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Disentangling the impacts of nutrient enrichment and climatic forcing as key drivers of change at Rostherne Mere

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Disentangling the impacts of nutrient enrichment and climatic forcing as key drivers of change at Rostherne Mere

by
Alan Radbourne

A doctoral thesis submitted in partial fulfilment of the requirements for the award of
Doctor of Philosophy of Loughborough University

April 2018



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Preface

This thesis presents the results of my Ph.D. studies conducted from October 2014 to April 2018, registered at the Department of Geography, Loughborough University.

The research studentship was funded by the Natural Environment Research Council (NERC), as part of the Central England NERC Training Alliance (CENTA) doctoral training partnership [grant number NE/L002493/1].

The thesis consists of a contextual introduction, four individual study chapters and a thesis synthesis, drawing together each individual study to provide the overall findings and implications. The structure of my thesis has taken this individual study approach because the research aims and objectives have successfully divided into these four distinctive chapters, providing a fresh assessment of the different aspects of nutrient and climate change on the lake system in the past, present and future. I believe the distinguishing features of each chapter, although individualistic, have a strong thread that tie them together as a whole, this evident through the cross-citation throughout, as well as the discussion provided in the thesis synthesis chapter.

Furthermore, with the individual study chapters being able to stand alone, they have offered the opportunity to be prepared for publication in peer-reviewed scientific journals. All four studies have been prepared for publication in an altered structure as is presented in this thesis, with those presented here being the pre-submission manuscripts with small changes made to each to fit the thesis style and flow. Below is the citation information for each manuscript. All writing and data analysis for each study has been completed by myself with published article contributors providing comment and direction only.

Study 1 - RADBOURNE, A. D., RYVES, D. B., ANDERSON, N. J. & SCOTT, D. R.
2017. The historical dependency of organic carbon burial efficiency.
Limnology and Oceanography, **62**, 1480 - 1497.

Study 2 – RADBOURNE, A. D., RYVES, D. B., MADWICK, G. & ANDERSON, N. J.
In progress (intended journal: Freshwater Biology). Nutrients and climate drive reduced nutrient load trajectories and ecological change in a deep stratifying eutrophic lake.

Study 3 – RADBOURNE, A. D., RYVES, D. B. & ANDERSON, N. J. *In progress* (intended journal: *Journal of Ecology*). Climate perturbations modulate planktonic diatom communities and phenology in a reduced nutrient load deep lake.

Study 4 – RADBOURNE, A. D., ELLIOTT, J. A., MABERLY, S. C., RYVES, D. B. & ANDERSON, N. J. *In review* (*Freshwater Biology*). The impacts of changing nutrient load and climate on a deep, eutrophic, monomictic lake.

All the data from this research has also been made available via the Environmental Information Data Centre (EIDC). The data has been published in four sections relating to the four studies outlined above and are available at:

Study 1 – Organic carbon burial calculation using sediment trap and sediment core records from Rostherne Mere, Cheshire, UK (1360-2016). DOI: 10.5285/8616c1a0-6c6d-441c-9b10-8464dc4ee346

Study 2 – Lake and catchment nutrient, ecology and hydrology monitoring of Rostherne Mere, Cheshire, UK (2016-2017). DOI: 10.5285/5c6b2bcb-6b10-4c57-a595-ce94a655e709

Study 3 – Sediment trap diatom assemblages from Rostherne Mere, Cheshire, UK (2004-2017). DOI: 10.5285/16f52064-a19d-4cf5-a388-aff04a592179

Study 4 – Potential future scenarios of nutrient and climate change using the model PROTECH at Rostherne Mere, Cheshire, UK (2016-2100). DOI: 10.5285/2f0eae1c-1512-4823-9cbe-cb54f05ee996

Alan Daniel Radbourne
Loughborough, April 2018

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I thank my parents who have shown me unwavering support throughout, despite it being some of the most challenging years of their lives.

To my supervisors, David Ryves and John Anderson, I offer my deepest gratitude. Thank you for always pushing me to improve my work, challenging me when you thought it could be better and releasing me to work in a way that best suits my strengths.

Thanks, go to Alex Elliott and Stephen Maberly at the Centre for Ecology and Hydrology in Lancaster for agreeing to work with me for a part of my research.

Many thanks to Rupert Randall and Natural England for allowing access to Rostherne Mere to complete my research. I have very much come to love standing by the boat house looking out over the lake, contemplating the mysteries beneath.

I thank CENTA for your support financially as well as through the wide range of training opportunities I was a part of.

Finally, I thank the Department of Geography at Loughborough University and all my colleagues there. Thank you for all the support you have provided, whether in the office, labs (special thanks here to Richard and Rebecca) or out on fieldwork. There are too many good friends here to mention, so I just say thanks to you all.

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1. Introduction

1.1. Background to study

Despite covering only a small portion of the earth's land surface (~3.7%; Verpoorter et al., 2014), lakes have a key role in earth surface processes. Located at the key interface of terrestrial nutrient exchange (Carpenter, 2005, Smith et al., 2006), they are sites of great physical, hydrological, chemical and ecological diversity (Wetzel, 2001). Due their capacity to respond rapidly to external change and their position within the landscape, lakes are recognised as (i) integrators of past change through the archival burial of environmental and ecological proxies into their profundal sediment; (ii) regulators of current change through the rapid limnological and ecosystem adjustment; and (iii) sentinels of future change from both climatological and anthropogenic impacts (Williamson et al., 2009b). Therefore, the study of lake systems provides an opportunity for the assessment of the past, present and future of the natural environment.

Lake eutrophication and management recovery

Wetzel (2001) provides a popular definition of eutrophication, being; aquatic systems that are enriched with nutrients and dominated by primary production. In many freshwater systems nutrient loading has caused significant change in ecosystem functioning (Sas, 1989), with many lowland freshwater catchments becoming eutrophic through the influence of anthropogenic nutrient enrichment, from activities such as agriculture, industry and waste water disposal (Jeppesen et al., 2005, Smith et al., 2006, Anderson et al., 2014). Biodiversity loss, ecological change and water treatment difficulties are some of the considerable environmental problems associated with eutrophication (Smith et al., 1999, Pretty et al., 2003), resulting in the legislative requirement within Europe for the ecological restoration of inland waters under the European Union Water Framework Directive (WFD, 2014), making the alleviation of eutrophication not only an important environmental requirement, yet also potentially politically sensitive and a costly process (Pretty et al., 2003).

As a result, many lakes have undergone catchment-scale management intervention to limit nutrient load and reduce lake nutrient concentrations (Schindler, 2006, Zamparas and Zacharias, 2014). The approach for restoring lakes has long rested on

the simple paradigm that a reduction of nutrient loading will, to an extent, create a solution to the problem of eutrophication (Moss et al., 2005, Kalff, 2002). While such management interventions have improved ecological condition in some lakes (Jeppesen et al., 2005, Sondergaard et al., 2005), many deep stratifying lakes have only witnessed a slow recovery, with plankton and nutrient biogeochemistry affected by stratification cycles, often due to the internal loading of soluble reactive phosphorus (SRP) derived from historic SRP inputs stored within the upper sediment (Schindler, 2006, Jarvie et al., 2013a). The process of internal legacy sediment loading, especially when in anoxic conditions, replenishes the water column with nutrients through the liberation of organic-bound compounds via the mineralisation of organic matter (OM), fuelling further primary production (Gale et al., 1992, Thomsen et al., 2004). A delayed recovery response following catchment intervention can cause great difficulties for the management practitioner, because intervention practices have often required a catchment wide approach to restricting some practices of agriculture and industry. Consequently, the importance of providing evidenced support for the intervention and ensuring continued management is enacted in the best way possible is significant both financially and practically. Thus, long-term (i.e. year to decadal) monitoring of nutrient change and ecological recovery is of great importance for informing the management debate of sustainable interventions and appropriate target setting, ensuring the expectation of recovery trajectory and timing meets the various political, financial and environmental demands.

The role of lakes in the organic carbon cycle

Conversely, it has recently been considered that while the negative effects of nutrient enrichment are considerable, with most ecosystem services being impaired with eutrophication (i.e. biodiversity, ecological resilience to drivers), the enhanced organic carbon (OC) sequestration as a function of increased lake productivity provides a positive aspect to the problem, with eutrophic lakes sequestering more OC now than at any other time in their history (Anderson et al., 2014).

The rate at which carbon is mineralised increases as primary productivity increases (Thunell et al., 2000). Dissolved organic carbon (DOC) is a key parameter in lakes that can affect numerous features, including microbial metabolism, light climate, acidity, and primary production (Sobek et al., 2009). The classical Redfield et al. (1963) ratio

of C106 : N16 : P1 is a cornerstone of biogeochemistry (Sterner et al., 2008), and it is often assumed that the C:P ratio of the seston in lakes corresponds to this ideal number. However, research has shown this C:P ratio does deviate systematically from this value (Gachter and Bloesch, 1985, Hecky et al., 1993, Sterner et al., 2008). Seasonal variations of nutrient uptake and release will result in variations in the actual C:P ratio. For example, summer algal production is limited by P supply depletion, whereas in winter P is available in abundance, yet production is limited by light (Gachter and Bloesch, 1985).

Lakes are increasingly recognised as extremely important sites for the transport, transformation and storage of considerable amounts of terrestrial carbon (Cole et al., 2007). Of the OC that is being transferred down the water column to the bottom sediment of a lake, a portion will undergo intense mineralization emitting significant amounts of CO₂ and potentially CH₄ into the atmosphere (Fahrner et al., 2008) and the remainder will be buried, removing C from the active cycling pools over geological timescales (i.e. 10³ – 10⁵ years). Estimates of global C burial are between 0.02 to 0.07 Pg C yr⁻¹, with most lakes burying between 4.5 - 14 g C m⁻² yr⁻¹ (Tranvik et al., 2009), although such estimates have not been corrected for the effects of sediment focusing which will lead to over-estimation of C burial when up-scaled (by ~45%; Anderson et al., 2014).

The lake OC burial efficiency debate has recently received considerable attention. Generalised as the ratio between OC burial and gross OC sedimentation (Sobek et al., 2009), the OC burial efficiency rate has rested on the paradigm that productivity (i.e. gross OC sedimentation) is generally assumed constant over time with an array of factors driving OC preservation within lakes. Some drivers of OC preservation are well established, such as the influence of anoxic hypolimnion control reducing the OC decomposition rate with a shorter oxygen exposure time (Laskov et al., 2002, Sobek et al., 2014). Other factors known to be important are still to be fully prescribed, for instance the influence of temperature on decomposition rates, especially when applied to future warmer climate scenarios (Sobek et al., 2009, Gudas et al., 2010). Organic carbon source (i.e. structural type) is also recognised as a potential driver of OC burial efficiency, with autochthonous OC previously been regarded as labile compared to assumed typically refractory allochthonous (terrestrial) OC. The study conducted by

Sobek et al. (2009) found lakes dominated by allochthonous inputs had a mean burial efficiency of 66%, whereas lakes dominated by autochthonous sediment had a mean burial efficiency of only 22%, leading to the assumption that autochthonous sediments are more labile and as such lakes dominated by autochthonous primary production will have a lower burial efficiency. However, the importance of this terrestrial OC supply vs. in-lake primary production within a eutrophic system dominated by autochthonous production is still uncertain, as previous studies have tended to focus on comparisons between the lability of different sources. Other drivers, such as basin morphometry influencing the OC storage potential (Ferland et al., 2012), adjusting seston and DOC settling rates (von Wachenfeldt et al., 2008), and sorption onto mineral surfaces with increased potential for decomposition (Maerki et al., 2006), have all been shown to have some importance for OC burial efficiency, yet this has to date only been applied on an individual lake basis, rather than larger (regional or global) scale.

While the factors driving OC preservation are of great importance in the OC burial efficiency debate, the traditional approach to lake OC primary production being at a steady state in all systems is outdated, as many culturally impacted lakes are in a non-steady state (i.e. inputs of OC, whether terrestrial or aquatic, have changed over time), through increasing OC burial rates attributed to the onset of lake eutrophication driving increasing aquatic primary production of autochthonous, labile OC (Anderson et al., 2014). Therefore, the changing state of such impacted lake systems (e.g. where production changes substantially on relatively short timescales of 10^0 - 10^1 yr), must play a major role in the fate of OC in the lake system, rather than simply dependent only on the drivers of OC preservation for quantification of burial rates.

As has been previously mentioned, lake systems can be an effective sink of terrestrial (allochthonous) and autochthonous OC, burying OC in their bottom sediments over geological timescales (i.e. 10^3 - 10^5 years). The sequestration of autochthonous OC in lake sediments is a function of both production and decomposition, and recently, there has been considerable focus on quantifying burial efficiency to estimate the global role of lakes for removing OC from the active carbon cycling pools (Tranvik et al., 2009). Various approaches to calculating burial efficiency have been proposed (Alin and Johnson, 2007a, Sobek et al., 2014). While burial efficiency is the ratio

between OC burial and OC gross sedimentation, there is debate as to where in the process of OC production, transport and deposition the OC sedimentation and burial should be measured (Sobek et al., 2009).

Sobek et al. (2014) calculates OC burial as the mean OC mass accumulation of sediments between 25 and 150 years in age, stating sediments <25 years in age are unsuitable due to continued diagenesis. However, for lakes that are becoming more or less eutrophic (e.g. undergoing oligotrophic recovery from recent cultural eutrophication) this method will result in a poor representation of the OC mass accumulation rate as it may use data that will predate the onset of eutrophication, or recovery from eutrophication (oligotrophication), leading to a potentially significant underestimation. Alternatively, Alin and Johnson (2007a) calculates the mean OC mass accumulation from sediments between 10-25 years in age. Arguably, this more recent range of sediment age, according to Sobek et al. (2014), will fall within the timeframe of continued diagenesis. Yet, other studies have shown diagenesis to slow from ~5 years, essentially stopping by ~10 years (Galman et al., 2008) providing support for the selection of the 10-25 year sediment age range. However, within a non-steady state system undergoing oligotrophication (or indeed increasing eutrophication), this method is also shown to be inaccurate, as the timespan of sediments used to generate the OC burial value will predate the declining OC accumulation rates, resulting in an OC gain, not loss. This highlights the imprecise nature of this OC burial calculation method in systems undergoing change.

Therefore previous methods for estimating OC burial efficiency may contain significant error when applied to lake systems with changing productivity due to the changing nature of lake trophic status. In fact this issue will not just impact a small number of lakes, it can be expected to influence many lakes that are experiencing changing productivity, whether through the influences of climate change affecting the production and inputs of OC into lakes (Sobek et al., 2009, Tranvik et al., 2009), eutrophication affecting nutrient recycling and productivity (Heathcote and Downing, 2012, Anderson et al., 2014), changes to hydrology through climate or human modifications affecting the lake water residence time and nutrient loading (Elliott and Defew, 2012, Cross et al., 2014), or oligotrophication through measures to reduce nutrient loading for ecological restoration of inland waters (Moss et al., 2005), particularly as the European

Water Framework Directive takes effect (Hering et al., 2010). Therefore, previous estimates of burial efficiency may contain substantial error, especially those that have been applied to global upscaling models. An improved method for estimating burial efficiency in non-steady state systems is therefore required for the application to modelled predictions of future change.

Climate as a driver of lake change

The environmental impact of climate change is increasingly becoming a priority for scientific research across the world, with future projections of UK annual average climatic warming of air temperatures rising by +1.4 °C from 2020 to 2060 and +3.4 °C from 2020 to 2100 (UKCP09 projections; Murphy et al., 2009), causing substantial effects on the entire environmental life cycle (i.e. ecosystem functioning, phenology) across the UK. Increasingly, climate change has been recognised as having a substantial impact on lake structure and function globally (Paerl and Huisman, 2008, Tranvik et al., 2009, Williamson et al., 2009b), with long-term incremental increase of air temperature being shown to influence lake thermal structure (Gauthier et al., 2014, Liu et al., 2014) and the timing of stratification (Meis et al., 2009, Izmet'eva et al., 2016). Adjustments in the physical forcing of a lake can cause large changes in lake system functioning because much of the ecological organisation and nutrient cycling relies on the interconnected relationship to physical cycling and thermal oscillations, causing both progressive (Titze and Austin, 2014, Zhang et al., 2014) and sudden shifts (Graham and Vinebrooke, 2009, Austin and Allen, 2011) in the lake ecological system. Abrupt ecological regime shifts are increasingly being used to describe changes in the environment. Theory suggests these shifts can occur either following an abrupt environmental forcing (extrinsic regime shift) or as a response to local-scale thresholds being breached (intrinsic regime shift) (Seddon et al., 2014).

Furthermore, climate change has been linked to the increasing frequency of climatological and meteorological extremes through the shorter-term impact of heatwaves, droughts and flooding, which in isolation can greatly affect the hydrological balance and ecological structure in many lake systems (Bakker and Hilt, 2016, Bertani et al., 2016, Wigdahl-Perry et al., 2016). Despite perturbations often being short lived, the projected increase in frequency and magnitude has the potential to cause substantial adjustments in a lake system, causing shifts in the planktonic ecological

organisation through altered hydrological, thermal, nutrient and chemical structure and availability (Hausmann and Pienitz, 2007, Meis et al., 2009, Kirilova et al., 2011, Elliott, 2012b).

Thus, if future projections of UK climatic warming come to pass (UKCP09 projections; Murphy et al., 2009) there are likely to be substantial effects on lakes across the UK. However, the precise direction and magnitude of change is uncertain since multiple stressors may interact in synergistic, antagonistic or additive ways (Coors and De Meester, 2008). Therefore, understanding of how both progressive and short-term perturbations impact the physical structure and ecological assemblages is of upmost importance to determine how future change is likely to impact the lake system and suggestively how this may support or delay management recovery trajectories and targets. The UK Lake Ecological Observatory Network (UKLEON) project buoy located on Rostherne Mere, being one of 11 host sites across the UK, provides an excellent opportunity to assess these changes both at an individual lake and national perspective, underlining the importance Rostherne Mere is an important site for freshwater ecological research in the UK.

Assessing change using the diatom assemblage

To assess ecological change over the long and short term, the study of lake sediments (both in sediment cores and sediment traps) is of great value due to their capability to accumulate and preserve large quantities of high quality ecological and chemical information (Anderson and Battarbee, 1994, Hall and Smol, 1999). Diatoms are a significant component of algal assemblages in freshwater lakes (Hall and Smol, 1999), containing a considerable fraction of total algal biomass across a broad spectrum of lake trophic status (Smol and Stoermer, 2010). Therefore, within sediments diatom records can be analysed to assist an examination of a number of ecological stressors such as acidification, climate change and eutrophication in aquatic ecosystems (Hadley et al., 2010). Assessment of the diatom assemblages in a sediment core can act as a paleoenvironmental archive for long-term environmental change beyond the historical record (Hadley et al., 2010). Whereas, the use of sediment traps enables the contemporary high-resolution assessment of seasonal downward settling diatom flux (Kulbe et al., 2006). Diatoms are photoautotrophic organisms, influenced by the availability of environmental resources such as nutrients and light (Tilman et al., 1982,

Gevrey et al., 2004), making them ideal biological indicators with many ecologically sensitive species (Stoermer and Smol, 1999). Due to the silica construction of diatom cell walls they are well preserved in most lakes (Ryves et al., 2006) and so are a useful tool to quantify ecological change as a result of eutrophication and any subsequent recovery (Hall and Smol, 1999). There are a great number of freshwater diatom taxa with no accurate estimate for the number of species as annually more are discovered (Smol and Stoermer, 2010), with different taxon recognised by their siliceous cell wall structure (Adler et al., 2010). However, with recent developments in eDNA approaches (Apotheloz-Perret-Gentil et al., 2017, Rivera et al., 2017), it is suggested the number of genetically different taxa could be an order of magnitude larger than that known through morphological analysis, as it is not limited by the variances that can be distinguished under a microscope (Stoof-Leichsenring et al., 2015, Van den Wyngaert et al., 2015, Chen and Ryneerson, 2016). Although it can be a time costly process, an accurate taxon count can provide key information for past and present water ecology as each taxon has a highly reliable optimum level of nutrient availability to bloom (Reavie et al., 1995), which in turn can have vital implications for other components of the aquatic ecosystem (Lewin, 1990). Diatom analysis has the capability to map long-term ecological change to employ in the increasingly important model of restoring a natural ecological balance (Moss et al., 2005).

Disentangling nutrients and climate as drivers of lake change

As climate (i.e. annual and seasonal variations in; temperature, precipitation, wind, humidity, cloud cover, etc.) and nutrients have individually been shown to have a potentially great impact on lake systems, together therefore they can be expected to result in major change. Yet, an appreciation of how the two drivers will interact, if they will work in tandem or opposition, is still unclear, with research into attempting to disentangle the implications only recently begun (Thackeray et al., 2008, Battarbee et al., 2012, Flaim et al., 2016). Additionally, these interactions are further complicated by variations in lake parameters, such as morphology, history and current ecological condition, making the task a challenging issue.

Freshwater lakes that have a long and detailed history of measuring the impact of anthropogenic eutrophication in freshwaters are extremely rare but recognised now as key sites for research into developing a greater understanding of how our changing

climate will influence lake systems. The rich historical understanding of nutrient impacts provides a trajectory that can be unpicked from any new trend of change likely caused by climate. However, it must also be considered that lakes that have undergone eutrophication and those who have a reduced biodiversity may have become progressively more sensitive to change with a loss of resilience (Scheffer et al., 2001), meaning further progressive or sudden extreme perturbation from either nutrients or climate could result in rapid changes in limnological and ecosystem state (Ruhland et al., 2015, Bertani et al., 2016, Yamoah et al., 2016).

Therefore, disentangling the key driving forces of lake change, be it from nutrients, climate or both, is vitally important as lake management plans are developed to plot the likely future trajectories of lake change in a variety of possible future scenarios. This information then can be used to implement further remedial management if necessary, in order to avert or minimise damaging, and possibly irreversible, ecosystem change that may be seen too late if responding reactively, even in a well monitored system.

1.2. Study objectives

The objective of this thesis is to:

Disentangle the impact of nutrients and climatic forcing as key drivers of change in deep eutrophic lakes in the UK.

The project focused specifically on Rostherne Mere, Cheshire, UK, assessing the driving force(s) behind the trajectories of ecological and limnological change in the past, present and future. To do this, four independent studies were conducted, assessing different proxies and timeframes of change, with the overarching synthesis connecting the four studies together to answer the research objective.

Each individual study had a specific research aim that went some way to support the overall study objective. These were:

Study 1: How has the history of nutrient enrichment impacted the organic carbon burial rate?

Many studies have viewed lakes as quasi-static systems with regard to the rate of organic carbon (OC) burial, assuming that the dominant control on burial efficiency (BE) is sediment mineralisation. However, in systems undergoing recent eutrophication or oligotrophication (i.e. altered nutrient loading), or climatic forcing, the changes in primary production will vary on both longer (>10 years) and shorter (seasonal) timescales, influencing the rate of OC accumulation and subsequent permanent burial.

Here, consideration of the extent to which permanent OC burial reflects changing production in a deep monomictic lake (Rostherne Mere, UK) that has a long history of cultural eutrophication (present annual average TP >200 $\mu\text{g L}^{-1}$), but has undergone recent reductions in nutrient loading over the last ~25 years. Comparison of multi-year dynamics of OC fluxes using sediment traps to longer-term burial rates was carried out using two ^{210}Pb -dated sediment cores. Assessment of autochthonous OC preservation is considered for the implications it may have upon the method for calculating BE for lakes which have undergone changes in primary productivity in recent decades, especially those responding dynamically to recent human impact and climate change.

Study 2: How has sewage treatment work diversion in 1991 driven the reduced nutrient load trajectory?

Understanding reduced nutrient load pathways of nutrient-impacted lowland freshwater systems is of great ecological and cultural impact and has economic implications for remediation. Thus, gaining a greater insight into how lakes respond to reduced nutrient loads and physical limnological cycling of available nutrients is vitally important for ecosystem and resource management.

This study re-examined the recovery status of a hypereutrophic freshwater lake (Rostherne Mere, Cheshire, UK) 25 years after sewage effluent diversion. Using newly collected (2016) nutrient and phytoplankton data and high resolution (5 minutely) hydrological monitoring of lake inflow and outflow, a nutrient budget for phosphorus (P) and catchment dissolved inorganic nitrogen (DIN) loading in the contemporary lake system is compared to previous budgets from 1990-2002, and assessment is made of the key drivers of recovery to inform debates on long-term lake management.

