes Water, UK. *Freshwater Biology*, 60(11), 2226-2247.

Wiik, E., Bennion, H., Sayer, C., Davidson, T., Clarke, S., McGowan, S., Prentice, S., Simpson, G. and Stone, L. (2015b). The coming and going of a marl lake: multi-indicator palaeolimnology reveals abrupt ecological change and alternative views of reference conditions. *Frontiers in Ecology and Evolution*, 3.

Wiik, E., Bennion, H., Sayer, C. and Willby, N. (2013). Chemical and Biological Responses of Marl Lakes to Eutrophication. *Freshwater Reviews*, 6(2), 35-62.

Wilby, R., Orr, H., Watts, G., Battarbee, R., Berry, P., Chadd, R., Dugdale, S., Dunbar, M., Elliott, J. and Extence, C. (2010). Evidence needed to manage freshwater ecosystems in a changing climate: Turning adaptation principles into practice. *Science of The Total Environment*, 408(19), 4150-4164.

Wilcke, W., Müller, S., Kanchanakool, N. and Zech, W. (1998). Urban soil contamination in Bangkok: heavy metal and aluminium partitioning in topsoils. *Geoderma*, 86, 211-228.

Williams, P., Whitfield, M., Biggs, J., Bray, S., Fox, G., Nicolet, P. and Sear, D. (2004). Comparative biodiversity of rivers, streams, ditches and ponds in an agricultural landscape in Southern England. *Biological Conservation*, 115(2), 329-341.

Williamson, C. E., Saros, J. E., Vincent, W. F. and Smold, J. P. (2009). Lakes and reservoirs as sentinels, integrators, and regulators of climate change. *Limnology and Oceanography*, 54, 2273-2282.

Winder, M. and Sommer, U. (2012). Phytoplankton response to a changing climate. *Hydrobiologia*, 698(1), 5-16.

Winfield, I., Fletcher, J. and James, J. (2008). The Arctic charr (Salvelinus alpinus) populations of Windermere, UK: population trends associated with eutrophication, climate change and increased abundance of roach (Rutilus rutilus). *Environmental Biology of Fishes*, 83(1), 25-35.

Winslow, L., Read, J., Hansen, G. and Hanson, P. (2015). Small lakes show muted climate change signal in deepwater temperatures. *Geophysical Research Letters*, 42(2), 355-361.

Wolfe, A. P., Baron, J. S. and Cornett, R. J. (2001). Anthropogenic nitrogen deposition induces rapid ecological changes in alpine lakes of the Colorado Front Range (USA). *Journal of Paleolimnology*, 25(1), 1-7.

Wolfe, A. P., Van Gorp, A. C. and Baron, J. S. (2003). Recent ecological and biogeochemical changes in alpine lakes of Rocky Mountain National Park (Colorado, USA): a response to anthropogenic nitrogen deposition. *Geobiology*, 1, 153-168.

Woodward, C., Potito, A. and Beilman, D. (2012). Carbon and nitrogen stable isotope ratios in surface sediments from lakes of western Ireland: implications for inferring past lake productivity and nitrogen loading. *Journal of Paleolimnology*, 47(2), 167-184.

Woolway, R., Jones, I., Feuchtmayr, H. and Maberly, S. (2015). A comparison of the diel variability in epilimnetic temperature for five lakes in the English Lake District. *Inland Waters*, 5(2), 139-154.

Worrall, F., Harriman, R., Evans, C., Watts, C., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P., Nisbet, T., Reynolds, B. and Stevens, P. (2004). Trends in Dissolved Organic Carbon in UK Rivers and Lakes. *Biogeochemistry*, 70(3), 369-402.

Wu, Y., Sklar, F. and Rutchey, K. (1997). Analysis and simulation of fragmentration patterns in the Everglades. *Ecological Applications*, 7(1), 268-276.

Xu, L., Lofts, S. and Lu, Y. (2016). Terrestrial ecosystem health under long-term metal inputs: modeling and risk assessment. *Ecosystem Health and Sustainability*, 2(5), p.e01214.

Yang, H. (2010). Historical mercury contamination in sediments and catchment soils of Diss Mere, UK. *Environmental Pollution*, 158(7), 2504-2510.

Yang, H. and Rose, N.L. (2003). Distribution of mercury in six lake sediment cores across the UK. *Science of the Total Environment*, 304, 391-404.

Yang, H. and Rose, N. L. (2005a). Temporal trends of toxic trace metals across the UK using ^{210}Pb-dated sediment cores. (ECRC Research Reports 104). UCL Environmental Change Research Centre: London, UK.

Yang, H. and Rose, N. (2005b). Trace element pollution records in some UK lake sediments, their history, influence factors and regional differences. *Environment International*, 31(1), 63-75.

Yang, H. and Smyntek, P. (2014). Use of the mercury record in Red Tarn sediments to reveal air pollution history and the implications of catchment erosion. *Environmental Science: Processes and Impacts*, 16(11), 2554-2563.

Yang H., Rose N. L., Battarbee R. W. and Boyle J. F. (2002). Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment. *Environmental Science and Technology*, 36, 1383-1388.

Yang, H., Turner, S. and Rose, N. (2016). Mercury pollution in the lake sediments and catchment soils of anthropogenically-disturbed sites across England. *Environmental Pollution*, 219, 1092-1101.

Zhang, Y., Su, Y., Liu, Z., Yu, J. and Jin, M. (2017). Sediment lipid biomarkers record phytoplankton dynamics of Lake Heihai (Yunnan Province, SW China) driven by climate warming since the 1980s. *Environmental Science and Pollution Research*, 24(26), 21509-21516.

Zolitschka, B., Francus, P., Ojala, A. and Schimmelmann, A. (2015). Varves in lake sediments – a review. *Quaternary Science Reviews*, 117, 1-41.