Study 3: How have climate perturbations modulated planktonic diatom communities and phenology during the reduced nutrient load trajectory?

Climate change and extreme meteorological perturbations are having an important impact on lake environments, driving long (inter-annual) and short (seasonal) term physical and ecological change.

This study utilises 6 years (2011-2016) of high resolution (2-4 week) sediment trap diatom data, lake physical data and regional climate data, to assess the stability and change of the seasonal diatom assemblage at Rostherne Mere, Cheshire, UK, a deep (30 m), seasonally stratifying, eutrophic ($>200 \mu\text{g TP L}^{-1}$) lake, following meteorological and climatological perturbation.

Study 4: What do the future possible nutrient and climate scenarios hold for Rostherne Mere?

Nutrient availability and climate have long been known to have substantial effects on the structure and function of lakes. With predicted changes to climate (particularly temperature) over the 21st century across the UK, and changes in nutrient loading, there is an increasing necessity to disentangle the effects of these two drivers on lakes.

This study uses monitoring of in-lake and catchment nutrient concentrations at Rostherne Mere over 1 year, to validate a lake biophysical model (PROTECH) which was then applied to assess the effect of future nutrient loading and climate change on the lake in a factorial modelling experiment. Future possible scenarios of adjustments in internal nutrient load, external nutrient load and a changing climate (air temperature) are assessed for the concentration of phosphorus and chlorophyll *a* for cyanobacterial blooms, and adjustments in the altering timing, depth and length of lake stratification.

Thesis synthesis

The thesis synthesis draws together the conclusions from each of the four studies (as described in the flow diagram below, Fig. 1.1.) to answer the major study objective for application to other deep, eutrophic temperate lake systems.

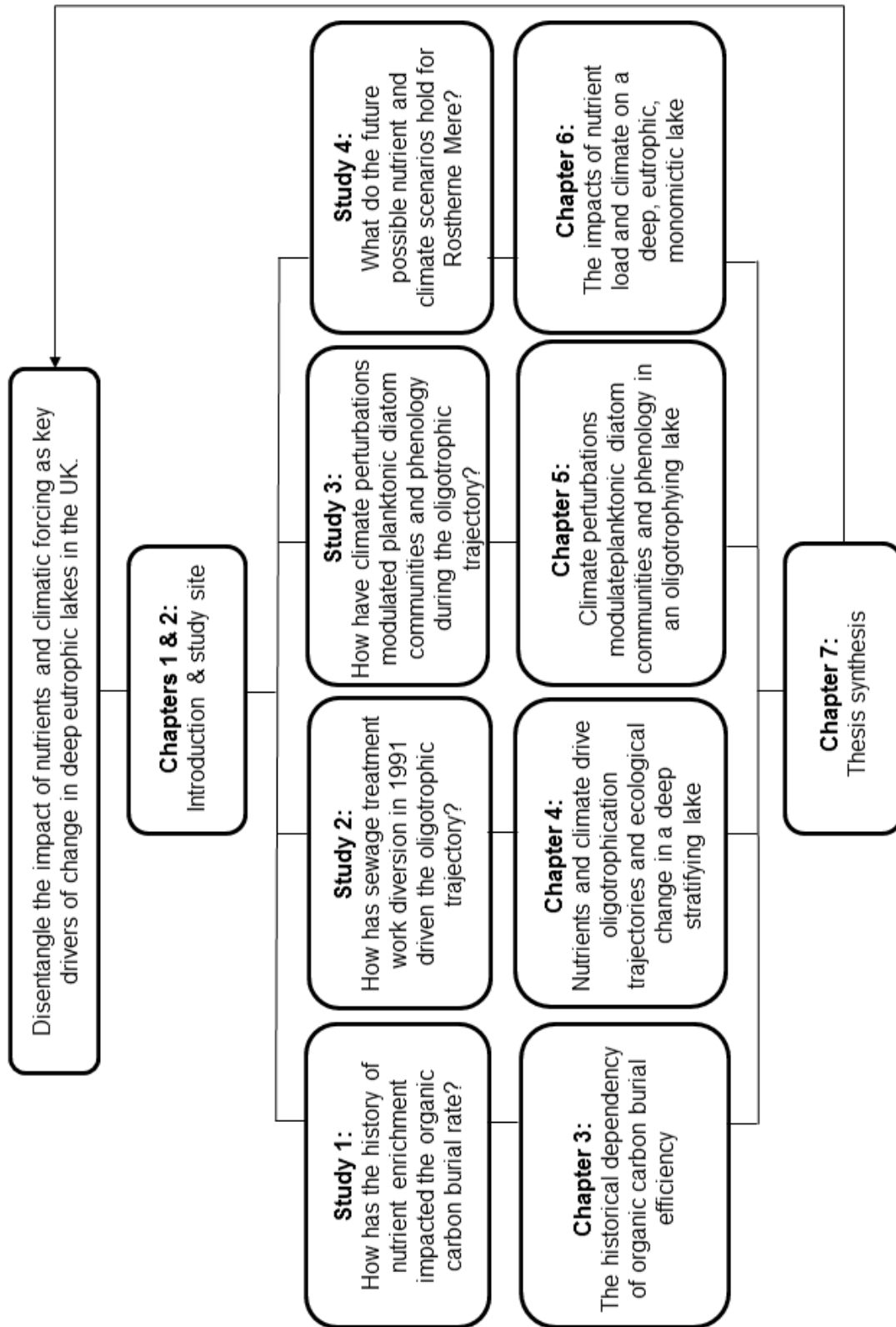


Figure 1.1.1. Flow diagram outlining thesis structure, research aims and individual studies.

2. Study site

Rostherne Mere (53° 20'N, 2° 24'W; Fig. 2.1.) is located in the north-west of England in the county of Cheshire, approximately 6 km from the town of Knutsford and 7 km from Manchester International Airport, on the edge of the small village of Rostherne. Rostherne Mere is part of the Cheshire and Shropshire Meres, a group of more than 60 freshwater lakes that lie on the glacial geology of the Cheshire-Shropshire Plain. Their varied size, morphometry and nutrient status have made the group of lakes popular with researchers, with a comprehensive review of the meres being conducted by Reynolds (1979).

Rostherne Mere is the deepest (maximum depth ~31 m; mean depth 13.6 m) and one of the largest (surface area of 48.7 ha; water volume of $6.8 \times 10^6 \text{ m}^3$) of the Cheshire and Shropshire Meres. Situated as the last of a chain of three meres lying sequentially along a single stream, draining a small catchment (940 ha) of agricultural, urban and parkland (Carvalho et al., 1995). Having a kettle basin morphometry, with one significant inflowing stream from the upstream Little Mere, numerous other small spring and groundwater-fed inflows and a single surface outflow, the water retention time is ~0.8 years (this study), with previous lower-resolution estimates of 1.6 - 2.4 years (Moss et al., 2005). A monomictic lake, Rostherne Mere stratifies annually with a long, stable summer stratification (thermocline average depth March to November ~10 m) and an anoxic hypolimnion developing as a result of organic matter decomposition rapidly utilising the oxygen in the lower water column within 1 month (Scott, 2014). The epilimnion, however, remains well oxygenated throughout stratification and nutrient dynamics are mainly influenced by biological uptake, replenishment from inflows and entrainment of hypolimnetic waters during periods of windy weather (Krivtsov et al., 2001), and overturn in late autumn.

Designated a Site of Special Scientific Interest, National Nature Reserve and Ramsar site due to protected bird roosting sites, Rostherne Mere is of great ecological value to the national natural environment and as such has been studied with much vigour for over a century (Tattersall and Coward, 1914, Pearsall, 1923, Lind, 1944). The lake has been hypereutrophic since the 1970s (defined as $>100 \mu\text{g P L}^{-1}$; Carlson, 1977), largely due to anthropogenic P loading from two catchment sewage treatment works (STW) that became overwhelmed by a growing surrounding population from the

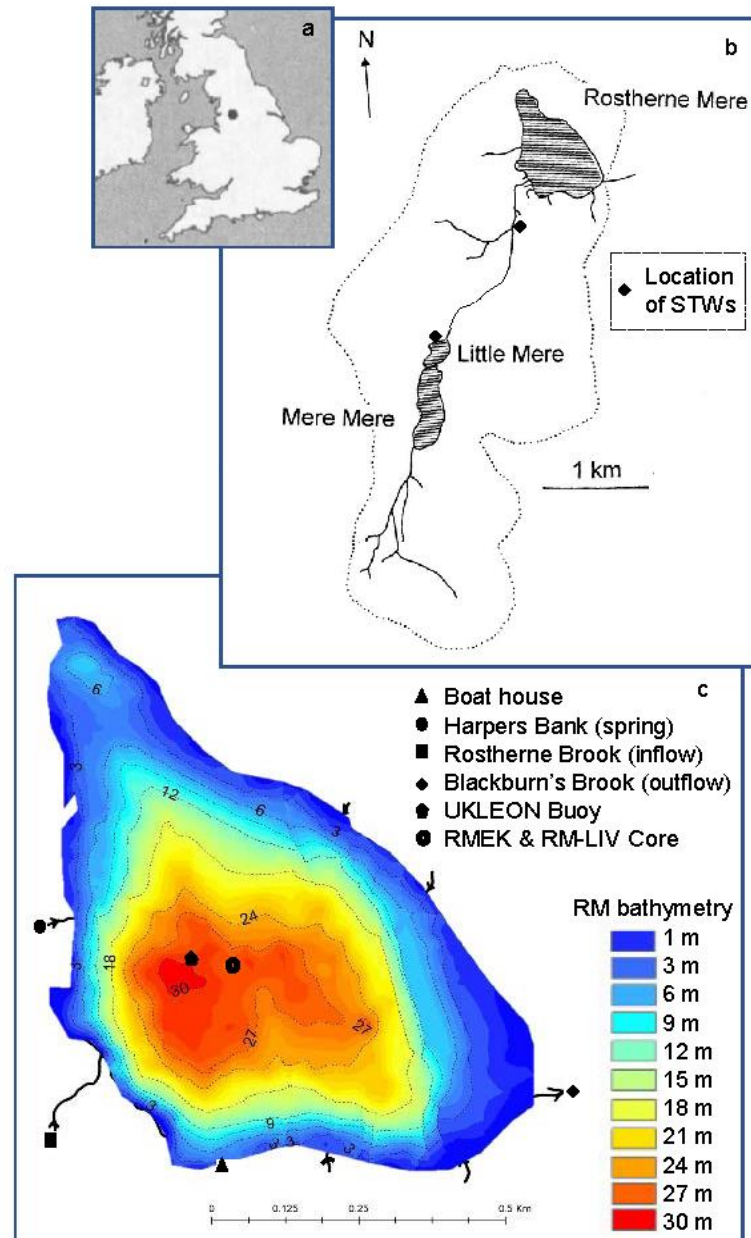


Figure 2.1. Location in UK (a), catchment map (b; adapted from Moss et al., 2005) and bathymetric map of Rostherne Mere with sample sites labelled (c; adapted from Scott, 2014).

1930s, leading to a particular renewal of scientific interest following the diversion of the STW in June 1991 with catchment restoration management efforts starting in earnest (Carvalho et al., 1995).

More recently, despite the removal of point-source sewage effluent, the lake is still hyper-eutrophic with high levels of P mobilised from the sediments below the anoxic hypolimnion, causing substantial internal loading and limiting the rate of ecological

recovery (Moss et al., 2005). Lake net primary production is high (NEP $\sim 130 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 2011-12 with individual algal blooms $>20 \text{ g m}^{-2}$ dry weight; Reynolds, 1979, Scott, 2014) with planktonic diatom blooms typically in spring and autumn, and a dominance of cyanobacteria in summer (Livingstone and Cambray, 1978, Livingstone and Reynolds, 1981, Moss et al., 2005). Submerged aquatic plant species diversity today is very low and in littoral areas $<1 \text{ m}$ deep dominated by *Callitriche hermaphrodita*. Lake margins are dominated by a narrow band of *Phragmites australis* with some *Typha angustifolia*, behind which is *Salix* scrub and alder carr (*Alnus glutinosa*) with areas of relatively species-rich wetland vegetation (G. Madgwick, pers. comm.). Since 2010, an automated water quality monitoring station has been located at a central buoy, being part of the UK Lake Ecological Observatory Network (UKLEON) project (see <https://www.ceh.ac.uk/our-science/projects/uk-lake-ecological-observatory-network-ukleon>).



Figure 2.2. Images of Rostherne Mere. Left: The UKLEON monitoring buoy (upgraded in 2014). Top right: Looking out over Rostherne Mere from the boat house. Bottom right: The automated sediment traps ready for re-deployment in the deeper part of the lake at two depths (10 m and 25 m), anchored by bricks and kept afloat by a couple of large buoys.

3. The historical dependency of organic carbon burial efficiency

3.1. Introduction

Despite covering only a small portion of the earth's land surface (~3.7%; Verpoorter et al., 2014), lakes are now recognised as key sites for the transformation and storage of considerable amounts of carbon (C) derived from either in-lake production or transfer from the catchment (Cole et al., 2007, Catalan et al., 2016). A portion of the organic carbon (OC) that settles to the bottom of a lake will be mineralised and either recycled or degassed as CO₂, or potentially undergo methanogenesis and degassed as CH₄ (Fahrner et al., 2008), and the remainder will be buried. Burial of this OC in lake sediments can be considered as removal of atmospheric or terrestrial C from the active pool over geological timescales. Estimates of global C burial by lakes are between 0.02 to 0.07 Pg C yr⁻¹, with most lakes burying between 4.5 - 14 g C m⁻² yr⁻¹ (Tranvik et al., 2009), although rates are considerably higher in agriculturally-dominated landscapes of Europe (~60 – 100 g C m⁻² yr⁻¹; Anderson et al., 2014) and North America (~7 – 554 g C m⁻² yr⁻¹; Heathcote and Downing, 2012, Anderson et al., 2013, Clow et al., 2015). Furthermore, many previous estimates based on lake sediment cores have not been corrected for the effects of sediment focusing, which will lead to overestimation when up-scaled (Buffam et al., 2011, Engstrom and Rose, 2013, Anderson et al., 2014). Clearly, understanding sedimentation processes in lakes, and the extent to which lakes preserve OC in their sediments (i.e. burial efficiency [BE]), is key to improving the accuracy of such estimates and clarifying the role of lakes in regional and global C cycling.

Approaches to estimating OC BE have received considerable attention in both limnology and oceanography (Alin and Johnson, 2007b, Sobek et al., 2009, Anderson et al., 2014) yet within limnology this attention is still sparse without much agreement on a standard method. Formalised as the ratio between the rate of OC burial and gross sedimentation at the sediment surface (Sobek et al., 2009), studies of BE have been largely concerned with the factors controlling OC preservation. Production has generally been assumed to be constant over time, a concept largely derived from the marine literature (Hedges et al., 1999, Burdige, 2007). While some drivers of OC preservation are relatively well understood, such as oxygen exposure time, with hypoxic or anoxic conditions in the hypolimnion reducing the OC decomposition rate

(Laskov et al., 2002, Sobek et al., 2014), other key factors are still to be fully constrained, for instance the influence of temperature on decomposition rates (Sobek et al., 2009, Kothawala et al., 2014). For example, while Gudas et al. (2010) have argued that warmer water temperatures result in more mineralization and reduced OC burial, Anderson et al. (2013) demonstrated little climatic effect on C burial rates across a temperature gradient in 116 Minnesotan lakes. In a study of lakes from West Greenland, Sobek et al. (2014) similarly found little effect of temperature on burial efficiency. The source and type of OC has also been recognised as a potential control of OC BE, with terrestrially-derived OC often assumed to be refractory, and autochthonous OC, labile (Sobek et al., 2009). Other drivers have also been argued to have a bearing on OC BE, such as basin morphometry (Ferland et al., 2012), changes in sunlight (Cory et al., 2014, Koehler et al., 2014, Tranvik, 2014), sediment flocculation (von Wachenfeldt et al., 2008, Sobek et al., 2009), OC molecular properties (Kellerman et al., 2015), and mineral sorption (Maerki et al., 2006).

Much of the current understanding of processes of lake OC burial (especially preservation) is based on studies from boreal lakes (Sobek et al., 2005), where production (OC input) is generally assumed to be constant in the recent past (steady-state conditions). In agricultural landscapes, long-term changes to land use intensity have led to the disruption of regional nutrient cycling with increased erosion, transportation and deposition of sediment from tilled agriculture (Clow et al., 2015), leading to the widespread development of freshwater eutrophication influencing autochthonous OC production and hence OC burial (Anderson et al., 2013, Dietz et al., 2015). While the factors controlling OC preservation are clearly important for OC BE, the implicit assumption that lake OC production is in a (quasi-) steady state in most systems is invalid, given the multiple stressors that lakes are subject to in all biomes (tropical, temperate and boreal) (Williamson et al., 2009a, Leavitt et al., 2009). Many culturally-impacted lakes are in a state of continual adjustment to increasing or decreasing nutrient loading (i.e. inputs of OC, whether terrestrial or aquatic, have changed over recent decades), and thus may influence OC burial rates together with those factors (i.e. temperature, O₂) influencing preservation.

Here, I utilise long-term (5-yr) high temporal resolution (2-4 week) sediment trap observations of OC flux in a strongly stratified, nutrient-rich lake that is recovering from cultural eutrophication (Rostherne Mere, UK), to generate estimates of OC flux to the

sediment surface at seasonal, annual, and sub-decadal scales (Douglas et al., 2002). Although traps (in the same way as sediment cores), are susceptible to focusing effects (i.e. over-trapping), trap fluxes can be corrected by comparison to monitored records of net ecosystem production (NEP) at the lake (Scott, 2014), and to contemporary OC accumulation measured from a well-dated, focusing-corrected sediment core. Furthermore, I compare the long-term high-resolution trap monitoring data to this sediment record of OC burial over the last ~150 years to examine historical patterns of OC burial and apply different methods to calculate OC BE at Rostherne Mere. Given the widespread occurrence of (seasonal) hypolimnetic anoxia among lakes globally (Kalff, 2002), Rostherne Mere provides an important test of the widely held assumption that labile OC is rapidly mineralised after sedimentation in such lakes. This distinction is critical in determining to what degree historical trends in OC burial are driven by changes to terrestrial OC supply and sedimentary OC preservation (the latter controlled by oxygen exposure time, temperature and OC lability), rather than long-term changes in autochthonous production. This study has broad implications for studies of OC BE and preservation in such dynamic, culturally-impacted lakes and other systems where direct and indirect impacts of human activity have altered autochthonous OC production and/or terrestrial OC inputs in the recent past.

3.2. Methodology

Sediment collection

Sediment trapping using both open tube and sequencing traps was carried out at Rostherne Mere from April 2010 to March 2015. Open tube sediment traps (KC Denmark, Silkeborg, Denmark; older variation of <http://www.kc-denmark.dk/products/sediment-trap-station/sediment-trap-station-oe80-mm-tubes.aspx>), comprising 4 clear plastic tubes (450 mm length/72 mm internal diameter, 1:6.3 trapping ratio, 0.016 m⁻² trapping area per 4 tubes), were deployed at 10 m and 25 m depth in the central, deepest part of the lake (~30 m). Some early tube trap collections (shallow trap April 2010 to June 2010; deep trap April 2010 to May 2011) used a funnel (to maximise absolute catch for a separate project) that resulted in a lower material capture per unit area (Bloesch and Burns, 1980). As a result, a series of calibration traps (paired traps with and without funnel) were deployed and a lake-

specific calibration factor (with:without funnel = 3.13) was calculated to correct tube trap collections on a unit area basis. Technicap PPS 4/3 automatic sequencing traps (1310 mm length/252 mm internal diameter, 1:5.1 trapping ratio, 0.05 m⁻² trapping area; <http://www.technicap.com/images/product/pps-4-3.pdf>) were also deployed at 10 m and 25 m water depths, sequentially opening into 12 individual 250 ml HDPE bottles, each representing a 2-week collection period (except in January and February longer collection periods of up to 4 weeks were used). The traps were reset every 6 months as dictated by the trapping interval used, with trap sediment kept cool, dark and sealed during transport to the laboratory where it was stored frozen prior to analysis.

A 112 cm long sediment core (RM-LIV-2011, hereafter the RML core) was collected at 26 m water depth in September 2011 using a Livingstone piston corer (Wright, 1967). The sealed core was transported vertically to the laboratory, and stored vertically in a dark cold room at 5° C, prior to extrusion at 1 cm intervals for the upper 50 cm of sediment, and then at 0.5 cm intervals for the remainder of the core.

Water column oxygen concentration and temperature were measured at 1 m intervals approximately every 3 weeks between May 2010 and April 2012 using a YSI 6600 V2 multi-parameter sonde (Scott, 2014). Hourly NEP estimates of the pelagic epilimnion at 1 m depth at the UKLEON buoy were calculated for 2011-12 by the free-oxygen method using daytime water column dissolved oxygen calculations (Odum, 1956). Precipitation data from the closest reliable Meteorological Office station (Shawbury, Shropshire, UK; situated 64 km south-west from Rostherne Mere) were utilised to generate 30-year monthly and annual means for comparison to the study period monthly and annual means. Average daily wind speed and surface water temperatures were taken from the UKLEON buoy.

Sediment analysis

All trap and core samples were freeze-dried prior to analysis. For all samples organic matter (OM) was determined using sequential loss-on-ignition, where OM was calculated by weight-loss after 3 hrs at 550°C (Dean, 1974). Percentage OC was calculated from %OM using a lake-specific conversion factor ($\%OC = \%OM \cdot 0.56$; see Appendix 1) estimated from analysis of 20 sediment samples with a range of %OM (14-65%) with total OC determined via mass-spectrometry elemental analysis.

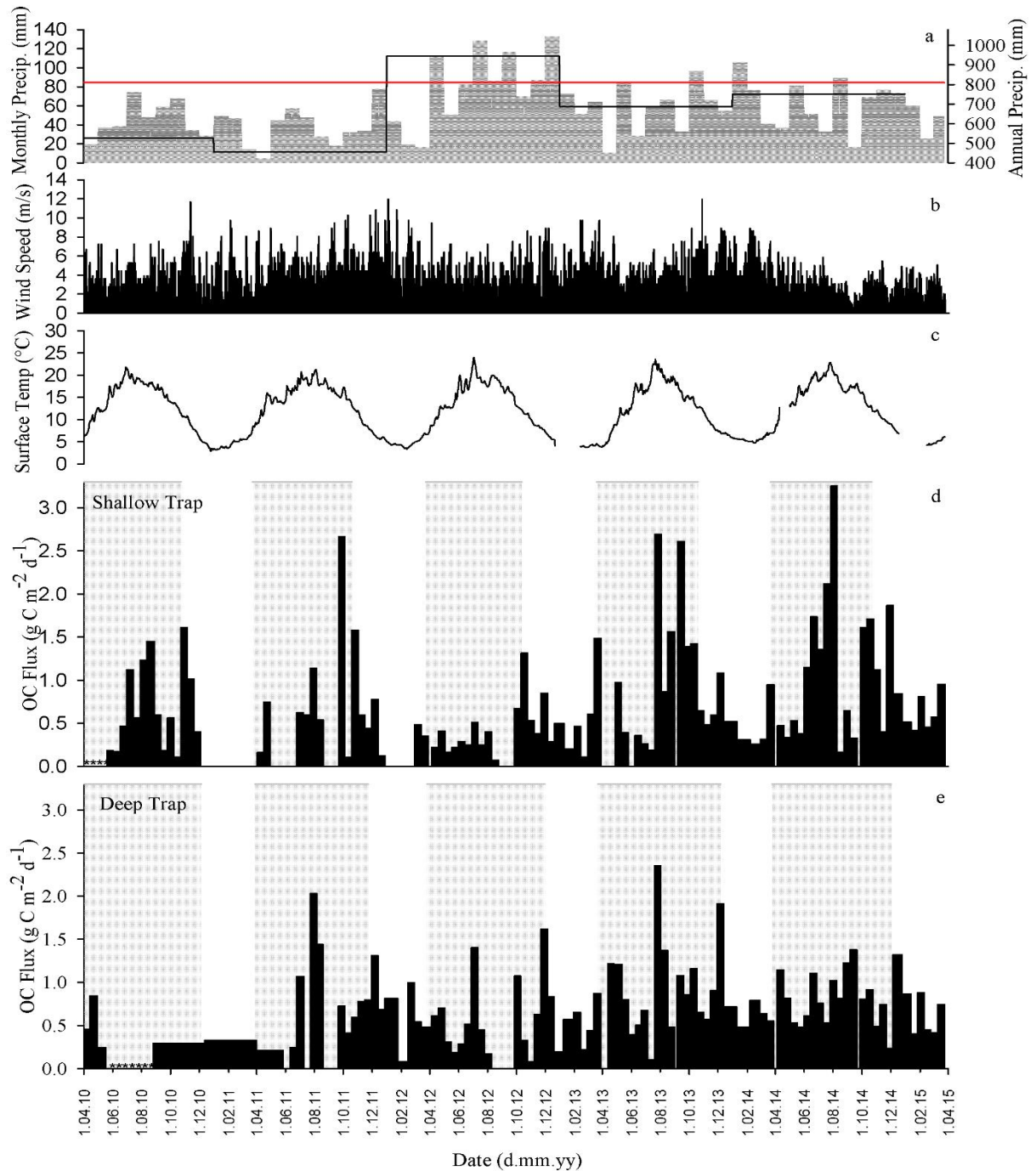


Figure 3.1. Rostherne Mere Organic carbon (OC) flux ($\text{g C m}^{-2} \text{d}^{-1}$) captured in sediment traps (uncorrected for over-trapping or mineralisation losses) at a depth of 25 m (e) and 10 m (d) overlaid with timings of stratification (grey bars stratified period) for respective depths. Daily average surface water temperature (c), daily average wind speed (b), and monthly (shaded grey area against the left y-axis) & annual total precipitation (single black line against right y-axis) with 30-year average (single red line against right y-axis) plotted (a) for comparison to changes in trapped OC flux. * = missing data.

Freeze dried and homogenised core samples were analysed via alpha spectrometry for ^{210}Pb activity to determine chronology and sediment accumulation rates according to the CRS (constant rate of supply) model with confidence intervals calculated by first-order error analysis of counting uncertainty (Appleby, 2001).

Data analysis

Preliminary analysis of the sediment trap OC flux showed a high winter sediment collection, especially in the deep (25 m) trap (Fig. 3.1d and 3.1e), despite little to no primary production during this time, as confirmed by high-resolution monitoring of NEP (Scott, 2014). Rostherne Mere has an intensely managed catchment, with restricted

Table 3.1. Uncorrected and corrected OC flux rates ($\text{g C m}^{-2} \text{yr}^{-1}$) for limnological years (1st April to 31st March) 2010-2015. Data from 1st November to 15th March have been removed to correct for over trapping of resuspended particles and a 10% trap OC mineralisation factor has been applied (see text for details). Net ecosystem production (NEP) for 2011-12 is estimated from the free-oxygen method (Scott 2014).

Year	Corrected		Uncorrected deep trap	Corrected deep trap	NEP
	Uncorrected shallow trap	shallow trap			
2010 - 11	225.15	167.69			
2011 - 12	157.72	133.74	208.52	122.56	135.6 ± 91
2012 - 13	154.09	106.81	183.00	112.98	
2013 - 14	306.14	279.78	313.39	227.01	
2014 - 15	355.61	280.58	287.93	215.36	
Total Means (2011-2015)	243.39	200.23	248.21	169.48	
Total Means (2010-2015)	239.74	193.72			

Table 3.2. Uncorrected and corrected trap OC flux ratios highlighting the changes applied with correction methods and the loss rate between sediment traps. Note the outlying 2012 ratio highlighting the impact of the annual variability from extreme meteorological behaviour.

Year	Shallow Corrected / Shallow Uncorrected	Deep Corrected / Deep Uncorrected	Deep Uncorrected / Shallow Uncorrected	Deep Corrected / Shallow Corrected
2010 - 11	0.74			
2011 - 12	0.85	0.59	1.32	0.92
2012 - 13	0.69	0.62	1.19	1.06
2013 - 14	0.91	0.72	1.02	0.81
2014 - 15	0.79	0.75	0.81	0.77
Total Means (2011-2015)	0.81	0.67	1.09	0.89
Total Means (2010-2015)	0.80			

land use and agricultural activity, so it can be assumed the terrestrial OC contribution is minimal and the NEP is the dominant OC source. Therefore, the high winter collection in the deep sediment trap implies over trapping is a significant issue within Rostherne Mere, as expected from its morphometry and stratification pattern (Hilton, 1985). Seasonal over trapping was corrected through the removal of the winter sediment collection (1st November – 15th March, as determined by comparison to the NEP analysis, i.e. the period when net production was ~0) from the calculated annual collection totals. Furthermore, a correction value of +10% was added to offset the OC loss rate in the sediment traps as a result of mineralisation in the traps themselves. The 10% correction factor is an arbitrary number taken from other similar studies that have previously suggested the figure to be a suitable correction with minimal error (Bloesch and Burns, 1980, Horppila and Nurminen, 2005). This approach was independently verified by comparison to the 2011-12 NEP (Scott, 2014) with the corrected trap fluxes fitting within the expected range of NEP values, assuming the terrestrial OC component within this study is minimal. Subsequently the corrected

values were summarised as annual totals (1st April to 31st March; Table 3.1.) and compared between years and trap depths (Table 3.2.).

Loss rates of OC in the water column were calculated by the difference between each sampling depth (NEP at ~0.5 m, traps at 10 m and 25 m; Fig. 3.2.). Both trap and core corrected data were used to calculate BE according to two published methods (Fig. 3.2.). Alin and Johnson (2007b) proposed burial efficiency (here denoted BE₂₅) as the ratio of OC burial (the mean OC mass accumulation of sediments between 10 and 25 years in age; see below) to NEP. Alternatively, Sobek et al. (2009) describes burial

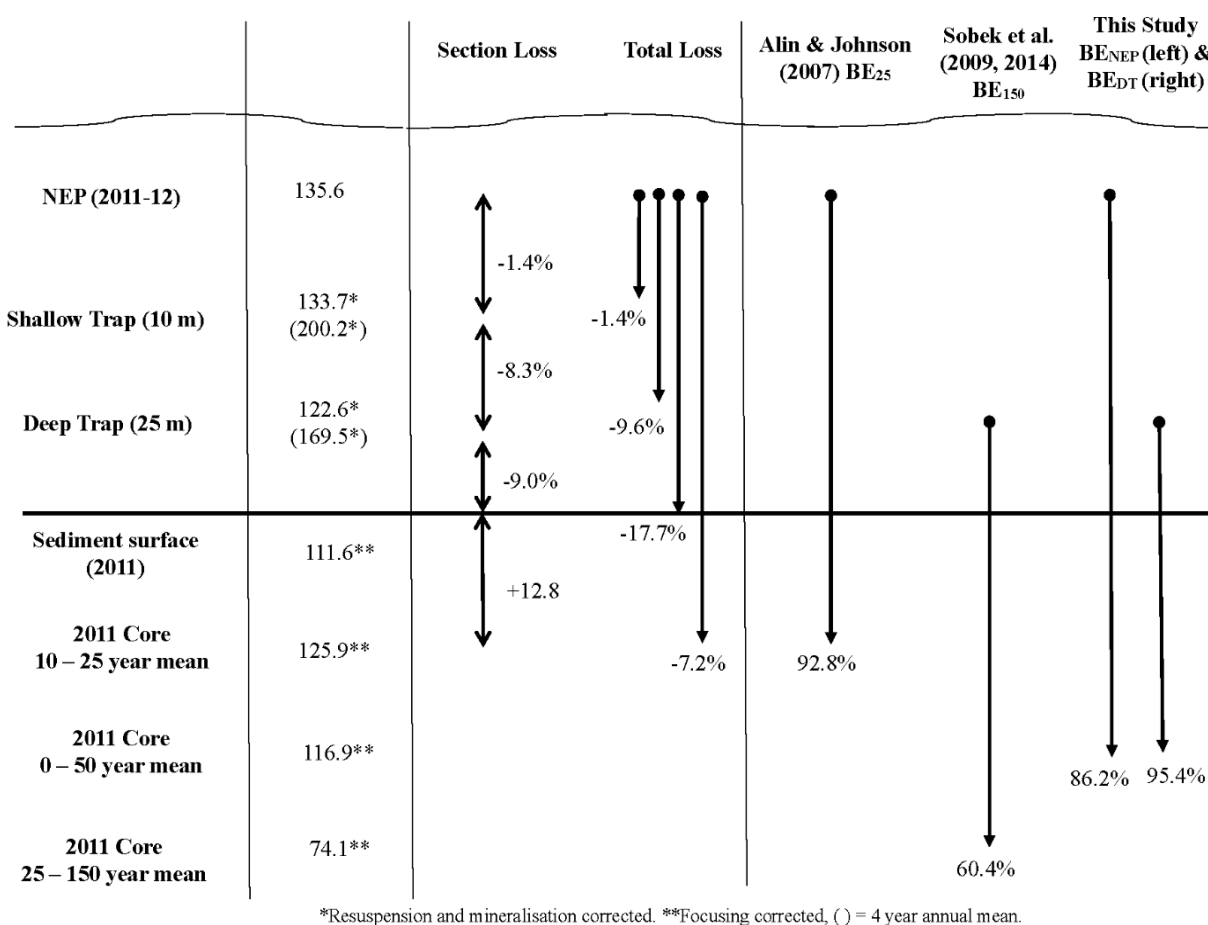


Figure 3.2. Rostherne Mere OC from NEP (2011-12), trap data (corrected 2011-12 and 4-year annual mean in brackets) and historical sediment core accumulation rate, showing the estimated losses through the water column and into the surface sediment. Various methods for calculating burial efficiency are shown (BE₂₅ [NEP to 10-25 year mean of core], Alin & Johnson 2007; BE₁₅₀ [deep trap to 25-150 year mean of core], Sobek et al. 2009; BE_{NEP} [NEP to 0-50 year mean of core], this study; BE_{DT} [deep trap to 0-50 year mean of core], this study), highlighting the difference in the methods. Values shown are g C m⁻² yr⁻¹.

efficiency (here denoted BE_{150}) as the ratio of OC burial (the mean OC mass accumulation of sediments between 25 and 150 years in age) to the OC delivery to the sediment surface (deep trap capture). The literature on calculating OCBE is sparse, with an agreement on a standard method elusive. Therefore, due to limitations found with both these methods when applied to Rostherne Mere due to its recent, and ongoing, changes in production over the timescales used in calculations of BE_{25} and BE_{150} , a revised method of calculating BE is proposed using sediments deposited over the last 50 years.

The use of sediment cores provides a long-term perspective on C burial rates. Sediment core OC accumulation rates were estimated by multiplying bulk sediment accumulation rates ($\text{g dry matter cm}^{-2}\text{yr}^{-1}$, derived from ^{210}Pb dating) by the OM% and the OM/OC conversion factor (see above) and are reported as $\text{g C m}^{-2}\text{yr}^{-1}$. Significant problems can arise with this approach for whole-basin upscaling if sediment focusing is not considered (Anderson et al., 2014), due to pelagic accumulation often overestimating whole-lake accumulation. Therefore, core sediment accumulation rates were focusing-corrected (by a factor of 0.7) using the ratio of the expected unsupported flux of ^{210}Pb (9.82 pCi cm^{-2}) to that found in the core (Anderson et al., 2013, Anderson et al., 2014). After deposition into the bottom sediments, the OC mineralisation rate slows exponentially towards zero with increasing depth below the sediment-water interface (Middelburg, 1989). Sediments younger than 5 years have the highest rate of decay, dropping dramatically after ~ 10 years (Thomsen et al., 2004, Galman et al., 2008). Therefore, the most recent 10 years of accumulation ($< 5 \text{ cm}$ sediment core depth, ^{210}Pb dated age $\sim \text{AD } 2001 \pm 2.04 \text{ yrs}$) was removed from flux calculations to avoid the influence of incomplete mineralisation (Galman et al., 2008, Heathcote et al., 2015).

For comparison to the RML core, a previous core taken from the central deepest part of Rostherne Mere in 1977 (Livingstone, 1979) using a Mackereth one metre minicorer (Mackereth, 1969) was used (hereafter referred to as the LIV77 core). A loess smoother was fitted to the LIV77 core data to reduce noise and enable clearer comparison to the RML core. Additionally, I compare the historical record of Rostherne Mere with 9 Danish lakes (all with independently dated ^{210}Pb records and focussing corrected; Anderson et al., 2014). These Danish lakes have been undergoing nutrient reduction over a similar time period to Rostherne Mere, as part of a wider national

policy to reduce nutrient loading to surface waters (Commission, 2012). A loess smoother was fitted through the aggregate Danish core data to reduce noise and highlight the trend, with a $p = 0.95$ confidence envelope calculated in R (using ggplot2 software; Wickham, 2009).

3.3. Results

During the study, total annual rainfall at Rostherne Mere (Fig. 3.4a) was below the 30-year average (study period = 676.7 mm yr⁻¹; 30-year annual mean = 810.2 mm), with the exception of 2012 where the total annual rainfall (1054.6 mm) was 30% higher than the 30-year average. This was largely due to an unusually wet summer, with a 55% higher June to September total rainfall in 2012 (413.2 mm) compared to 30-year mean (267.1 mm). Daily wind speed was variable (daily average range 0 to 11.9 m s⁻¹) with slight increases over the winter months, as expected in this location (Fig. 3.4b). Surface water temperature reflects air temperature (range ~3 to 24 °C; see Figs. 3.1a and 3.2c).

The shallow and deep trap uncorrected OC flux shows high capture is not restricted to summer, although the stratified and productive summer period commonly had higher catches than the winter and spring (Fig. 3.4d and 3.4e), with greater fluxes recorded in 2013-15 than earlier years (Table 3.1.). Despite being suspended only 15 m apart in the water column, the two traps sometimes showed large differences in individual 2-weekly catch, as observed in other multiple trap studies (Moschen et al., 2009). At times, simultaneous peaks in collection in both traps indicate rapid settling (e.g. early August 2013; Fig. 3.4d and 3.4e), while other periods are characterised by a slow downward flux of particles (e.g. August 2011 and August 2014; Fig. 3.4d and 3.4e). This variation in settling rate results in the signal in the shallow trap being blurred in the deep trap on a 2-weekly timescale (e.g. summer 2012; Fig. 3.4d and 3.4e). Across the study the uncorrected winter OC collection mean is similar between the shallow trap and deep trap (5-year average 243.4 and 248.2 g C m⁻² yr⁻¹ respectively; Table 3.1.), with the deep trap collecting more in three of the four years (2011-14; Table 3.2.). This is typical where intermittent complete mixing (ICM) dominates sedimentation processes (Hilton, 1985), resuspending unconsolidated organic matter into the water column during the mixed period. After correction for both ICM (i.e.

removing the winter collection) and a fixed 10% mineralisation loss in the collecting bottles, the shallow trap mean value was $200.2 \text{ g C m}^{-2} \text{ yr}^{-1}$, and $169.5 \text{ g C m}^{-2} \text{ yr}^{-1}$ in the deep trap over the study period (Table 3.1.). Calculated NEP from high-frequency monitoring in 2011-12 ($135.6 \text{ g C m}^{-2} \text{ yr}^{-1}$; Scott, 2014) differs by $< 5\%$ with the corrected trap catch in 2011-12 for both shallow and deep traps, supporting the approach taken to adjust trap catch here. The difference between the corrected shallow trap flux in 2011-12 ($\sim 134 \text{ g C m}^{-2} \text{ yr}^{-1}$) and the surface sediment accumulation rate (from the core collected in September 2011; $\sim 112 \text{ g C m}^{-2} \text{ yr}^{-1}$) is $22.1 \text{ g C m}^{-2} \text{ yr}^{-1}$, which is close to the C efflux as calculated from lake profile CO_2 measurements in 2011-12 ($33.5 \text{ g C m}^{-2} \text{ yr}^{-1}$; Scott, 2014). I therefore conclude that corrected trap flux is a good estimate of NEP (shallow trap) and OC delivered to the surface sediments (deep trap) for calculation of BE, assuming the terrestrial OC contribution is minimal as previously suggested.

The average OC loss through the water column in 2011-12 was 1.4% (lake surface to shallow trap at 10 m), 8.3% (shallow trap to deep trap at 25 m) and 9.0% (deep trap to surface sediment at 26 m) with about 10% of NEP lost through the water column to 25 m, and a further $\sim 8\%$ at the sediment surface (Fig. 3.2.). Using the Alin and Johnson (2007b) method comparing NEP in 2011-12 to average sediment accumulation rate from the previous 10-25 years, BE_{25} is estimated at 92.8% (Fig. 3.2.). Alternatively, the Sobek et al. (2009) method, comparing deep trap flux to average sediment accumulation rate from the previous 25-150 years, gives an estimate of BE_{150} as 60.4%, or two-thirds of the Alin and Johnson (2007b) method (Fig. 3.2.).

The burial rate from the RML core (focusing-corrected; Fig. 3.3.) shows an increase in OC burial from $24 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 1900 to $138 \text{ g C m}^{-2} \text{ yr}^{-1}$ in the late 1980s (a 7-fold increase). Both the temporal pattern and burial rates of the RML core are very similar to the focusing corrected LIV77 core (Fig. 3.3a), demonstrating the consistency of the deep water sediment archive across the lake. Small discrepancies between the two cores are likely due to differing core locations and depths (Anderson, 1990) as well as the incomplete mineralisation in the upper part of the 1977 core compared to sediments this age in the 2011 core (Fig. 3.3b). Since the 1990s, the RML core OC accumulation rate has declined to approximately $110 \text{ g C m}^{-2} \text{ yr}^{-1}$. The temporal pattern of OC burial at Rostherne Mere corresponds to the historical record of intensification

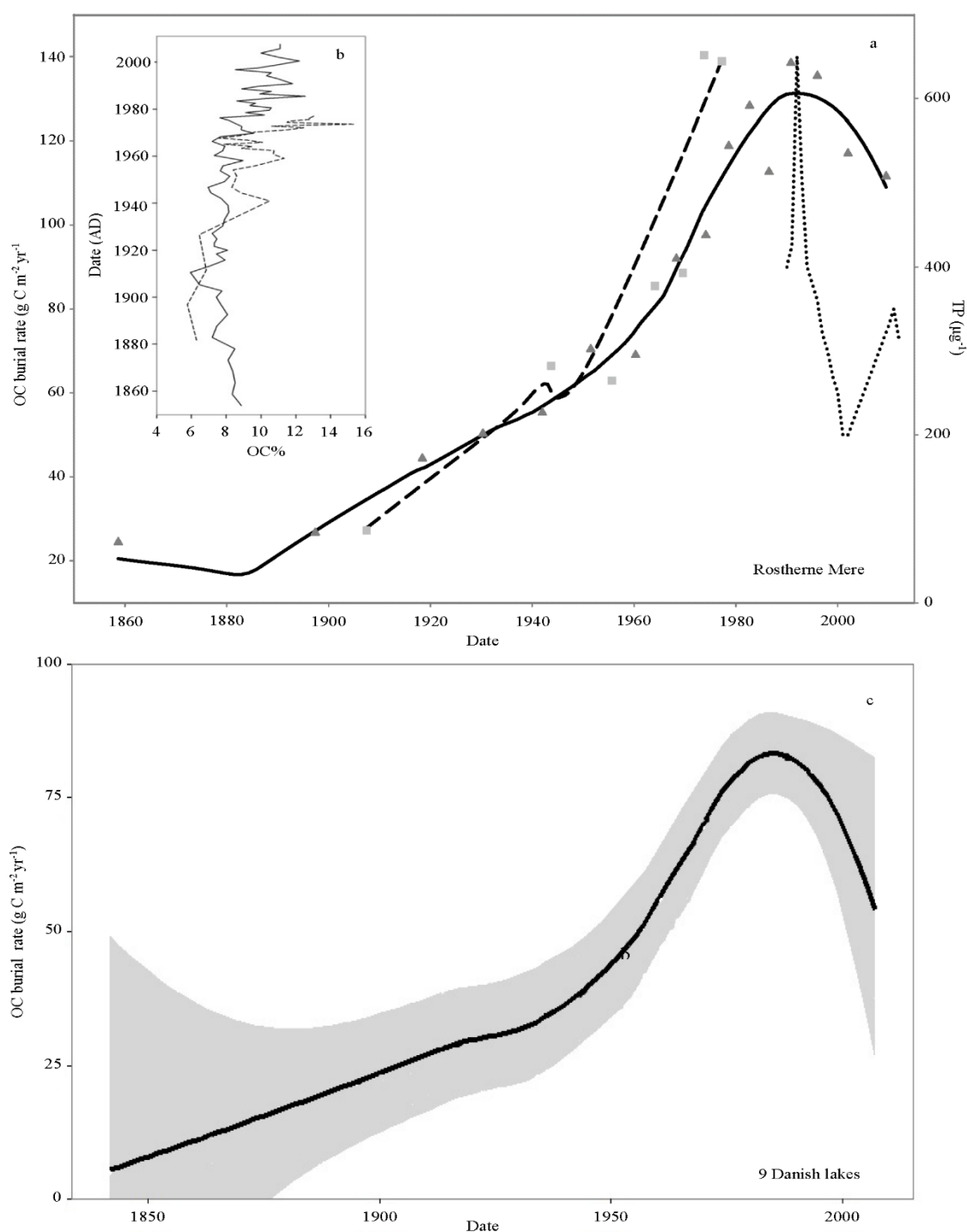


Figure 3.3. (a) Loess smoothed focusing corrected OC burial rate from core RML (solid line, dark grey triangles, collected in 2011) and LIV77 core (dashed line, light grey squares; collected in 1977), compared with mean surface water annual TP concentration (dotted line). (b) OC% down core profiles for RML (solid line) and LIV77 (dashed line) cores. (c) Aggregated sedimentary records of 9 Danish lakes over the last ~150 years showing 20th century eutrophication and oligotrophication (taken from Anderson et al., 2014). Lake records have been independently ²¹⁰Pb-dated and focussing-corrected. A loess smoother with 0.95 confidence envelope has been fitted through the data.

of eutrophication over the last century associated with sewage treatment works development, and the recent diversion of effluent from the inflowing stream in 1991, initiating a gradual recovery (Moss et al., 2005). This recent decline in sedimentary OC accumulation rate shows good agreement with the decline in the measured TP concentrations from a maximum of 400 to 600 $\mu\text{g P L}^{-1}$ at the peak of eutrophication in the late 1980s, to approximately 200 to 300 $\mu\text{g P L}^{-1}$ in recent years (Fig. 3.3a). Although the exact timing differs slightly and accumulation rates are lower, changes over the 19th and 20th centuries at Rostherne Mere (with nutrient enrichment followed by reduction) are mirrored in many Danish lakes (Fig. 3.3c) which have undergone similar experiences of human impact and recent management over the last 100-150 years. Trajectories of change in lake OC production and burial are clearly shared across industrial and post-industrial landscapes across Europe.

3.4. Discussion

Inter-annual variability in OC dynamics

Culturally impacted lakes are not only prone to longer term changes (>10 years) in OC burial potential (due to varying nutrient loading), but also show short term fluctuations on inter-annual timescales (Reynolds and Reynolds, 1985, Gibson et al., 2000). At Rostherne Mere, for example, trap fluxes were atypically low in 2012-13, only 106.81 $\text{g C m}^{-2} \text{ yr}^{-1}$ in the shallow trap, which is 50% lower compared to the mean of the other four years (Table 3.1.). Although there are several episodes of negligible trap catch over the 5-year record in either or occasionally both traps, consistently and unusually low flux was most evident during the summer of 2012, with trap catch negligible in both traps in September 2012 (Fig. 3.4d and 3.4e). The reason for this seasonal anomaly can most likely be attributed to extreme meteorological conditions. Rainfall was 66.2% higher in September 2012 (the wettest summer period for the UK since 1912) and 30.2% higher in total for the year 2012-13, compared to the 30-year average (Fig. 3.4a). The exceptional hydrological conditions of that summer will have resulted in a combination of factors limiting algal growth. Light for photosynthesis would have been reduced by greater cloud cover (Brooks and Zastrow, 2002) and increased turbidity from greater inflows of turbid flood water (mean minerogenic fraction in shallow sediment trap was 9.1% higher [56.3%] than the study period mean [47.2%]), while

reduced lake water residence time would decrease phytoplankton standing crop by outflow washout (Reynolds et al., 1982, Cross et al., 2014). Together, this would reduce total algal production in the lake, and hence reduce OC burial potential.

In recent years (2013-15), the sediment trap total collections have shown an increase in total yield (Table 3.1.), aligning to an increase in TP levels (Fig. 3.3a) and the impact of climatic variability mentioned previously. This rise suggests a short-term increase in production despite a longer-term trend to oligotrophication and recovery. These seasonal and inter-annual fluctuations highlight the importance of combining trap and sediment core studies allowing the variability in OC dynamics (production, sedimentation and burial) to be assessed across a range of temporal scales, from seasonal to decadal, and emphasise the benefits of sediment trap studies that last more than one limnological cycle (Kulbe et al., 2006, Moschen et al., 2006).

Preservation controls on OC burial efficiency

Rostherne Mere is very efficient at storing OC, with an estimated BE of between 60 – 93%, as calculated using the Sobek et al. (2009) and Alin and Johnson (2007b) methods, respectively (BE_{150} and BE_{25} ; Fig. 3.2.). This falls within the upper end of BE reported in a range of other lakes with and without focussing-correction, with ~31% in two lakes in West Greenland (BE_{150} method used for Lake SS4 & Lake SS8; Sobek et al., 2014), 23.2-26.1% (BE_{150} method) and 44.7% (BE_{25} method) in eutrophic Baldeggersee, Switzerland (Teranes and Bernasconi, 2000, Muller et al., 2012)(not focussing corrected). Brothers et al. (2013) reported ~100% efficiency in Kleiner Gollinsee, Germany (deep trap to uncorrected sediment surface accumulation), yet here application of the BE_{150} method gives a 28.5% efficiency. Previously, discussion of variability in OC BE between lakes has focussed on the processes driving preservation, with consensus that the dominant controls are oxygen exposure time, temperature and the dominant OC type (i.e. labile autochthonous versus refractory allochthonous carbon) (Calvert et al., 1991, Sobek et al., 2014).

When considering the controls on OC preservation in Rostherne Mere, the long, stable periods of stratification and associated hypolimnetic anoxia are a key factor. The high levels of production in the lake lead to increased oxygen consumption rate in the hypolimnion following the sedimentation of the spring algal bloom (Rippey and McSorley, 2009), with rapid deoxygenation of the hypolimnion (within 4-6 weeks after

stratification; Fig. 3.4b) and low OC mineralisation rates in the deeper water column and at the sediment surface in the profundal zone (Laskov et al., 2002, Sobek et al., 2014). Once the available dissolved O₂ is depleted (within a few weeks of stratification; Scott, 2014; Fig. 3.4b), denitrification, methanogenesis and manganese reduction will be stimulated (Davison and Woof, 1984, Thomsen et al., 2004, Fahrner et al., 2008).

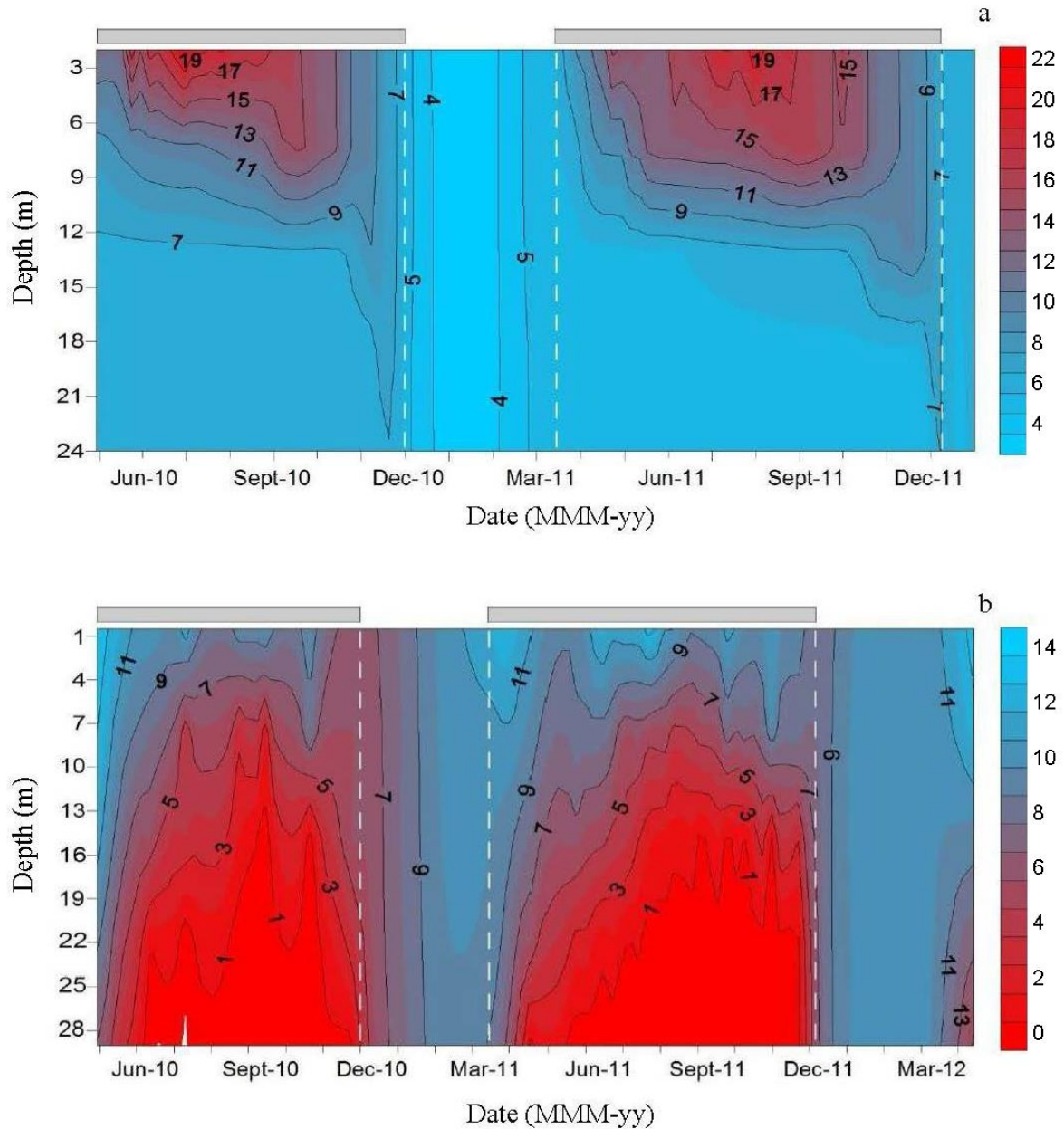


Figure 3.4. The seasonal cycle of stratification at Rostherne Mere during 2010 and 2011 (adapted from Scott 2014). Periods of lake stratification are shown with grey bars and dashed lines. (a) Depth-time plot of temperature (°C) and (b) depth-time plot of dissolved oxygen (mg L⁻¹) between May 2010 to December 2011.

However, within Rostherne Mere the redox sequence observed in other systems may only reach the initial stages due to a lack of available electrons (Davison and Woof, 1984, Davison et al., 1985), adding to the high BE potential of the lake. While research in marine systems has questioned the role of anoxia in promoting high OM preservation (Calvert et al., 1991), anaerobic respiration of OM is generally less efficient than aerobic (Sobek et al., 2009). Additionally, given the year-round low temperature ($\sim 6^{\circ}\text{C}$; Fig. 3.4a) in the hypolimnion of Rostherne Mere (and other mid- and higher latitude stratifying lakes), kinetic rates affecting biogeochemical and biological processes involved in OC respiration and diagenesis will also be reduced, enhancing OM preservation (Tison and Pope, 1980).

Interestingly, the OC loss rates in the water column at Rostherne Mere are seen to increase with depth, with the representative loss rates of the warmer oxygenated epilimnion (NEP to shallow trap, Fig. 3.2.) being lower than the colder anoxic deeper water column sections (shallow trap to sediment surface, Fig. 3.2.). Preliminary results from in-trap decomposition experiments using Rostherne seston (see Appendix 2) show little mineralisation in a sealed container during the first 7 days after sedimentation. Therefore, I propose a week is enough time for sedimenting particles to be deposited in the shallow trap relatively intact (thus only a 1.4% loss found, Fig. 3.2.), whereas, the particles sedimenting to the deep trap will take longer to be captured. The deep trap seston thus includes organic matter that has been partially mineralised within the water column during sedimentation, explaining reduced deep trap flux of OM despite colder and less oxic ambient waters at this depth.

Finally, autochthonous OC derived from algal production is generally regarded as labile compared to more refractory, allochthonous (terrestrial) OC. Sobek et al. (2009) found that BE was one-third that in lakes where OC was predominantly composed of autochthonous matter (mean $\text{BE}_{150} = 22\%$) compared to lakes in which OC was composed predominantly of allochthonous inputs (mean $\text{BE}_{150} = 66\%$). However, some eutrophic lakes that are dominated by autochthonous production, such as Rostherne Mere (this study), Baldeggersee (Teranes and Bernasconi, 2000) and Kleiner Gollinsee (Brothers et al., 2013), can be highly efficient OC sinks, implying that OM source may not be a major control in all lakes. For example, previous work at Rostherne Mere has shown that the preservation of non-siliceous algae is excellent,

potentially leading to higher burial rates with increasing production (Livingstone and Cambray, 1978).

Quantifying OC burial efficiency

Recently, there has been considerable focus on quantifying burial rate to estimate the global role of lakes in removing C from the active carbon pool (Tranvik et al., 2009). Two methods for calculating OC BE were employed in this study; Alin and Johnson (2007b) compared recent (previous 10 – 25 years) OC accumulation rate against NEP (BE_{25} ; Fig. 3.2.), and Sobek et al. (2009) who used the long term mean OC accumulation rate (25 – 150 years) and the delivery to the sediment surface (here the deep trap capture; BE_{150} , Fig. 3.2.). When applied to Rostherne Mere using focussing-corrected core RML, the BE_{25} method gives an estimated efficiency of 92.8%, and BE_{150} 60.4% (Fig. 3.2.). This discrepancy of 32.4% (i.e. about half the BE_{150} value) highlights inadequacies in using either method in systems where OC production has not been constant. This indeed will be the case in many post-industrial landscapes where nutrient loading issues are now being addressed (such as under the EU Water Framework Directive; e.g. Denmark, Fig. 3.3c), in regions where production is increasing with progressive nutrient enrichment, and where terrestrial OC loading is increasing due to landscape or climate change, as in boreal regions (Evans et al., 2005, Monteith et al., 2007). For example, it is reported that Baldeggersee's organic carbon delivery to the sediment surface (as net export from the epilimnion is very similar to deep trap collection; Muller et al., 2012) is between 90 - 103.5 g C m⁻² yr⁻¹ (Teranes and Bernasconi, 2000, Muller et al., 2012), which implies steady burial of 24.3 – 40.1 C m⁻² yr⁻¹, given a BE of 23 - 45% (BE_{150} & BE_{25} , respectively) over recent decades. However, since the 1960s there has been a burial of ~50 g C m⁻² yr⁻¹, rising to >75 g C m⁻² yr⁻¹ in the 1990s (Teranes and Bernasconi, 2000), and although some continued mineralisation would be expected in the 1990s sediments, this demonstrates the methodological mismatch of comparing contemporary productivity with historical accumulation (during lower productivity).

There are two main differences between the two methods; the calculation of inputs (denominator in BE ratio) being either from NEP (BE_{25}) or the deep trap catches (BE_{150} , i.e. surface sediment) and the choice of numerator in the BE ratio for the sediment core historical mean (10-25 years or 25-150 years; BE_{25} and BE_{150}

respectively). At Rostherne Mere, it is the choice of historical record (BE numerator) that drives the burial efficiency value due to the changing production of the lake influencing the core mean value (Fig. 3.2.), with the input (BE denominator) being very similar, as little OC is lost within the water column, although this will not be the case for all lakes. However, OC loss rates during sedimentation down the water column reported from eutrophic Swiss lakes up to 90 m deep have also been shown to be relatively minor, as here (Muller et al., 2012; Fig. 3.2.).

Application of the Sobek et al. (2009) method (BE_{150}) to lakes undergoing change in production (i.e. due to changes in nutrient loading, such as its reduction or redirection) will result in an unrepresentative BE, due to the changing OC accumulation rate (Fig. 3.3a and 4.3b). As the method uses average OC burial between 25 and 150 years in age, this may include sediments that were deposited under very different ecological or trophic conditions. In much of NW Europe and North America, lakes in agricultural landscapes over the last 100-150 years have experienced progressive nutrient loading, greater allochthonous OC inputs and increasing eutrophication (Teranes and Bernasconi, 2000, Brothers et al., 2013, Anderson et al., 2014, Clow et al., 2015, Heathcote et al., 2015). In Europe, for example, average OC burial rates have increased by a factor of 2.2 over the last 100 – 150 years, with a significant rise in hyper-eutrophic lakes from a mean of $59 \text{ g C m}^{-2} \text{ yr}^{-1}$ pre-1950 to $\sim 100 \text{ g C m}^{-2} \text{ yr}^{-1}$ post-1950 (Smith, 2003, Anderson et al., 2014).

Given widespread cultural eutrophication across the globe, it is unsurprising that similarly sharp increases in OC burial rates have been found elsewhere. Comparable patterns are found in 9 Danish lakes (Fig. 3.3c), and although not corrected for sediment focussing, similar relative increases in OC burial have been reported from lakes in Mexico (3-fold increase) and Germany (4-fold increase) in the modern period (Brothers et al., 2013, Carnero-Bravo et al., 2015). At Baldeggersee, Teranes and Bernasconi (2000), found an increase in OC burial rates, rising from $15 \text{ g C m}^{-2} \text{ yr}^{-1}$ pre-1960 to $103.5 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 1995-1996. At Rostherne Mere a similar pattern emerges; with severe cultural eutrophication accelerating post-1900 resulting in a 7-fold rise in OC burial during the 20th century (Fig. 3.3a). Therefore, the application of the Sobek et al. (2009) method (BE_{150}) to lakes undergoing change in production will underestimate burial efficiency by comparing contemporary nutrient-enhanced production with largely pre-impact burial rates, when production was commensurately

lower too. Further, it is likely that preservation of OC in historical periods was in fact lower than in the contemporary system as the speed and severity of hypolimnetic deoxygenation will have increased with cultural eutrophication over the last 100-150 years (exceeding any marginal increase in mineralisation from warming hypolimnia in the last ~50 years; Dokulil et al., 2006), leading to greater underestimation using the BE₁₅₀ method.

Recent oligotrophication is leading to reductions in production in many lakes as nutrient loading is controlled and reduced, as seen at Rostherne Mere (Fig. 3.3a) and in Denmark (Fig. 3.3.c). At both Rostherne Mere and the 9 recovering Danish lakes, a decline in OC burial rate begins following a reduction in nutrient loading (Fig. 3.3a and 3.3c). Comparison of the LIV77 core taken at Rostherne Mere in 1977 confirms the long-term pattern found in the RML core from 2011, and agrees closely with the focussing-corrected values (Fig. 3.3a), suggesting that mineralisation losses do not continue after permanent deposition. Indeed, comparison of the burial rate and OC% for the two cores (Fig. 3.3a and 3.3b) suggests that mineralisation is largely complete after ~10 years, in agreement with recent studies on lake sediments (Galman et al., 2008). While there will be some variability expected even from cores collected in close proximity (Rippey et al., 2008), the good agreement between these cores supports the approach of using sediment focussing (independently applied to both ²¹⁰Pb-dated cores) to estimate a basin-mean value from a single core. Moreover, the LIV77 core OC data also support the contention that OM mineralisation effectively ceases ~10 years after deep water sedimentation in such lakes: OC burial rates in the LIV77 and RML cores from the 1960s are essentially the same (within methodological and within-basin variability), while OC%, initially higher in the uppermost section of the LIV77 core, falls to similar values in both cores by ~1965 (Fig. 3.3b), as expected if OM mineralisation was still incomplete at that time (Fig. 3.3b). The fall in productivity following reduced nutrient loading seen at Rostherne Mere and the 9 Danish lakes is mirrored in the pattern of OC burial rate in their lake sediment records, despite mineralisation processes in the uppermost sediments, in agreement with simulations of OC burial under various models of mineralisation (Heathcote et al., 2015).

It is clear that the OC burial rate in lakes undergoing recent changes in nutrient loading will respond dynamically to changes in both production and preservation environment. However, as decomposition of organic matter continues after deposition onto the lake

bed and during incorporation into the lake sediment record, the use of recent sediments (possibly <25 years and certainly <10 years in age; Galman et al., 2008) should be avoided due to potential continued diagenesis after deposition (Sobek et al., 2009). However, comparing contemporary production with pre-20th century sediment records is also problematic. Consequently, application of the Alin and Johnson (2007b) method that uses a more recent time period of OC accumulation (10-25 year mean) may result in a more realistic estimate for lakes where major changes in production have occurred over ~25 years, and have since stabilised. At Rostherne Mere and other lakes undergoing recent recovery over this timescale (cf. Danish lakes; Fig. 3.3c), it is clear from the trends of the OC burial rates (Fig. 3.3a and 3.3b) that recent diagenesis does not remove the signal of changes in recent lake production recorded in the sediment record. From Figure 3.2, comparison of the 2011 sediment surface OC burial rate from the core ($112 \text{ g C m}^{-2} \text{ yr}^{-1}$) to the mean from 1985 – 2000 ($126 \text{ g C m}^{-2} \text{ yr}^{-1}$; i.e. the BE₂₅ method) shows a 12.8% higher historical burial rate, and generates a paradoxical BE over 100%. In this case, it is happenstance that the BE₂₅ method included the period of maximum lake production, pre-sewage diversion, at this site. Nonetheless, this highlights the problems inherent in any such historical approach to estimating contemporary OC sedimentary dynamics in systems undergoing recent change.

Updated OC burial method: BE_{DT} and BE_{NEP}

This study suggests the current methods for estimating OC BE may be inappropriate when applied to lakes that have recently undergone, or are undergoing, changes in their trophic status and production due to anthropogenic impacts (such as nutrient loading) or global change drivers (such as climate change) (Evans et al., 2005, Monteith et al., 2007). The implications for errors in up-scaling lake OC burial rates for regional and biome-scale C cycling without an effective methodology are substantial (Heathcote et al., 2015).

The fundamental issue with both methods discussed here (BE₂₅ and BE₁₅₀) is the calculation of a contemporary OC burial rate via a historical sediment mean OC burial value that will either underestimate BE in increasingly productive lakes (e.g. those becoming more nutrient enriched) or overestimate it in lakes that are recovering from eutrophication (Fig. 3.5.). Therefore, here I propose adapting previous approaches for

assessing the OC burial in lakes that are in a state of trophic flux, by reducing the historical dependency in the sediment core mean value by using the 0 to 50-year mean (Fig. 3.2.; labelled BE_{DT} & BE_{NEP}), using delivery of OC to surface sediment as estimated from a deep trap or surface sediment accumulation (BE_{DT}) or epilimnetic export of OC as estimated by NEP respectively (BE_{NEP}). Using this time frame will reduce the historical dependency inherent in the BE_{150} method and capture the most recent lowered accumulation rates found in recovering lakes, addressing issues of the BE_{25} method. This new approach using surface sediment accumulation (BE_{DT}) was applied to 36 stratifying (> 10 m maximum depth) European lakes known to have been impacted by nutrient enrichment over the last 100-150 years, extracted from the

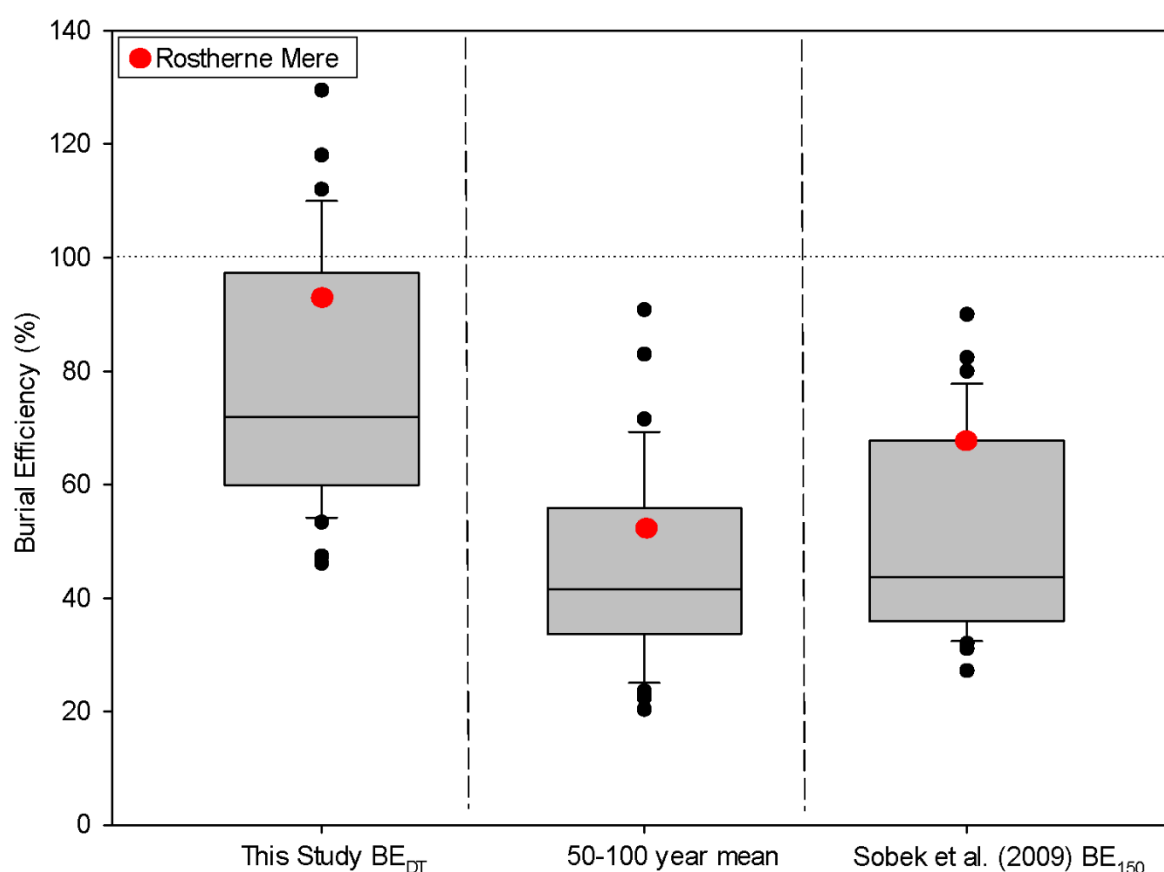


Figure 3.5. Burial efficiency (BE%) for 36 stratifying European lakes (> 10 m) that have been impacted by recent nutrient enrichment (data from Anderson et al. 2014). Three methods for BE% are calculated; this study's BE_{DT} (last 50 years of accumulation), 50 to 100-year sediment core mean representing the early/pre-impact BE, and the BE_{150} method (Sobek et al. 2009). All cores are ^{210}Pb -dated and focussing-corrected. Rostherne Mere's BE is marked with a red dot. Lakes >100% BE are those with net oligotrophic recovery in the last 50 years. See text for details.

dataset of Anderson et al. (2014; Fig. 3.5.). All these lakes have independently dated, focussing-corrected sediment records, with delivery to the sediment surface estimated from surface sediment accumulation rate. I argue that BE_{DT} values are better estimates of true, current BE than those methods using historical sediment data from earlier (pre- or early impact) periods, with mean BE_{DT} ~75% compared to ~40% using either sediment records from 50-100 years or 25-150 years ago (Sobek et al., 2009; Fig. 3.5.). For example, Kleiner Gollinsee is estimated to have an efficiency of 28.5% using the BE_{150} method, inexplicably low compared to BE of ~100% calculated from deep trap flux to sediment surface accumulation (Brothers et al. (2013). However, the BE_{DT} method proposed gives BE as 70.7%, fitting within the range of other eutrophic lakes (Fig. 3.5.), and representing a more realistic value for contemporary BE.

Similarly, Baldeggersee (Teranes and Bernasconi, 2000, Muller et al., 2012) is calculated with a BE of 41.8 – 48.1% (BE_{DT} & BE_{NEP} , respectively), compared to BE_{150} of ~23%. While these are relatively low figures compared to other such lakes (Fig. 3.5.), this may be due to over-trapping within the sediment traps as the reported net export from the epilimnion in Baldeggersee in 1996 was $90 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Muller et al., 2012), compared to delivery to the sediment surface (via deep trap collection) of $103.5 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Teranes and Bernasconi, 2000). Over-trapping will underestimate BE (by overestimating production), which highlights the need for effective trap corrections, as mentioned previously.

Rostherne Mere's BE using this updated method is estimated as ~95% (BE_{DT} ; Fig. 3.2.), and fits within the range of this larger dataset (Fig. 3.5.). Some lakes are shown to have a $BE_{DT} > 100\%$ (Fig. 3.5.), which are those that have undergone rapid oligotrophication at some point over the last 50 years, resulting in a higher mean organic carbon accumulation rate (OCAR) in the sediment core compared to the current sediment surface OCAR. To account for this, individual adjustments of the BE_{DT} or BE_{NEP} methods can be made to quantify the rate of trophic recovery over different time scales, by adjusting the sediment core mean OCAR date range. This adjustment will generate an improved representation of the sediment core OCAR mean, enabling a more realistic BE to be calculated.

This study has focused on a lake system dominated by autochthonous production and minimal terrestrial OC inputs. However, most of the world's lakes are boreal systems

(Tranvik et al., 2009), and those with significant peatland, forest and organic rich soil in their catchments typically have high loadings of terrestrial DOC (Jonsson et al., 2001, Sobek et al., 2007, Ferland et al., 2012), while temperate lowland lakes, such as Rostherne Mere, have much less (due to both the lack of such sources of terrestrial OC and the agriculture practised in the catchment). The BE_{NEP} method proposed in this study relies on autochthonous contribution representing the majority of total OC inputs to the lake, as such it will be susceptible to substantial overestimation of the total OC load. Therefore, research design for lake systems with a high terrestrial contribution must also consider that the BE_{NEP} may not be a suitable method to use without adding the estimate for the terrestrial OC component. This can be done through direct field study of major inflows and lake DOC and POC pools or utilising the literature to estimate load of OC. Below, I estimate terrestrial OC loadings to Rostherne Mere as a worked example of method alteration for systems with high terrestrial loading.

The allochthonous loading of DOC from Rostherne's catchment can be estimated from major river inflow and outflow concentrations from 2011-12 (Scott, 2014; 8 mg L⁻¹ DOC) and the inflow and outflow volumes measured in 2016 (see chapter 4) and up-scaled to account for missing sources (Carvalho et al., 1995), plus a small amount released from the lake sediment (Scott, 2014), giving a total DOC loading of 3.67 g C m⁻² if all DOC was sedimented to the lake floor. Terrestrial POC (TPOC) input is more difficult to estimate but there is consensus that loadings are less than for DOC (Worrall and Moody, 2014, Barry et al., 2016). Even if catchment losses are set as high as 50% of values for DOC, given significant mineralisation in transit to and while in the lake (Worrall and Moody, 2014), I conservatively estimate a TPOC loading of 6.88 g C m⁻² to the lake floor. Combining the DOC and TPOC values I estimate that terrestrial OC may account for 10.55 g C m⁻² yr⁻¹. This figure likely overestimates the contribution of terrestrial OC to the sediment traps and lake floor at Rostherne Mere as the lake is third in a chain in its catchment, which (though both smaller than Rostherne) would act both as sinks for TPOC and provide further opportunities for mineralisation. However, even if terrestrial OC loading was this significant at Rostherne Mere, there would only be a minor effect on the calculation of BE_{NEP}, as adding the terrestrial OC loading of 10.55 g C m⁻² yr⁻¹ to the NEP of 135.6 g C m⁻² yr⁻¹ would change the BE from 86.2% to 80.0%.

The BE_{DT} method already accounts for terrestrial inputs as the deep trap collection will include all in-lake and terrestrial OC contributions. However, there must be a consideration of the relative importance of terrestrial OC inputs against resuspension in trap collections, especially during the winter high flow events (which are considered the dominant periods of terrestrial OC loading, as catchment runoff is at its highest). In this study the removal of the winter collection corrected for resuspension in the deep trap, a suitable correction in systems with low terrestrial OC inputs and high winter resuspension, like Rostherne Mere, as evident in the shallow and deep trap correction comparison (see Table 3.2.). Removal of this inter collection would also therefore preferentially remove terrestrial OC inputs and therefore underestimate the total OC input. To account for this discrepancy, an addition of the estimated terrestrial OC input during this winter period (as discussed above, based on catchment loading) could be included in the calculation.

It is clear this updated approach will contain some error due to the continued diagenesis of OC in the upper sediment before permanent incorporation into the sediment archive (Galman et al., 2008) and thus (under steady-state production) will on some level overestimate the true burial efficiency. However, as mentioned above, this may be only a minor issue in deep seasonally hypoxic lakes, such as Rostherne Mere (this study), Baldeggersee (Teranes and Bernasconi, 2000) and Kleiner Gollinsee (Brothers et al., 2013), where OC mineralisation rates are already suppressed. In other lake systems (e.g. warmer, shallower, less prone to stratification) this overestimation may be larger and needs further examination. While no method in lakes that are changing rapidly will be perfect, the approach proposed here does at least recognise the role of recent lake ecosystem history and attempt to take this into account, and can improve the estimation of lake OC burial efficiency over previous approaches.

3.5. Conclusions & implications

Much of the current literature on the role of lakes in global C cycling assumes constant OC burial rates, but it is clear from the present study and others (Heathcote and Downing, 2012, Anderson et al., 2013, Anderson et al., 2014) that OC burial rates have fluctuated historically, increasing in lakes as they have become more eutrophic,

but also declining following recovery (Fig. 3.3.). It is evident that OC BE is subject to both the controls of preservation as well as production, and varies over a range of timescales, from seasonal to multi-annual and over longer timescales (decadal and centennial). Productive, stratifying lakes with seasonally anoxic hypolimnia also demonstrate that autochthonous OC, although labile, can be well preserved and buried in lake sediments over long time periods (Livingstone and Cambray, 1978, Livingstone and Reynolds, 1981).

Future work requires the wider utilisation of long term lake monitoring programmes to understand further the extent to which seasonal, inter-annual and multi-annual variability and changing external stressors, such as nutrient loading and climate change, will have upon organic carbon dynamics in lakes, such as increasing terrestrial OC loading through hydrological and land use change. A greater appreciation of the variable nature of OC burial rates will improve our understanding of C cycling in the large (and growing) number of impacted, non-steady state lakes and give greater confidence to up-scaling models that estimate the role of lakes as important regional and global sinks of OC. Furthermore, changes in autochthonous production are a key control on historical patterns of OC burial and need to be considered for a deeper understanding and evaluation of the role of lakes in global C dynamics.

4. Nutrients and climate drive reduced nutrient load trajectories and ecological change in a deep stratifying eutrophic lake

4.1. Introduction

Eutrophication is a well-known problem in lowland freshwater catchments, with many in the last century receiving excessive nutrient loads from anthropogenic sources, such as wastewater effluent, agricultural runoff and other nutrient sources, leading to shifts in trophic state (Carpenter, 2005, Smith et al., 2006, Spears et al., 2012). As understanding of the catchment-scale issues developed, management intervention has attempted to reduce point source nutrient loads entering freshwater systems with the purpose of restoring surface waters to a good ecological status, as required by law across the EU for example (European Commission, 2000).

Previously, the oligotrophication trajectory of impacted freshwater systems has been predominantly focused on the management intervention of anthropogenic nutrient loading, with efforts successful in some lakes, especially those that are shallow flush quickly, while others have been slow to respond (Jeppesen et al., 2005, Jarvie et al., 2013b, Zamparas and Zacharias, 2014). Understanding why in-lake nutrient reduction is delayed in some instances has become a crucial issue for management research, with a need to understand the most suitable long-term approaches and the necessity of setting realistic recovery targets becoming of great importance, because the cost of mitigating the impacts of eutrophication for any single system is large and for multiple lakes therefore, prohibitive (Pretty et al., 2003). Therefore, assessment of long term management applications in systems that are known to show a delayed recovery trajectory is of great interest, not just limnologically, but also to appreciate the impact of management intervention over a broader timescale and inform future management initiatives for continued recovery.

However, it is becoming increasingly clear that climate change is impacting the physical limnology of many deep, stratifying lake systems across the globe through warming and changes in seasonal precipitation (Dokulil et al., 2006, Williamson et al., 2009b, Verburg and Hecky, 2009) and stratification timing adjustment (Thackeray et al., 2008, Meis et al., 2009). Gradual changes to physical limnology in turn can alter

the cycling and availability of nutrients, having an influence on biological uptake and algal bloom development, re-directing the trophic pathway of recovering lake systems.

This study re-examines the recovery status of Rostherne Mere 25 years after sewage effluent diversion, and uses an updated P budget to examine two drivers of change; oligotrophication driven by nutrient load change and oligotrophication driven by physical limnological change from climatic forcing. To do this, newly collected nutrient and phytoplankton data from 2016, equivalent to those collected in 1990-2002 (Carvalho et al., 1995, Moss et al., 2005), were combined with high resolution hydrological monitoring of lake inflow and outflow, to update the nutrient budget for P (and catchment loading of dissolved inorganic nitrogen, DIN) in the contemporary lake system and compare these to previous budgets, for assessing the recent lake oligotrophication. Furthermore, physical limnological and hydrological changes on epilimnion nutrient flushing and availability are assessed for their impact on primary (algal) production, using high resolution hydrological and limnological monitoring from 2016. Changing timing (onset and overturn) and duration of stratification over the last ~50 years may shed light on the importance of climate change as a driver of physical limnology for seasonal nutrient availability in deep, eutrophic stratifying lakes.

4.2. Methodology

Climate and lake temperature data

Air temperature, wind speed and precipitation data were taken from the closest reliable meteorological station (Manchester Airport, UK; situated 7.4 km north-east of Rostherne Mere), with wind speed at the airport (V_{MA}) corrected for local sheltering (V_{RM}) through comparison to the available partial study period wind speed data from the UK Lake Ecological Observatory Network project buoy (UKLEON; see <http://www.ceh.ac.uk/our-science/projects/uk-lake-ecological-observatory-network-ukleon>; comparable daily data from February 2013 to January 2017; correction factor of $V_{RM} = 0.55V_{MA} - 0.12$, $R^2 = 0.82$, $n = 1417$, $p < 0.001$). Additionally, the UKLEON buoy measures various in-lake parameters (e.g. temperature profiles, chlorophyll) and lake-surface meteorological variables at high resolution (every 1 minute) with data uploaded in real-time. This provided daily average water column temperatures since 2010, from thermistor readings at 2 m intervals from 2 m to 24 m depth in a central

lake location (Fig. 2.1.). The date of stratification onset was taken as the day a >3% difference in epilimnion and hypolimnion temperature develops and is maintained throughout the summer, with stratification end taken as the first day the difference in epilimnion and hypolimnion drop to a <3% range.

Sample collection and analysis

Two 250 ml water samples were collected for nutrient analysis into new PTFE sealable bottles approximately every 3 weeks for each sampling location from January 2016 to January 2017. Sampling locations included Rostherne Brook (main inflow, 250 m upstream from the lake), Harper's Bank Spring (ground water inflow), Blackburn's Brook (outflow, 350 m downstream from the lake) and surface water samples from a central lake location, with multiple water column depth samples (6 m, 12 m, 18 m and 24 m) added to the collection programme from September 2016 (Fig. 2.1.). Additionally, an 8 m integrated water column sample from the central lake location (Fig. 2.1.) was collected into two opaque 500 ml bottles and two opaque 250 ml bottles, with 2 ml of Lugol's iodine added to each 500 ml bottle to preserve phytoplankton for identification. All samples were sealed and placed in a cool box for transport back to Loughborough University. Secchi depth was recorded at this central lake location during each visit.

On the same day as collection, one of the 250 ml water samples per site was frozen as collected, with the other filtered using GF/F filter paper (0.45 μm) before being stored frozen. Periodically (~2 month intervals) samples were shipped to an external certified laboratory (National Laboratory Service, UK) for orthophosphate (i.e. soluble reactive phosphate, SRP), DIN and total P (TP) nutrient analysis.

Nutrient budget and water residence time

There was no relationship between discharge (inflow and outflow) and nutrient concentration (TP, SRP and DIN; data not shown) as inflow concentrations are controlled by seasonal nutrient cycling of the upstream lakes. Therefore, discharge into and out of Rostherne Mere was estimated by measuring the cross-sectional profile and sectional velocities for a range of stage heights for both inflow (Rostherne Brook) and outflow (Blackburn's Brook) at the water sampling points. This discharge/stage

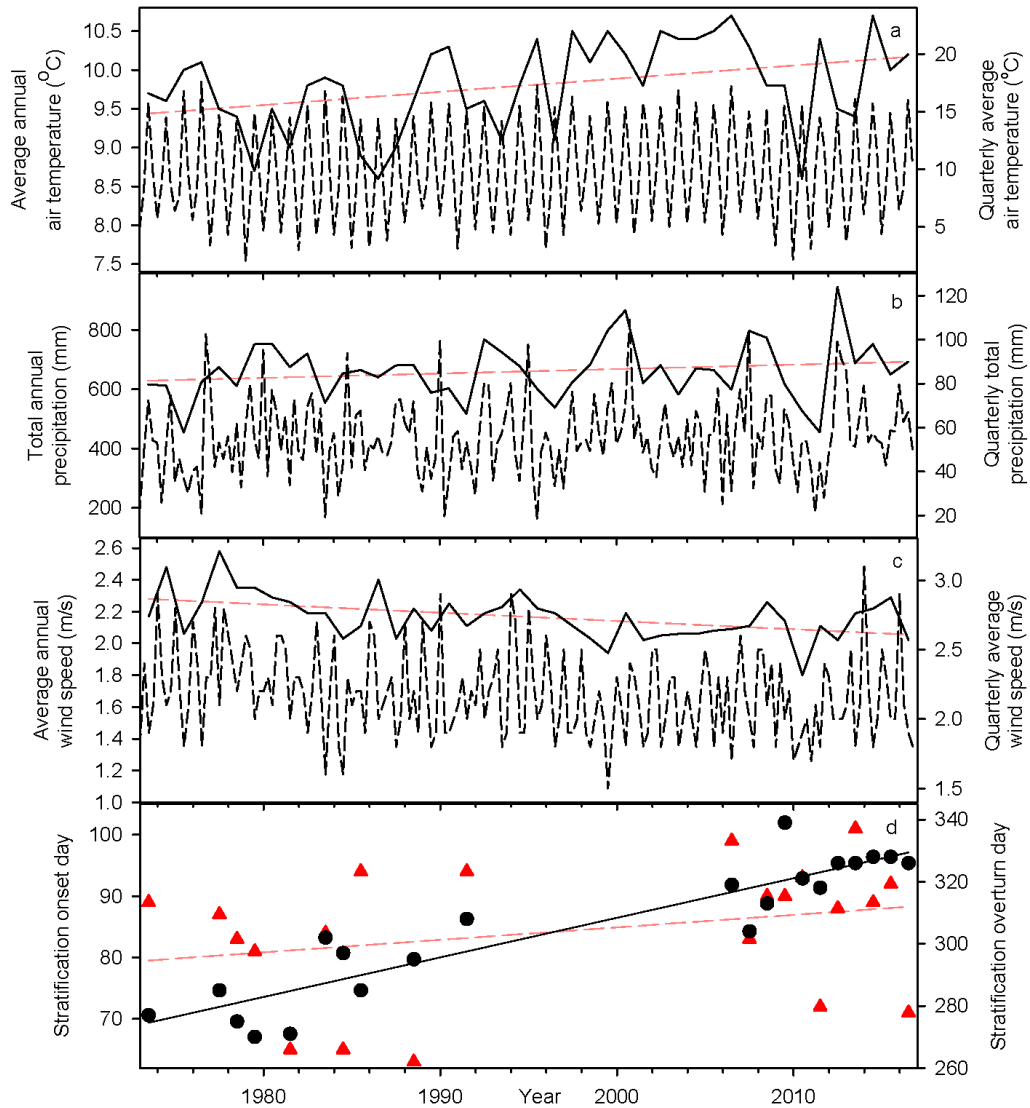


Figure 4.1. Climate and stratification timing data. a-c) Annual (solid black line) and quarterly (dashed black line) climate and meteorological data at Rostherne Mere over the last 43 years, including the 43 year regression line (dashed red line), for a) average air temperature, b) total precipitation, c) average wind speed. d) stratification onset (red triangles) and overturn dates (black circles) including regression lines (onset = dashed red line, overturn = solid black line), with data from 1973 - 1988 taken from Reynolds and Bellinger (1992), 1991 from Carvalho (1993) and 2006 - 2016 from the UKLEON thermistor data.

relationship was then applied to continuous stage height recordings taken throughout the study period (Jan 2016 – Jan 2017) from the inflow and outflow using a Van Essen mini-diver data logger (www.vanessen.com), recording water pressure every 5 minutes corrected to changes in air pressure by a barometer located in the boat house (Fig. 2.1.). Application of the measured discharge to stage relationship to the mini-

diver data provides a high-resolution total discharge measurement for both the inflow and outflow. Total nutrient fluxes were calculated by applying a daily nutrient concentration estimate through linear interpolation between two sample dates. The estimated daily nutrient concentration was then multiplied by monitored average daily flow rate to provide a total inflow and outflow load of each nutrient on a daily basis (SRP, TP, DIN). Loadings from the 21% of the lake catchment not drained by the inflow (“catchment north drainage” and “catchment north groundwater”) were estimated using the same methods as Carvalho et al. (1995), with estimation of cormorant bird roost nutrient inputs kept the same as 1992 estimates in the absence of evidence to suggest substantial changes in lakeside cormorant activity.

The TP budget was calculated using a mass balance equation as in Carvalho et al. (1995), with flux balance as follows:

$$\text{Output} = \text{external inputs} \pm \text{internal sources/sinks} - \Delta \text{lake storage} \quad (\text{eqn. 4.1.})$$

The internal sources represent the legacy sediment release of P in the hypolimnion and the sinks include sedimentation of particulate matter. The internal source/sink contribution was calculated by balancing eqn. 4.1.

The standard outflow method for water residence time (WRT) was estimated as the annual outflow discharge ($8.33 \cdot 10^6 \text{ m}^3 \text{ yr}^{-1}$) against the total lake volume ($6.85 \cdot 10^6 \text{ m}^3$). As the lake is strongly seasonally stratified (following the classic monomictic pattern), a second, adjusted WRT for the mixed part of the water column (WRT_m) was calculated. This is the monthly average outflow rate against the monthly available mixed lake volume (during the stratified period from April to November, this is the epilimnion, but during the mixed period from December to March, this the entire lake; UKLEON buoy data was used for stratification timing estimation for the years 2010 to 2016).

Chl-a and phytoplankton data collection

Chl-a analysis took a standard spectrophotometer approach. Pigments were extracted from filtered water samples using an 80% acetone solvent (Sartory and Grobbelaar, 1984), centrifuged and analysed using a spectrophotometer, with recordings taken at wavelengths of 750 nm, 665 nm, 645 nm and 630 nm. Chl-a was calculated using eqn. 4.2.:

$$\text{chl-a} = (11.85 \times (665\text{nm} - 750 \text{ nm}) - 1.54 \times (645 \text{ nm} - 750 \text{ nm}) - 0.08 \times (630 \text{ nm} - 750 \text{ nm})) \times 8 / 0.25 \quad (\text{eqn. 4.2.})$$

Samples were kept away from direct light throughout.

Phytoplankton analysis was conducted through the concentration of the total 1 L sample to 50 ml through a sequence of settling procedures. The concentrated sample was then well mixed and a measured 1 ml sub-sample was extracted and placed on a gridded cell (Sedgwick-Rafter cell) for identification and absolute abundance counts under an inverted microscope at 400x magnification (Lund et al., 1958), counting all

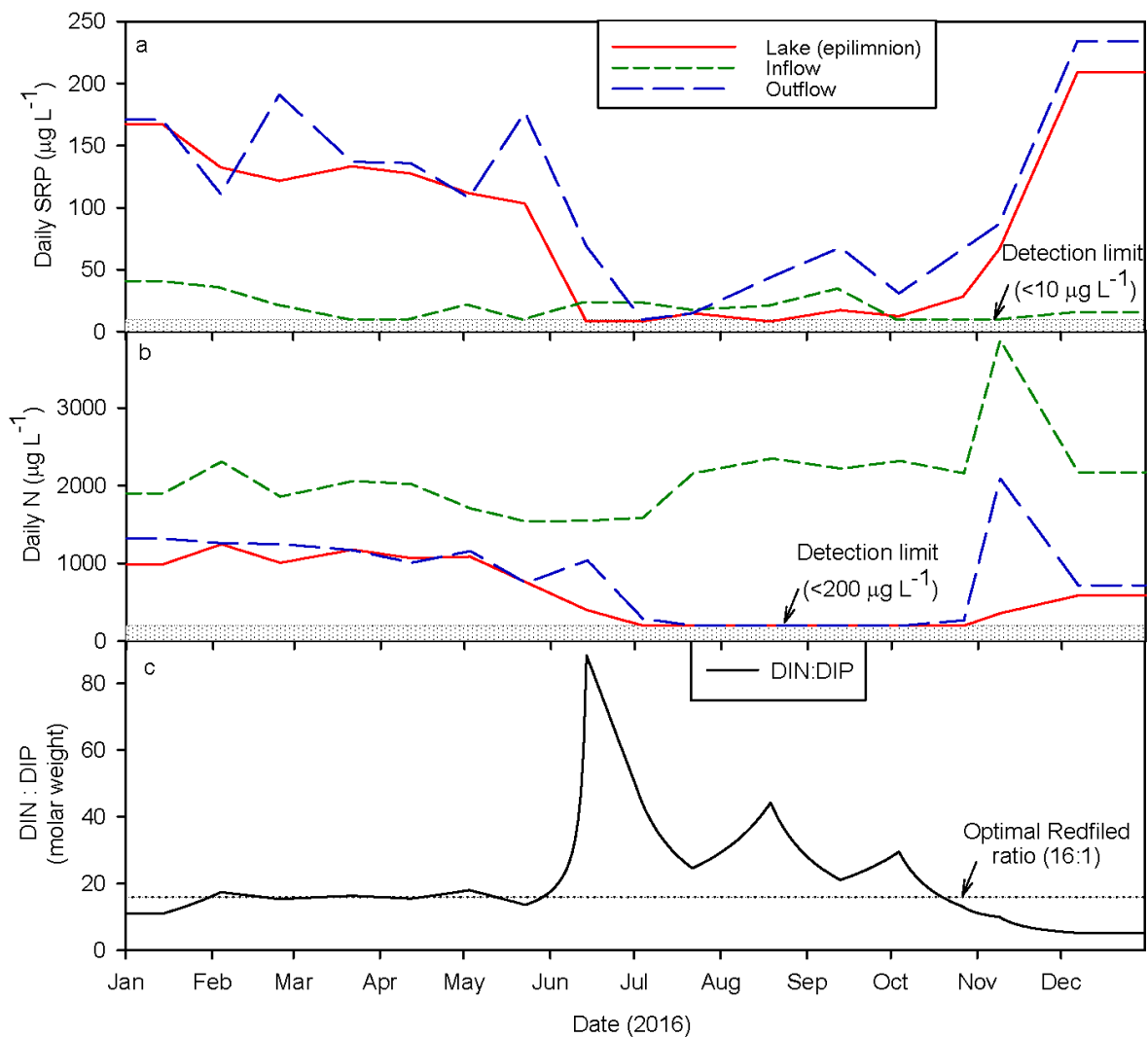


Figure 4.2. Estimated daily SRP (a) and N (b) concentrations for the major inflow, lake (epilimnion) and outflow. Analysis detection limits $<10 \mu\text{g SRP L}^{-1}$ and $<200 \mu\text{g N L}^{-1}$, samples below detection values set as $10 \mu\text{g}$ or $200 \mu\text{g}$, respectively. DIN:DIP (molar weight) ratio (c) with optimal Redfield ratio (16:1) reference line (dotted line).

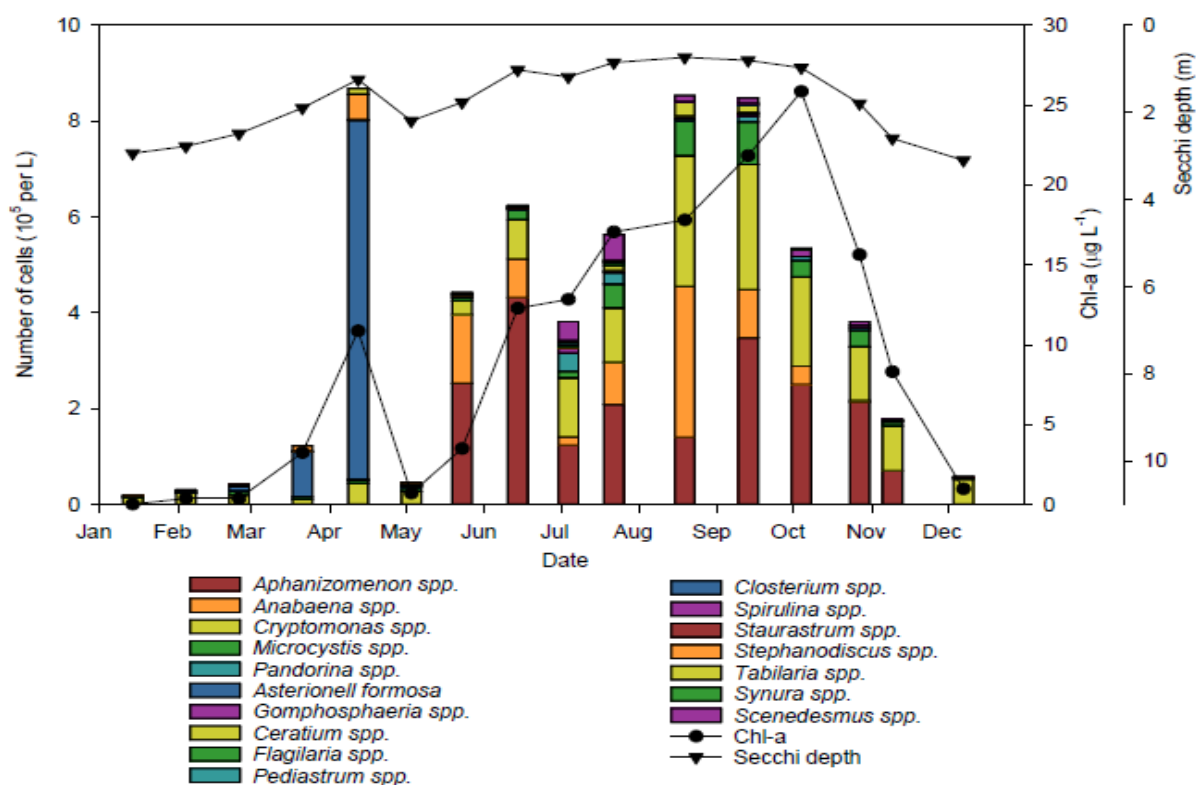


Figure 4.3. Epilimnion integrated samples total algal cells present (including triplicate count error bars for samples 4, 8, 12 and 16), chl-*a* concentration and measured Secchi depth.

algae present within a cell grid. Filaments of *Aphanizomenon* spp., colonies of *microcystis* spp. And cells of all other algae were counted. Four of the initial 16 algal samples were counted in triplicate to allow an estimate of sample reproducibility and count variation error ($\pm 15\%$ total number of cells).

4.3. Results

Climate and meteorological data

Air temperature, precipitation and wind speed varied seasonally during the past 43 years (Fig. 4.1.). Air temperature showed seasonal and inter-annual variability, with a warming trend present ($+0.72\text{ }^{\circ}\text{C}$ between 1973 and 2016; $y = 0.02x - 23.99$, $R^2 = 0.14$, $p < 0.001$; Fig. 4.1a). Precipitation varied greatly, with successions of drier and wetter years, with a trend towards increasing annual precipitation since 1973 ($+62\text{ mm}$ between 1973 and 2016; $y = 1.48x - 2290.5$, $R^2 = 0.04$, $p < 0.001$; Fig. 4.1b). Wind

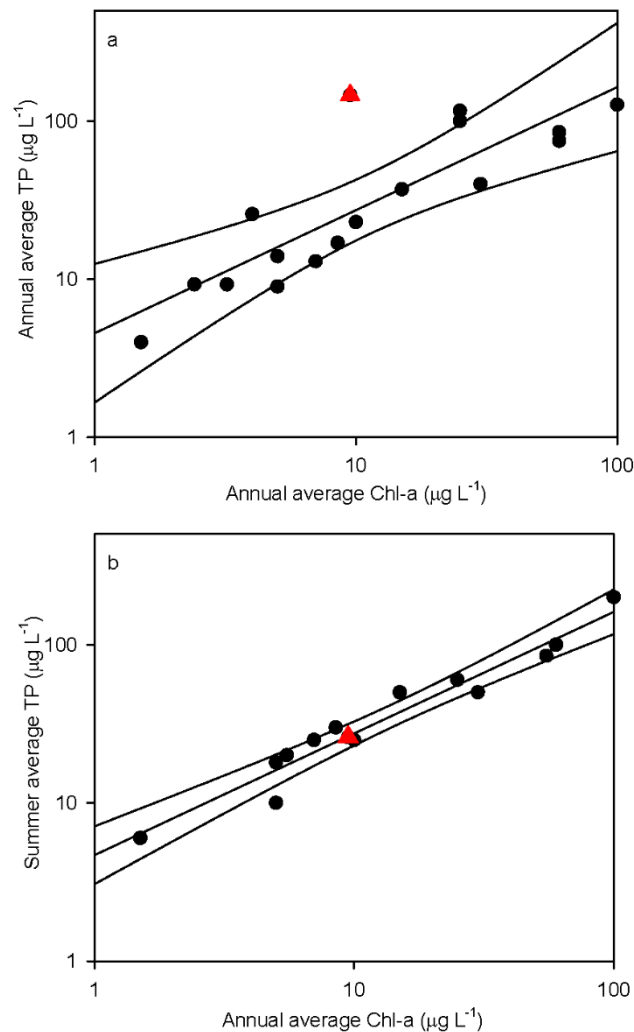


Figure 4.4. Synthesis of published data for deep lake systems (n=398) undergoing oligotrophic recovery (Cattaneo et al., 1998, Hansson et al., 1998, Guildford and Hecky, 2000, Jeppesen et al., 2005, Langdon et al., 2006) including this study. Annual average TP against annual average chl-a (a) and summer average TP against annual average chl-a (b). Reference lines represent linear regression line and 99% confidence intervals. Red triangle represents Rostherne Mere.

highlighting the sheltered position the lake sits in (~45% lower wind speed on the lake compared to Manchester Airport).

Physical limnological data

The UKLEON thermistor data show stratification onset and overturn date during the last 10 years has varied year to year (Fig. 4.1d) and comparison to stratification timings in Reynolds and Bellinger (1992) and Carvalho (1993) confirm stratification onset has

frequently ranged from early-March to mid-April. The stratification overturn date is shown to have become gradually later in the year ($y = 1.27x - 2240.5$, $R^2 = 0.84$, $p < 0.001$), extending the total time of stratification at Rostherne Mere by ~40 days over the past 43 years ($y = 1.07x - 1918.9$, $R^2 = 0.66$, $p < 0.001$; Fig. 4.1d).

The WRT estimated in this study (0.82 years) suggests Rostherne Mere flushes quicker than was previously thought (estimated as 1.6 - 2.4 years; Harrison and Rogers, 1977, Moss et al., 2005). Furthermore, the mixed lake WRT (WRT_m) that takes account of the strong stratification for 8.5 months (mid-March to end-November) which limits the available lake volume for outflow export, increases the summer flushing rate to an annual estimate of 0.57 years (Table 4.1.), suggesting the epilimnion will flush completely during stratification (7-8 months, ~0.65 yr). The discrepancy in residence time to previously published estimates is thought likely due to the availability of increased flow data frequency undertaken in this study (with stage height intervals measured every 5 minutes) compared to that of previous studies (~2 week intervals with correlation to daily precipitation). Comparison of the precipitation values for the two study periods show the 2016 precipitation was ~10% higher than 1990-92 (1990-92 = 630 mm yr⁻¹, 2016 = 693 mm yr⁻¹; Fig. 4.1b), which may result in a slightly faster flushing rate for 2016 but does not explain the difference present here.

2016 nutrient cycling and algal assemblages

At the beginning of 2016, lake P and N concentrations were high (>150 µg L⁻¹ SRP and >1000 µg L⁻¹ DIN; Fig. 4.2.), with in-lake SRP concentration being diluted by the inflow although inflow N concentrations are substantially higher (<50 µg L⁻¹ SRP and >1300 µg L⁻¹ DIN; Fig 4.2.). Nutrient draw-down from the spring diatom bloom (predominantly *Asterionella formosa* Hassall, Fig. 4.3.) and the early summer cyanobacterial blooms (predominantly *Aphanazomenon* and *Anabaena*, Fig. 4.3.) utilises the available P & N within the mixed part of the lake (epilimnion), which is rapidly being flushed out of the lake and diluted by the reduced inflow nutrient concentrations, consequently reducing levels to near (or below) detection limits by mid-June (Fig. 4.2a and 4.2b). The faster reduction in June SRP concentrations (Fig. 4.2a) compared to the DIN concentrations (Fig. 4.3b) results in a high DIN:DIP Redfield ratio (maximum 88:1; Fig. 4.2c), before DIN reduction later in the summer reduces the ratio to values slightly above the optimal Redfield ratio until mid-October.

Table 4.1. 2016 monthly and annual water retention time using revised method (WRT_m) of available lake volume over outflow rate.

Month	Revised WRT method		Monthly WRT (yr)
	Available volume ($L \cdot 10^9$)	Outflow rate (L per month $\cdot 10^8$)	
January	6.85	7.45	0.92
February	6.85	6.96	0.98
March	4.69	3.43	1.37
April	2.67	3.66	0.73
May	2.82	6.18	0.46
June	2.97	6.20	0.48
July	3.12	6.68	0.47
August	3.27	6.84	0.48
September	3.41	6.37	0.54
October	3.71	6.35	0.58
November	4.31	7.07	0.61
December	6.85	8.24	0.83
<i>Annual totals</i>	<i>4.29</i>	<i>75.4</i>	
WRT_m (yr)	0.57		

The phytoplankton summer maxima ($25.8 \mu g \text{ chl-a } L^{-1}$; Fig. 4.3.) is potentially limited by the available summer P, with summer P to chl-a production consistent with other similar lake systems (Fig. 4.4b), despite the much higher annual P to chl-a values (Fig. 4.4a). The shift from high annual P:chl-a to an expected summer P:chl-a relationship highlights the effective nutrient flushing mechanism evident in the WRT_m estimations (Table 4.1.), reducing the high concentrations early in the year to those typical of the inflow. Therefore, in the absence of significant mixing with the hypolimnion (Fig. 4.5.), late-summer algal growth is sustained by the inflowing SRP load. Secchi depth correlates to chl-a and algal biomass, highlighting the changing light climate in the lake with an increase of spring and summer production leading to increased light shading despite more incident sun insolation in the summer (Fig. 4.3.).

Concentrations of N from the inflow were regularly higher than the lake and outflow concentrations (Fig. 4.2b). Conversely, monthly concentration of SRP in the inflow was substantially below that of both the lake and outflow, with one short period when inflow SRP concentration was higher than outflow in early July, and higher inflow concentration compared to lake concentrations between mid-June and October (Fig.

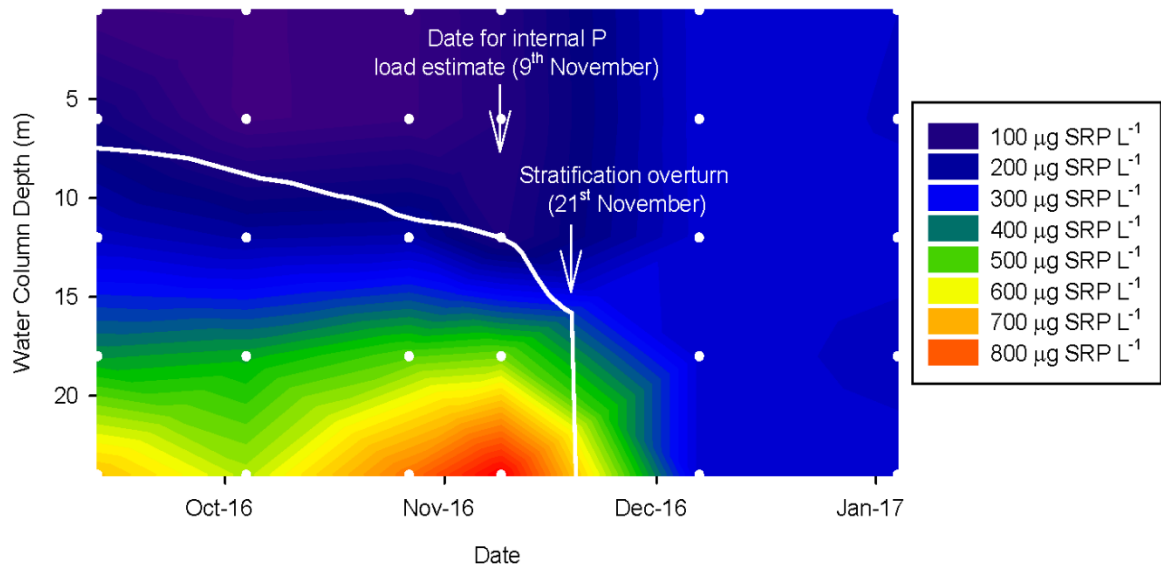


Figure 4.5. Internal concentration of SRP building in the hypolimnion during stratification and released into the whole water column upon stratification overturn in 2016. White dots represent sampling points. White line represents thermocline depth estimated using UKLEON daily thermistor data.

4.2a). With consistently higher outflow compared to inflow, the net export of P (635 kg TP; Table 4.2.) is driven by internal loading, with a large store of P developing during stratification in the hypolimnion (maximum $>800 \mu\text{g SRP L}^{-1}$ in deepest water; Fig. 4.5.) and dispersed throughout the water column at stratification overturn, replenishing the system to high concentrations once more for the following year ($\sim 250 \mu\text{g SRP L}^{-1}$; Figs. 4.2a and 4.5.). The outflow N and P concentrations were often greater than the epilimnion (Fig. 4.2.) due to the impact of an additional water source contributing nutrients from the catchment between the lake and the site of outflow sampling. This additional source is most notable in November with an inflow and outflow DIN peak, showing the impact of the localised catchment source in these water courses.

Updated Rostherne Mere phosphorus budget

With the faster WRT estimate in this study compared to previously published records, it can be assumed the previous nutrient budget calculations for the inflow and outflow were substantially underestimated. Therefore, the previous budget from 1990-92 was adjusted by comparison of 2016 measured flow data to flow data provided in Carvalho (1993) and corrected for the higher precipitation in 2016, which suggests a x1.73 factor difference to account for the increased flow rates. This correction increases the TP

Table 4.2. Total phosphorus budget for Rostherne Mere. Values in kg, except loads in kg day⁻¹. 1990 to 1992 data taken from Carvalho et al. (1995). A correction of inflow x1.73 based on comparison of water budgets from this study and Carvalho (1993). 2016 direct rainfall, catchment north drainage and catchment north groundwater all calculated as Carvalho et al. (1995), with bird roost estimate using the same value as 1992. Percentage of external input contribution in parenthesis.

Period	Days	Inflow	Inflow load	Catchment North drainage	Catchment north groundwater	Direct rainfall	Bird roost	Total inputs	Δ P lake	Out flow	Outflow load	Balance
5/2/90 - 14/5/91	377	2250 (96)	6.0	55 (2)	7 (0)	21 (1)	23 (1)	2356	-100	1830	4.8	-626
23/7/91 - 21/7/92	365	504 (85)	1.4	42 (7)	5 (1)	19 (3)	20 (3)	590	-345	1990	5.5	+1055
5/2/90 - 14/5/91 (WRT corrected)	377	3893 (97)	10.4	55 (1)	7 (0)	21 (1)	23 (1)	3999	-100	3166	8.3	-933
23/7/91 - 21/7/92 (WRT corrected)	365	872 (91)	2.4	42 (4)	5 (1)	19 (2)	20 (2)	958	-345	3443	9.5	+2140
14/1/16 - 4/1/17	356	864 (88)	2.4	49 (5)	5 (1)	21 (2)	20 (2)	959	+178	1416	3.9	+635

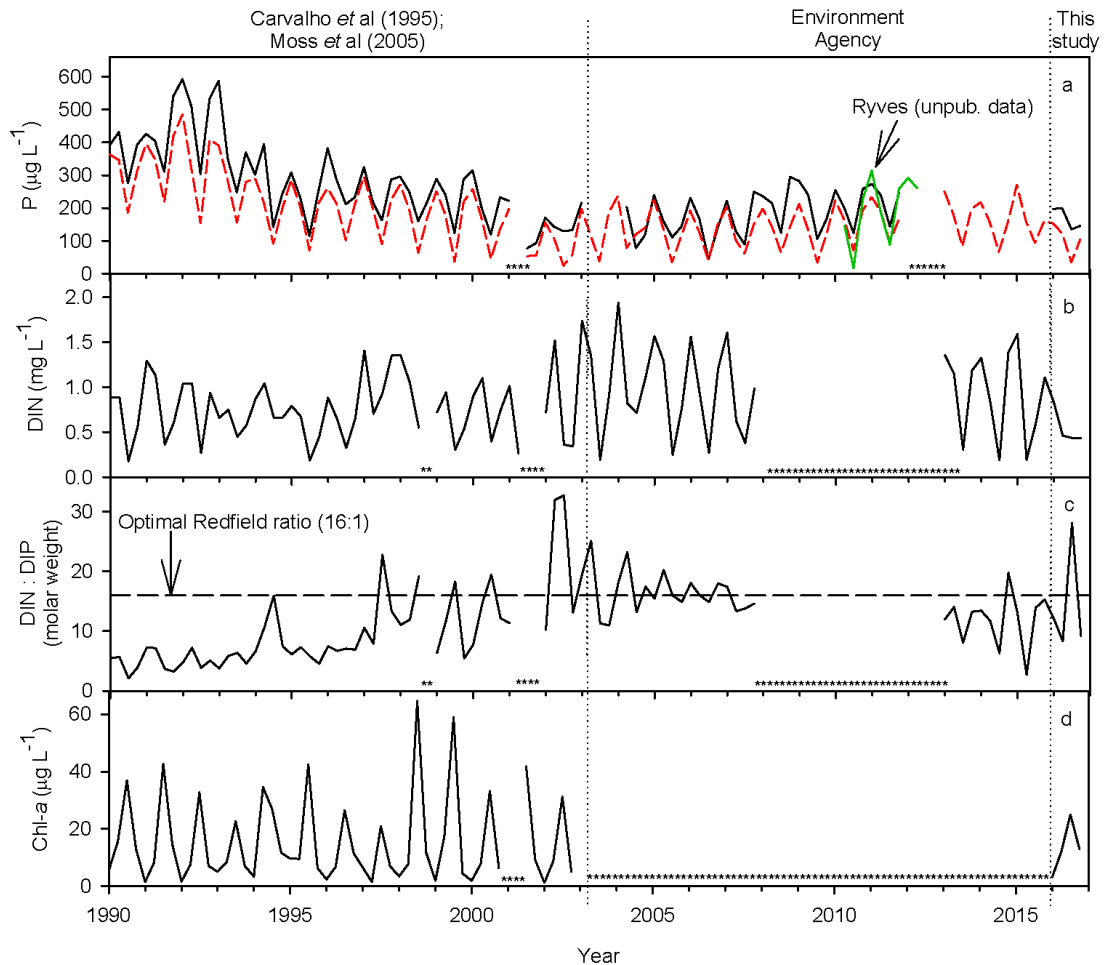


Figure 4.6. Seasonal nutrient, nutrient ratios and chl-a values at Rostherne Mere during the last 25 years. Data sources include Carvalho et al. (1995), Moss et al. (2005), Environment Agency and this study, with independent SRP data from 2010-12 confirming data reliability from D. B. Ryves. Dashed red line in 'c' signifies SRP. Asterisks signify unavailable data.

loading to the lake pre-STW diversion (933 kg TP; Table 4.2.) and the net export post-STW diversion (2140 kg TP; Table 4.2.). I use these corrected figures hereafter.

In comparison, the 2016 nutrient budget showed an almost identical TP external source total input as the post-STW diversion values in 1991-92 (1991-92 total external inputs 958 kg TP, 2016 total external inputs 959 kg TP; Table 4.2.), dominated by the inflowing load from the Rostherne Brook catchment (88-91%; Table 4.2.). These post-STW values are substantially reduced from the pre-STW diversion external inputs (1990-91 total external inputs 3999 kg TP; Table 4.2.), driven by inflow load (97% total external inputs; Table 4.2.). The outflow load between 1990-91 and 1991-92 did not

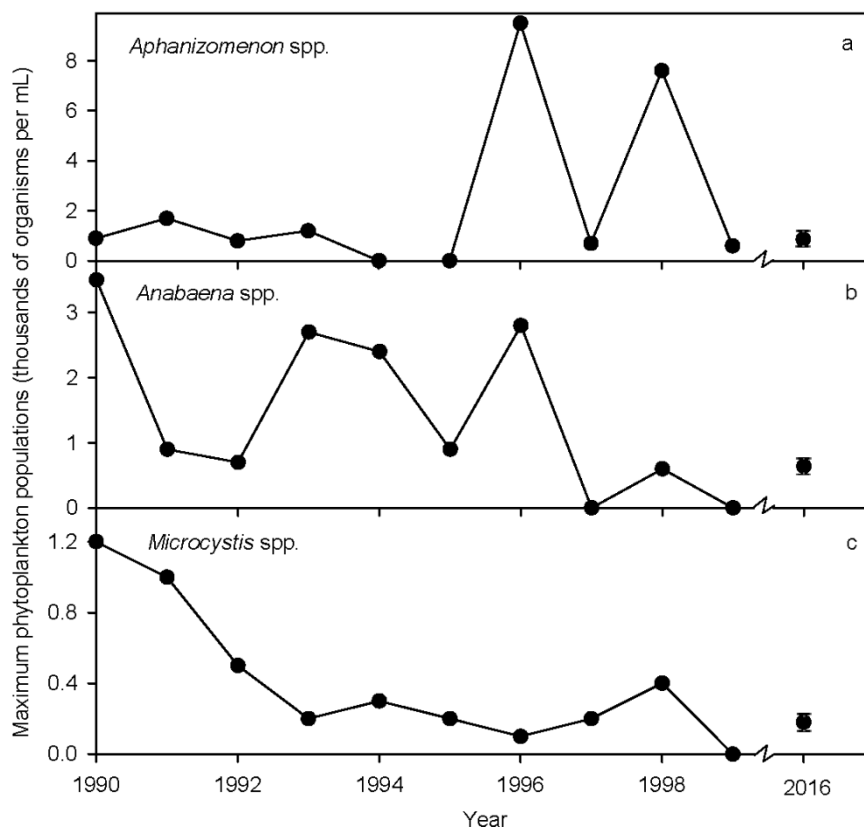


Figure 4.7. Maximum annual cyanobacteria populations for the three most abundant species. 1990s data taken from Moss et al. (2005), with 2016 data from this study.

fall in the same way as the inflow load, however, by 2016 the outflow load had substantially decreased (1991-92 outflow 3443 kg TP, 2016 outflow 1416 kg TP; Table 4.2.), resulting in a reducing net TP balance (i.e. loss of TP to the system, 1991-92 balance +2140 kg TP, 2016 balance +635 kg TP; Table 4.2.).

Nutrient, chl-a and phytoplankton change over the last 25 years

Following STW diversion upstream of Rostherne Mere, the concentration of in-lake P (TP and SRP) declined rapidly for approximately 11 years, with values stabilising to current levels (annual average $\sim 160 \mu\text{g P L}^{-1}$; Fig. 4.6c) from ~ 2002 , the end of the study period considered by Moss et al. (2005). With a reduction in the external TP loads following STW diversion (Table 4.2.), the annual replenishment of P at Rostherne Mere has been driven by internal sediment P loading, as evident in the 2016 water column TP profile (Fig. 4.5.). DIN showed seasonal peaks and troughs with no long-term trend in concentration change following STW diversion (Fig. 4.6b).

A trend of increasing DIN:DIP ratios highlights the stable DIN and decreasing P concentrations, with values over the last 25 years increasing from those suggestive of N limitation in the 1990s to those suggestive of P limitation, especially in the summer for some years (e.g. 2002-2004 and 2016; Fig. 4.6d). Chl-a showed annual peaks each summer, yet no change of note is seen in the 2016 data compared with the 1990s and early 2000s (mean annual chl-a: 1990-2003 = 15 $\mu\text{g L}^{-1}$, 2016 = 13 $\mu\text{g L}^{-1}$; Fig. 4.6a). However, long term trends in the chl-a data were difficult to assess due to a large period (2003-15) when data were not available.

Cyanobacterial summer blooms initially following STW diversion in 1991 showed a rapid decline in *Microcystis* spp. (Fig. 4.7c), a gradual decline in *Anabaena* spp. (Fig. 4.7b), and a consistent presence of *Aphanizomenon* spp. with two years of high abundance (1996 and 1998; Fig. 4.7a). Phytoplankton collections in 2016, showed summer phytoplankton communities still include the same cyanobacterial species at abundances consistent with earlier observations (Fig. 4.7.).

4.4. Discussion

Nutrient driven change: updated phosphorus budget 25 years post-STW diversion

To test the nutrient driven change, an updated nutrient budget for the Rostherne Mere catchment was calculated and the 25 year data set assessed for trends of change.

The P budget for Rostherne Mere calculated by Carvalho et al. (1995), likely underestimated the inflow and outflow of nutrient loads. High-resolution 5-minute stage height data collected during 2016 indicates the main inflow and outflow of the lake to have a high flow range. Therefore, previous water budget calculations without this high-resolution data have likely missed the variable flow at the lake, and have underestimated the nutrient load, by about 75%. Without correction of the previous nutrient flow values, the nutrient budget suggests the inflowing P load would have increased between 1992 and 2016 (Table 4.2.), which is unlikely given the history of continued action in the catchment to reduce agricultural nutrient inputs. However, the corrected nutrient loads show an identical inflow load as that estimated in 1992 (2.4 kg day^{-1} ; Table 4.2.). Although the correction factor is an estimate based on single year's WRT with a ~10% higher total annual precipitation, without considering the

influence of catchment saturation and run off rates (Moore, 2007, Marchi et al., 2010), it results in a similar estimation of catchment P loading following STW diversion, suggesting it is plausible.

The TP mass balance changes between pre-STW diversion, immediately post-STW diversion and 25-years post-STW diversion highlight the dynamic response of Rostherne Mere to management intervention (Table 4.2.). There was a rapid reduction in external TP load following STW diversion (3999 kg pre-STW diversion to 958 kg post-STW diversion; Table 4.2.), which has been sustained to present day with continued catchment management (959 kg; Table 4.2.). However, following STW diversion, the outflow load did not decrease in the same way as the inflow load, remaining at a similar value to the pre-STW diversion loads (3166 kg export pre-STW diversion, 3443 kg export post-STW diversion; Table 4.2.). This is a relic of the high lake nutrient load already *in situ*, leading to a higher net export of TP from the lake as seen in the change in lake value (-345 kg; Table 4.2.).

A key change in Rostherne Mere's P budget following STW diversion was the reduction of total inputs, yet a stable outflow load (Table 4.2.). Pre-STW diversion, Rostherne's TP balance suggests a large net burial of TP (-933 kg in 1990-91; Table 4.2.), yet following the reduction of inflow load post-STW diversion, the budget suggests a net loss from the system, initially very high (outflow load +2140 kg in 1991-92; Table 4.2.) but falling to a smaller, yet still substantial, net loss in more recent years (+635 kg in 2016; Table 4.2.).

The consistent export of P from Rostherne Mere since STW diversion is a result of the internal sediment P release that has replenished the lake P values annually at stratification overturn (Fig. 4.5.). This study finds during stratification in 2016 an accumulation of legacy P (maximum concentration $>800 \mu\text{g L}^{-1}$; Fig. 4.5) developed in the hypolimnion, while concentrations in the epilimnion dropped below detection levels (Fig. 4.3.a). As in many other such eutrophic and stratifying lakes, upon stratification overturn, the large legacy P load is diluted across the whole lake, replenishing available P and increasing lake SRP concentration to $\sim 250 \mu\text{g L}^{-1}$ (Fig. 4.2a), a common issue for lake management in deeper, stratifying lakes during oligotrophication (Jeppesen et al., 2005, Sharpley et al., 2013). Sediment P release in Rostherne Mere is high due to the strong stratification and anoxic conditions for a long

time period (~8.5 months thermal stratification with anoxia within ~3 weeks of stratification onset; Scott, 2014), with anoxia promoting the sediment release of iron-bound P for replenishment into the water column (Nurnberg, 1984). This morphometrically-enhanced anoxic release, linked with a long history of eutrophication sedimenting large quantities of P-rich organic matter for over a century (see chapter 3; Radbourne et al., 2017), means there is a large accumulation of P in the sediment that can be released over a long time-frame. From a management intervention perspective, the consistent net export of P since STW diversion, although serving the purpose of reducing in lake TP for lake recovery, will have significant implications for regional eutrophication problems downstream of the lake and nutrient flux to the coastal zone (Zhang et al., 2012, Soranno et al., 2015, Buquet et al., 2017).

In their study reviewing the initial 11 years following STW diversion at Rostherne Mere, Moss et al. (2005) showed after an initial 2-year increase in maximum P values, likely due to the impact of catchment disturbance from the STW diversion (i.e. engineering groundworks in the catchment), a rapid decline in in-lake P values followed, with the rate slowing towards the end of the study in 2002 (Fig. 4.6c). This study suggests the slowdown in recovery witnessed previously was the start of a stabilisation of in-lake P concentrations, with annual P replenishment sustained by the internal sediment legacy P (Fig. 4.5.). The stabilisation of in-lake P concentrations shortly after the diversion of the major point source nutrient load is a concern for management practitioners. While the recovery from extremely high P concentrations pre-STW has been successful, with a reduction in total external inputs from 3999 kg in 1990 to 959 kg in 2016 (Table 4.2.), further reductions in nutrient concentrations have not happened, leaving Rostherne Mere still classified as highly eutrophic and far outside management targets. Yet, this is not an unusual scenario, with other deep stratifying lake systems undergoing managed catchment nutrient recovery having shown a comparable stabilisation of annual in-lake P concentrations, similarly driven by major internal legacy source contributions (Jeppesen et al., 2005, Jarvie et al., 2013b), far above target levels.

The 25-year DIN concentrations at Rostherne Mere show no trend of change following STW diversion (Fig. 4.6b). Therefore, with a reduction in P over this time (Fig. 4.6c) there has been a shift in the DIN:DIP ratio (Fig. 4.6d), from the previously suggested potential for N limitation (i.e. 1990-1994; as previously suggested by Moss et al., 1997), to a potential summer P limitation, especially in certain years (i.e. 2002-04 and

2016; Fig. 4.6d). This change in available nutrients during the summer months can directly influence the lake phytoplankton assemblage causing cascading impacts across the lake ecosystem. At Rostherne Mere a change in algal community is evident with the abundance of *Anabaena* spp. and *Microcystis* spp. blooms (Fig. 4.7.) declining in line with the reducing lake P concentrations (Fig. 4.6.), as has been found in other experimental and observation studies (De Nobel et al., 1997, Downing et al., 2001, Ghaffar et al., 2017). However, chl-a showed little change over this time (Fig. 4.7.), possibly due to the impact of climate change offsetting the decline driven by nutrients as has been found in other systems such as Loch Leven (Carvalho et al., 2012). Reynolds and Bellinger (1992) suggested that a reduction in light as an influence of self-shading from high biovolume production, has an important limiting effect on summer algal blooms in Rostherne Mere, especially for *Microcystis*. However, this study was conducted during the time of extremely high nutrient concentrations in the 1970s and 1980s, when total algal biovolume production was higher (evident in higher organic carbon burial rate in chapter 3; Radbourne et al., 2017) and nutrient depletion (of P) would not have been a potential limiting factor. During 2016, secchi depth results do not show any relationship to changing abundances of phytoplankton species (Fig. 4.3.), therefore is unlikely to still be a major driver of species limitation in Rostherne Mere.

In summary, the diversion of the STW nutrient load from Rostherne Mere resulted in a nutrient driven change in lake system functioning throughout the 1990s and early 2000s, through reduced summer and autumn epilimnion P concentrations, altering the DIN:DIP ratios from an N limitation to a predominant summer P limitation, adjusting the seasonal dominance present in the summer cyanobacterial blooms. However, from ~2003, the total annual nutrient concentrations have stabilised with a slight return to a predominant N limitation, yet with changes in seasonal nutrient availability and algal communities there are instances of P limitation (e.g. 2016), suggesting Rostherne to be in a quasi-stable state (see chapter 5).

Climatic driven change: the impact of increasing flushing efficiency

There is evidence that climate has driven physical limnological change altering the stratification and flushing rates within the lake. Rostherne Mere during the last 43 years has undergone warming, and like many other lakes globally (Williamson et al.,

2009b) has dynamically responded to this warming through physical limnological change. Predominantly, Rostherne Mere's stratification has extended through a delay in the autumnal overturn date. Changing stratification timing is a common feature under global warming for deep freshwaters, with previous studies showing a change in timing as stratification onset becomes earlier in the year (Thackeray et al., 2008, Meis et al., 2009) and an increasing duration of stratification (Liu et al., 2014, Izmet'eva et al., 2016).

As mentioned above, the flushing rate of Rostherne Mere is much faster than was previously thought, to the extent that stratification is longer than the WRT_m (i.e. available water column flushing rate), thus the lake has the potential to completely flush the epilimnion each summer. Therefore, with the reduced nutrient (P) concentrations in the inflow following management intervention, there is the potential for P limitation in late summer. Additionally, an increase in stratification length, as a result of climatically forced change, will extend the period of nutrient depletion, altering the cycling and availability of nutrients during the latter (autumn) growing season and impacting lake ecology.

The 2016 monitoring data highlight the importance of nutrient flushing at Rostherne Mere, with high early year concentrations being diluted by flushing out of the system and algal uptake. Nutrient draw down and flushing is substantial, with the available P concentration falling rapidly (DIN remains higher due to inflow load replenishment), resulting in a spike in the DIN: DIP ratio. The rapid reduction of available P in the epilimnion over summer is shown to impact algal development and timing, with cyanobacterial blooms of *Aphanizommon* spp. and *Anabaena* spp. beginning while the DIN:DIP ratios are near optimal Redfield ratios, yet ending when the ratio exceeds ~30:1 due to a reduction in the available P.

The process of Rostherne Mere becoming P limited during 2016 is driven largely by the importance of the efficient flushing rate and low concentrations of P in the managed inflow. Comparison of the sizable range in TP concentrations at Rostherne Mere to other similar lakes highlights the remarkable drop in of TP in the epilimnion in the early part of the year (Fig. 4.4.). Annual average chl-a values are below those expected when assessed against annual average TP concentrations (i.e. including winter high; Fig. 4.4a), yet fall within an expected range when only the available summer TP

concentrations are included (Fig. 4.4b), supporting the inference of nutrient dilution from increased flushing rates (i.e. disparity of high annual and low summer TP concentrations) and potential summer TP limitation (i.e. fitting within expected summer TP to chl-a ratio).

The findings of this study have major implications for other stratifying, eutrophic lakes given future climatic projections. If the current projections of climatic warming come to pass (Murphy et al., 2009), it will have a direct impact on Rostherne's physical limnology (Williamson et al., 2009b), resulting in a change in stratification timing and length that will lead to longer summer and autumn periods of nutrient depletion, as has been seen in this study. Lakes that have shown an inclination to alter to an earlier onset of stratification, such as Windermere (Thackeray et al., 2008), will flush and utilise the available nutrient loads earlier in the growing season, resulting in greater limitation of summer algal blooms, potentially causing cascading effects on ecological succession. Lakes that tend to extend their stratification later into autumn, as seen at Rostherne Mere in this study, will show a longer depletion of available nutrients later into the year, delaying autumnal blooms (e.g. diatom blooms) potentially to an extent where other factors such as ambient (seasonal) light may become an important factor in limiting bloom development.

In summary, climate has impacted Rostherne Mere's physical limnology over at least the last 43 years, shifting the timing and length of stratification, resulting in an adjustment of the nutrient cycling and availability, which in turn has impacted the seasonal ecological production, causing changes in the algal bloom size, timing and dominance.

4.5. Conclusions

Nutrient loads have long been understood to have a key role in driving ecological change and this assumption is found to be correct here too. Yet this study also demonstrates that climate change is also having an impact on deep, stratifying eutrophic lakes, especially those undergoing catchment management intervention such as Rostherne Mere, with climate altering the physical limnology and flushing patterns, influencing the cycling and availability of nutrients for biological uptake. The climatic influence on the lake ecology, although potentially having an impact for

decades, is only clearly evident since nutrient load stabilisation following STW diversion, with the large nutrient concentration reduction being the major driver of change initially following management intervention.

5. Climate perturbations modulate planktonic diatom communities and phenology in a reduced nutrient loading deep lake

5.1. Introduction

Anthropogenic activity and climate change are altering aquatic ecosystems globally. Human impacts have driven lake systems into potentially irreversible state change (Butzer, 2015, Mills et al., 2017), with nutrient loading causing whole ecosystem change in many lake systems (Jeppesen et al., 2005, Moss et al., 2005, Anderson et al., 2014). More recently the impacts of climate, together with nutrient enrichment (or reduction: oligotrophication), has been increasingly cited as a major cause of further change (Thackeray et al., 2008, Battarbee et al., 2012, Flaim et al., 2016). Gradual (decadal-scale) climatic warming and greater variability in seasonal weather extremes, are both leading to rapid changes in physical and ecological state in aquatic systems across the globe, especially those that have become progressively more sensitive from historical nutrient loading, (Ruhland et al., 2015, Yamoah et al., 2016, Bertani et al., 2016). The increasing frequency and intensity of climatological and meteorological extreme variability (Easterling et al., 2000, Ekstrom et al., 2005, Jones et al., 2013) is being reflected in freshwater systems, adjusting thermal regimes and physical processes (such as stratification), in turn causing shifts in planktonic ecological organisation (Hausmann and Pienitz, 2007, Meis et al., 2009, Kirilova et al., 2011, Elliott, 2012b). Therefore, if the trend of increased climatic perturbation continues throughout the 21st century, it is important to understand how lake systems will respond dynamically from both ecological and management perspectives (Battarbee et al., 2012, Bertani et al., 2016).

Diatoms as an algal group are a well-used biological proxy for ecological and physical change in lake systems and provide key insight into patterns of primary production critical for lake ecosystem functioning (Battarbee et al., 2001). These ubiquitous ecological indicators show strong species response to changes in their environment (Smol and Stoermer, 2010), with temperate lake blooms tending to show seasonal peaks in the spring and autumn (Winegardner et al., 2014) linked to light, nutrients (mainly N, P and Si) and stratification in deep lakes (Wang et al., 2015). Their morphologically diverse silica valves generally preserve well in lake sediments and

enable identification to species level (Battarbee et al., 2012) and have broad application in reconstructing ecological responses to climate change and trophic status on both contemporary (10^{-1} to 10^1 yr) and long-term (10^1 to 10^5 yr) timescales (Bigler et al., 2007, Thackeray et al., 2008, Battarbee et al., 2012, Wang et al., 2015, Beck et al., 2016).

This study assesses temporary state changes in the seasonality of planktonic diatom assemblages using sediment traps at Rostherne Mere, a eutrophic, deep, stratifying UK lake undergoing oligotrophication over the last 25 years, for a six-year period between 2011 and 2016. Short term (seasonal/inter-annual) meteorological and climatic perturbations are assessed for their impact on trap sediment capture and diatom assemblage change, especially in relation to an extreme high summer precipitation in 2012 and changes to stratification over the 6 year period.

5.2. Methodology

Sample collection and analysis

Sediment trapping using sequencing traps was carried out at Rostherne Mere from January 2011 to January 2017. Technicap PPS 4/3 automatic sequencing traps (<http://www.technicap.com/>; 1310 mm length, $\varnothing 252$ mm internal diameter, 1:5.1 trapping ratio, 0.05 m^2 trapping area) were deployed in a central lake location at 10 m and 25 m water depths, sequentially opening into 12 individual 250 ml HDPE bottles, each representing a ~2 week collection period (in January and February longer collection periods of 3-4 weeks were used). The traps were reset every ~6 months as dictated by the trapping interval used, with trap sediment kept cool, dark and sealed during transport to the laboratory where it was stored frozen prior to analysis. All trap samples were freeze-dried prior to analysis and weighed for total trap sample dry sediment flux.

All samples were analysed for organic matter (OM) and CaCO_3 using sequential loss-on-ignition, where OM was calculated by weight-loss after 3 hrs at 550°C and CaCO_3 by weight-loss after 3 hrs at 925°C (Dean, 1974). Minerogenic flux (F_m) was calculated as: $F_m = \text{Total trap flux} - \text{OM flux} - \text{CaCO}_3 - \text{biogenic silica flux}$, with biogenic silica content estimated using diatom biovolume converted with a density $\sim 2 \text{ g cm}^{-3}$

(DeMaster, 2003, Sañé et al., 2013). Percentage organic carbon (%OC) was calculated from %OM using a lake-specific conversion factor ($\%OC = \%OM \cdot 0.56$) estimated from analysis of 20 sediment samples with a range of 14-65 %OM (A. Radbourne, unpublished data) with total OC determined via mass-spectrometry elemental analysis.

Freeze-dried sediment was prepared for diatom analysis using standard methods (Renberg, 1990, Battarbee et al., 2001) with material being left overnight in the concentrated H_2O_2 solution at room temperature, as labile algal organic matter reacted violently if heated before this time. Additionally, a known quantity of microspheres was added to the cleaned diatoms before slide preparation (Battarbee and Kneen, 1982). Microspheres and at least 300 diatom valves per slide were identified following standard methods (Battarbee et al., 2001), with percentage valve breakage categorised into 4 classes (as 100% intact, >0.75, >0.5 or >0.25; valves <0.25 were not counted) and valve dissolution recorded using the pristine/dissolved binary scheme (**F** index; Ryves et al., 2003, Ryves et al., 2006). If a minimum of 100 microspheres was not reached by the 300th diatom valve, counting was continued (without species identification) until 100 microspheres was reached. Total diatom abundance was calculated from relative percentage counts to known microsphere abundances using methods outlined in Battarbee and Kneen (1982). Diatom biovolume was calculated for taxa >3% abundance in an individual sample. Biovolume calculations followed methods outlined in Hillebrand et al. (1999), with 25 representative examples from a range of slides measured to determine a mean biovolume figure for each taxon (Table 5.1.).

Limnological and meteorological data

Average daily air (2 m above water level) and water temperatures (at 12 depths, every 2 m between 2 m to 24 m) were taken from the UKLEON buoy for the study period (2011-2016). Lake thermal analysis was conducted as whole lake (mean temperature of all 12 thermistor depths), epilimnion average (mean temperature of 2, 4 and 6 m during stratification) and hypolimnion average (mean temperature of 18, 20, 22 m during stratification). The date of stratification onset was taken as the day a >3% difference in epilimnion and hypolimnion temperature develops and is maintained

Table 5.1. Mean cell biovolume of common taxa at Rostherne Mere from 25 representative examples calculated using method provided in Hillebrand et al. (1999).

Taxon	Biovolume (μm^3)
<i>Amphora pediculus</i>	50.5
<i>Asterionella formosa</i>	380.4
<i>Aulacoseira ambigua</i>	562.1
<i>Aulacoseira granulata</i>	636.8
<i>Aulacoseira subarctica</i>	401.5
<i>Cocconeis placentula</i> var. <i>euglypta</i>	942.9
<i>Cyclostephanos dubius</i>	134.7
<i>Cyclostephanos tholiformis</i>	243.2
<i>Cyclotella atomus</i>	76.6
<i>Cyclotella meneghiniana</i>	368.2
<i>Cymbella silesiaca</i>	355.3
<i>Cymbellonitzschia diluviana</i>	55.0
<i>Denticula elegans</i>	1225.2
<i>Fragilaria bidens</i>	317.3
<i>Fragilaria brevistriata</i>	108.2
<i>Fragilaria crotonensis</i>	434.3
<i>Fragilaria lapponica</i>	57.2
<i>Gomphonema olivaceum</i>	206.6
<i>Gyrosigma nodiferum</i>	2429.4
<i>Navicula angusta</i>	1172.4
<i>Navicula capicata</i>	185.9
<i>Navicula pupula</i>	256.5
<i>Navicula rhynchocephala</i>	364.5
<i>Navicula seminulum</i>	84.8
<i>Nitzschia lanceolata</i>	135.0
<i>Nitzschia recta</i>	701.3
<i>Stephanodiscus hantzschii</i>	398.2
<i>Stephanodiscus neoastraea</i>	4180.1
<i>Stephanodiscus parvus</i>	94.7

throughout the summer, with stratification end taken as the first day the difference in epilimnion and hypolimnion temperatures drop to a <3% range. The relative resistance to thermal mixing (RTRM) was calculated using standard water temperature to density methods (see Wetzel, 2001) with the total strength of stratification being the difference between the average epilimnion density and average hypolimnion density.

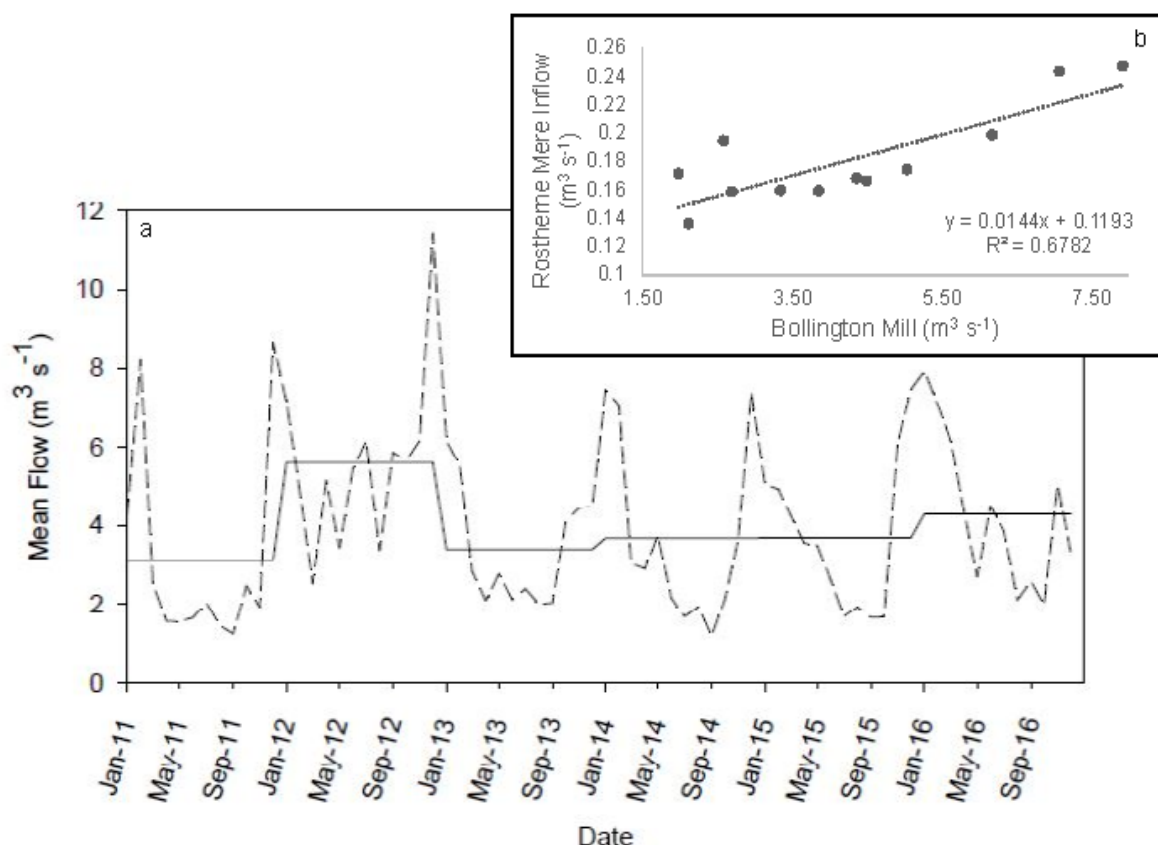


Figure 5.1. a) Mean monthly (dashed line) and annual (solid line) flow data from an Environment Agency flow station, Bollington Mill, 3.2 km downstream from Rostherne Mere. b) 2016 monthly mean flow ($\text{m}^3 \text{s}^{-1}$) of Rostherne Mere (inflow) and Bollington Mill.

Precipitation and wind speed data used the closest reliable meteorological station (Manchester Airport, UK; situated 4.6 miles north-east of Rostherne Mere). Wind speed at the airport (V_{MA}) was corrected for local sheltering (V_{RM}) through comparison to the available partial study period wind speed data from the UKLEON buoy (comparable data from February 2013 to January 2017; correction factor of $V_{\text{RM}} = 0.55V_{\text{MA}} - 0.12$, $R^2 = 0.82$, $n = 1417$, $p < 0.001$). Soluble reactive phosphorus (SRP) and dissolved silica (Si) were obtained for January 2011 to April 2012 from a separate study conducted by D.B. Ryves and from January 2016 onward as part of this study's wider objectives, with only SRP available between April 2012 to December 2015 from the Environment Agency.

To ascertain flow rate (discharge) into and out of Rostherne Mere, discharge was estimated by measuring the cross-sectional profile and the sectional velocities for the main inflow (Rostherne Brook, draining ~80% of the catchment) and the outflow

(Blackburn's Brook) over a range of stage heights during 2016. This discharge / stage relationship was applied to continuous stage height recordings taken throughout 2016 from Rostherne Brook and Blackburn's Brook using a Van Essen mini-diver data logger (www.vanessen.com) recording water pressure every 5 minutes, corrected to changes in air pressure by a barometer located in the boat house. Application of the measured discharge to height relationship of the mini-diver data provides a high-resolution total discharge measurement for both the inflow and outflow. An adjusted water residence time (WRT_m ; see chapter 4) method was used to estimate the residence time of the mixed part of the water column for 2016, calculated as the monthly average outflow rate against the monthly available mixed lake volume (during the stratified period from April to November, the epilimnion, but during the mixed period from December to March, the entire lake). Flow data from a nearby Environment Agency flow station at Bollington Mill (reference number 69045; 3.2 km downstream of Rostherne Mere; data for 2011 – 2016 available; Fig. 5.1a and 5.1b) was used to generate a monthly difference factor between 2012 and the 2011-2016 mean flow rates, and applied to monitored 2016 flow rates to estimate WRT_m during 2012.

5.3. Results

Sediment trap flux and diatom assemblages

Diatom assemblages showed two seasonal peaks each year, in spring and autumn (Fig. 5.2a), with clear seasonal distinction between spring and autumn species' composition. Spring each year began from similar conditions, dominated by *Asterionella formosa* Hassall (Fig. 5.2b) and/or *Stephanodiscus parvus* Stoermer & Håkansson (Fig. 5.2d), with smaller blooms of *Stephanodiscus neoastraea* Håkansson & Hickel (Fig. 5.2c). Autumn was more varied with dominance by *Aulacoseira granulata* Simonsen (Fig. 5.2e), *Cyclostephanos dubius* Round (Fig. 5.2f) and/or *Cyclostephanos tholiformis* Stoermer, Håkansson & Theriot (Fig. 5.2g). Inter-annual variability in diatom blooms was great. *Asterionella formosa* was abundant in the spring (March to May) of 5 of the 6 study years (>55% abundance), but only reached a maximum of <10% in 2012 (Fig. 5.2b). *Stephanodiscus parvus* showed a

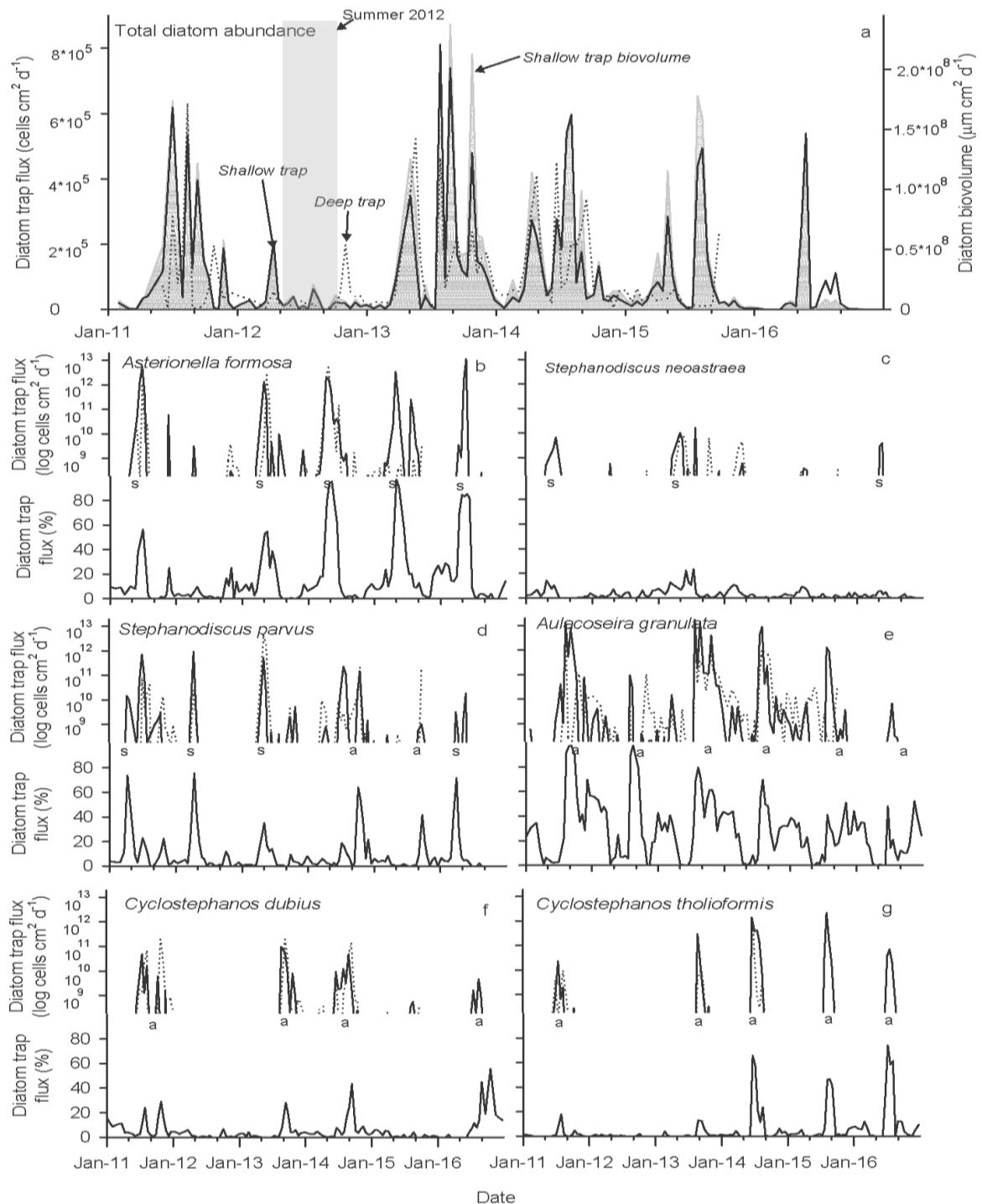


Figure 5.2. High-resolution sediment trap diatom assemblages. a) total diatom trap flux (shallow trap: solid black line; deep trap: dashed black line; valves $\text{cm}^{-2} \text{d}^{-1}$) and diatom biovolume flux (filled area; $\mu\text{m}^3 \text{cm}^{-2} \text{d}^{-1}$), with summer of 2012 highlighted by shaded area. b-g) Six most abundant individual diatom taxa total flux (upper; $\ln(x)$ valves $\text{cm}^{-2} \text{d}^{-1}$) for shallow trap (solid line) and deep trap (dashed line) and percentage taxon flux for the shallow trap (lower; % sample abundance). Label s = spring bloom, label a = autumn bloom b) *Asterionella formosa*, c) *Stephanodiscus neoastraea*, d) *Stephanodiscus parvus*, e) *Aulacoseira granulata*, f) *Cyclostephanos dubius*, g) *Cyclostephanos tholiformis*.

Table 5.2. Annual average shallow and deep trap flux. Total organic carbon (OC) flux, total diatom flux, total diatom biovolume estimate and minerogenic flux, with average annual diatom dissolution (pristine) and diatom breakage (unbroken).

Year	Shallow trap					
	OC flux (g m ⁻² d ⁻¹)	Diatom abundance (valves 10 ⁵ cm ⁻² d ⁻¹)	Diatom biovolume (µm 10 ⁷ cm ⁻² d ⁻¹)	Diatom dissolution (fraction pristine)	Diatom breakage (% unbroken)	Minerogenic flux (g m ⁻² d ⁻¹)
2011	2.1	1.5	4.7	0.61	52.1	0.5
2012	2.0	0.3	0.8	0.48	33.5	1.1
2013	3.8	1.6	5.9	0.57	42.6	0.6
2014	4.3	1.4	4.5	0.55	45.3	0.9
2015	2.7	0.8	3.0	0.77	64.7	0.8
2016	3.9	0.5	1.0	0.85	78.8	0.9
<i>Study mean</i>	3.1	1.0	3.3	0.64	52.8	0.8
Year	Deep trap					
	OC flux (g m ⁻² d ⁻¹)	Diatom abundance (valves 10 ⁵ cm ⁻² d ⁻¹)	Diatom biovolume (µm 10 ⁷ cm ⁻² d ⁻¹)	Diatom dissolution (fraction pristine)	Diatom breakage (% unbroken)	Minerogenic flux (g m ⁻² d ⁻¹)
2011	-	-	-	-	-	-
2012	2.5	0.3	1.1	0.53	40.3	1.3
2013	4.0	1.4	5.0	0.58	42.9	1.1
2014	3.5	1.4	5.8	0.56	44.6	0.5
2015	1.6	0.4	1.7	0.56	45.5	1.1
2016	-	-	-	-	-	-
<i>Study mean</i>	2.9	0.9	3.4	0.56	43.3	1.0

dominant early season trap capture in 2011 and 2012 (>70%), appearing later in spring/early summer of 2013 (<35%), then switching timing to autumn in 2014 and 2015, before returning to a principle trap capture in the early spring of 2016 (>70%; Fig. 5.2d). Autumn variability at the start of the study was driven by the substantial trap capture of *A. granulata* in 2011 to 2013, when importance began to decline (>90% in 2011 & 2012, <48% in 2016; Fig. 5.2e), in favour of *C. dubius* (~44% in 2014 & 2016; Fig. 5.2f) and the increasing prevalence of *C. tholiformis* (>70% in 2016; Fig. 5.2g).

During the six-year study period, annual OC flux ranged from 2.0 g m⁻² d⁻¹ in 2012, to 4.3 g m⁻² d⁻¹ in 2014 (Table 5.2.). Annual mean minerogenic flux also varied from 1.1 g m⁻² d⁻¹ in 2012 to 0.5 g m⁻² d⁻¹ in 2011 (Table 5.2.). The annual average shallow trap total diatom flux ranged greatly, from 0.3•10⁵ valves cm⁻² d⁻¹ (2012; Table 5.2.) to 1.6•10⁵ valves cm⁻² d⁻¹ (2013; Table 5.2.), with a study period mean of 1.0•10⁵ valves

$\text{cm}^{-2} \text{d}^{-1}$ (Table 5.2.). Diatom biovolume flux co-varied with diatom valve flux, with relatively higher biovolume in 2013 and 2015 due to the presence of larger sized taxa (see Table 5.1. and Table 5.2.). Diatom preservation (higher **F** index and lower % of broken valves) was generally good, especially in the upper trap, as expected (Ryves et al., 2003), and was also poorest in both traps in 2012 (Table 5.2.). The shallow and deep traps showed good agreement in annual flux totals (Table 5.2.) and in temporal patterns, even at high-resolution (2 weekly intervals) (Fig. 5.2a). In two of the four years (2012 and 2013), when both shallow and deep trap data were available, the deep trap had higher sediment and diatom fluxes, which is presumed to be as an influence of sediment resuspension and sediment focussing into the deep traps, as previously noted by Radbourne et al. (2017) (see chapter 3) and as expected from the morphometry of Rostherne Mere (Hilton, 1985, Hilton et al., 1986).

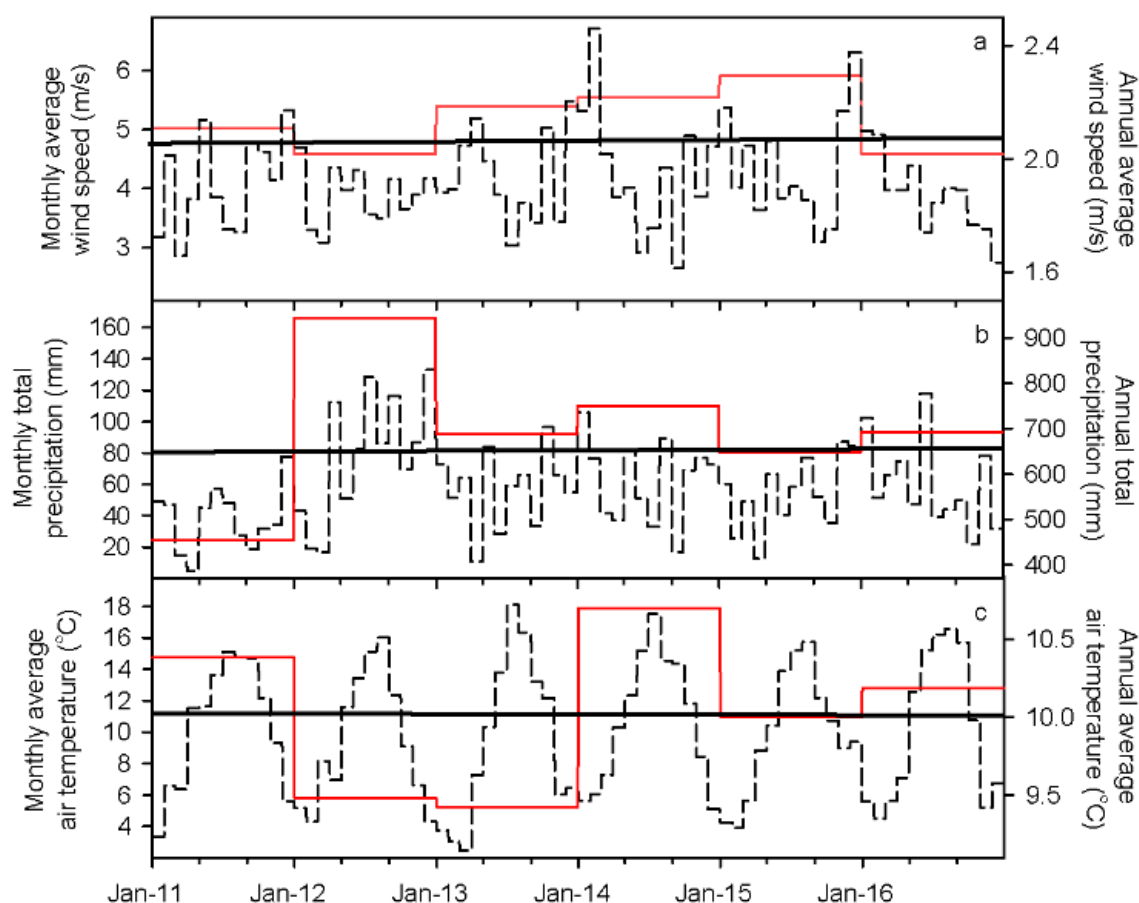


Figure 5.3. Climate data at Rostherne Mere for study period (2011-2016). Monthly mean dashed black line, annual mean solid red line and 30-year mean solid black line, for; a) wind speed (m s^{-1}), b) total precipitation (mm), c) air temperature ($^{\circ}\text{C}$).

Table 5.3a. 2016 WRT_m. Flow calculated from monitoring campaign data and monthly mixed water volumes estimated using UKLEON thermistor data.

Month	Available volume (L · 10 ⁹)	Outflow rate (L yr ⁻¹ · 10 ⁸)
January	6.9	7.5
February	6.9	7.0
March	4.7	3.4
April	2.7	3.7
May	2.8	6.2
June	3.0	6.2
July	3.1	6.7
August	3.3	6.8
September	3.4	6.4
October	3.7	6.4
November	4.3	7.1
December	6.9	8.2
<i>Annual</i>	<i>4.3 (mean)</i>	<i>75.4 (sum)</i>
WRT_m (yr)	0.57	

Table 5.3b. Estimated 2012 WRT_m. Flow estimated from the difference in 2012 flow to study period mean at a nearby Environment Agency river flow station and applied as a monthly factor to monitored 2016 data. Water volumes estimated using UKLEON thermistor data.

Month	Available volume (L · 10 ⁹)	Outflow rate (L yr ⁻¹ · 10 ⁸)
January	6.9	8.6
February	6.9	5.1
March	6.5	2.3
April	2.7	6.5
May	2.8	7.5
June	3.0	12.9
July	3.1	17.6
August	3.3	12.2
September	3.4	21.4
October	3.7	14.6
November	4.3	10.3
December	6.9	15.0
<i>Annual</i>	<i>4.5</i>	<i>134.0</i>
WRT_m (yr)	0.34	

Meteorological data

Wind speeds showed an expected seasonal progression with higher wind speeds over winter and calmer periods during summer (Fig. 5.3a). Average air temperatures also showed a seasonal progression, with a range of annual average temperatures from 9.4 °C (2013; Fig. 5.3c) to 10.7 °C (2014; Fig. 5.3c). Monthly and annual total precipitation varied, with 2012 total precipitation values (945 mm) being 36% higher than the study period mean (697 mm) and 41% higher than the 30-year mean (669 mm; Fig. 5.3b). Correlation of the 2016 Rostherne Mere monitored inflow rates to the Bollington Mill data (Fig. 5.1a and 5.1b), enabled the estimation of the higher flow rates that would have been experienced at Rostherne Mere during the wetter year of 2012. Application of this higher discharge rate to the WRT_m method implies that flushing rate was much faster in 2012 (0.34 years, ~4 months; Table 5.3b), compared to that calculated for 2016 (0.57 years, ~7 months; Table 5.3a).

Table 5.4. Stratification onset and overturn date taken from UKLEON buoy thermistor records. Day of year in brackets (Jan 1st = day 1). March epilimnion temperature difference from study period mean.

Year	Stratification Onset	Stratification Overturn	Total Days of Stratification	Mean difference March epilimnion temperature
2011	13-Mar (72)	14-Nov (318)	246	0.6
2012	28-Mar (88)	21-Nov (326)	238	0.4
2013	11-Apr (101)	22-Nov (326)	225	-2.0
2014	30-Mar (89)	24-Nov (328)	239	0.9
2015	02-Apr (92)	24-Nov (328)	236	-0.3
2016	11-Mar (71)	21-Nov (326)	255	0.7

Lake physical and nutrient data

Lake water column temperatures clearly showed the seasonal patterns in the timing, development and strength of stratification (Fig. 5.4c) Upper water temperature followed that of air temperature (Fig. 5.3c), with bottom water temperatures showing a similar annual cycle of warming and cooling (Fig. 5.4c). Stratification onset day varied throughout the 2011-2016 study period (range 31 days from 11th March to 11th April; Table 5.4.), with stratification overturn around a similar 10-day period in mid to late November (Table 5.4.). The earliest onset of stratification was seen in years with

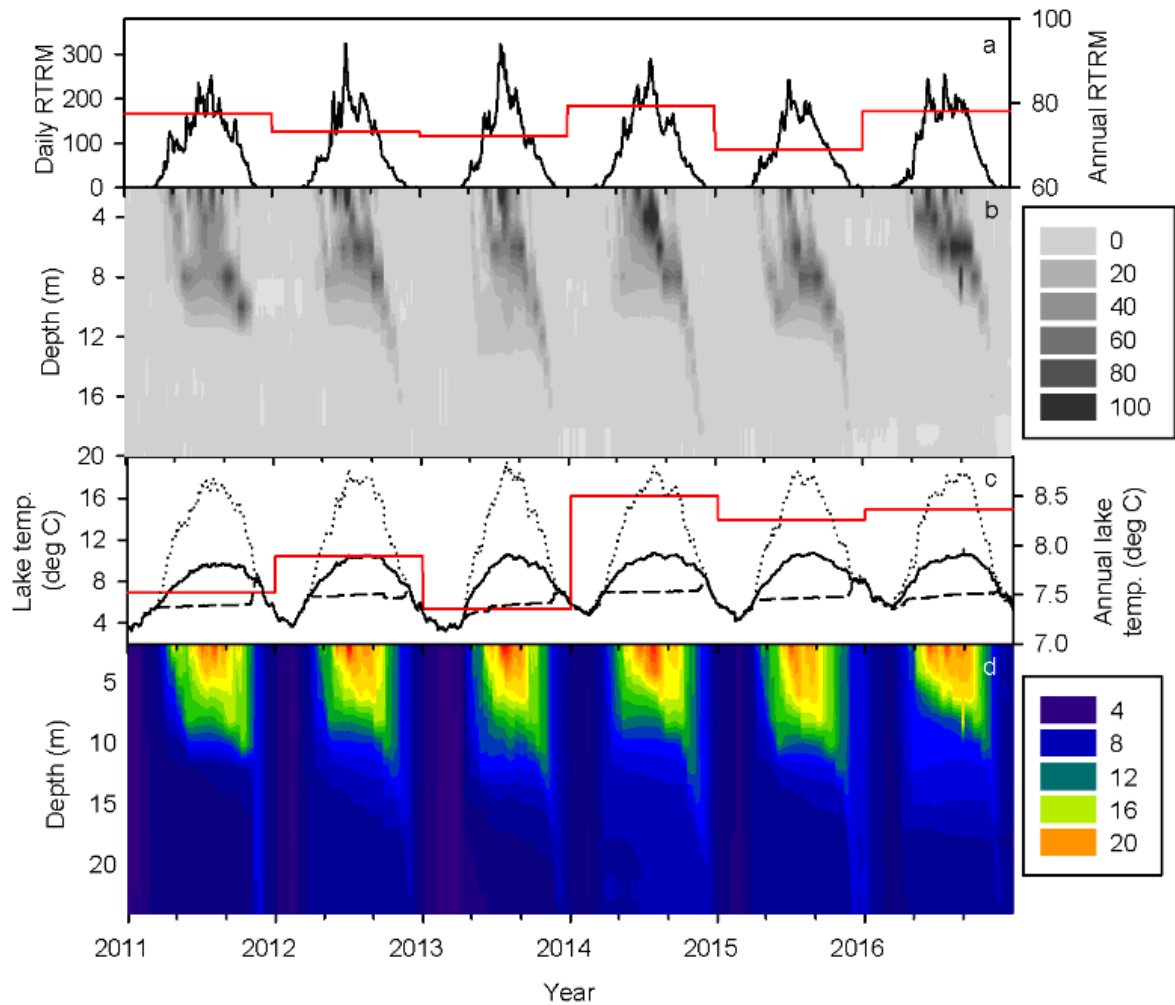


Figure 5.4. Water column temperatures and relative thermal resistance to mixing (RTRM) for study period (2011-2016). a) Mean daily and annual RTRM, b) water column density profile, c) mean daily lake temperatures for the whole lake (solid black line), epilimnion (dotted line), hypolimnion (dashed line) and mean annual whole lake temperature (solid red line), d) daily water column temperature.

a warmer late winter / early spring upper water column temperatures (e.g. 2011 and 2016; Table 5.4.), with the later onset of stratification corresponding to colder late winter / early spring temperatures (e.g. 2013 and 2015; Table 5.4.).

Lake RTRM showed an increase each spring to a maximum in summer, representing a strong stratification (>100 RTRM), before reduction during autumn to zero RTRM (mixed) at stratification overturn (Fig. 5.4a). In-lake RTRM values through the water column highlight the strong stratification each year, with the metalimnion forming around 7 m depth and gradually deepening through the summer to around 12 m depth,

allowing a small amount of nutrient replenishment from the deeper waters, before rapid breakdown of stratification and overturn (Fig. 5.4b).

Lake nutrient concentrations showed an annual cycle of depletion throughout the summer and replenishment during the winter (Fig. 5.5.). Si data were only available for selected times of the study period, but show a similar seasonal depletion and replenishment in the years data were available (Fig. 5.5a). SRP in the summers of 2013, 2014 and particularly in 2016 reached the lowest concentrations observed over the 6 years, with summer concentrations remaining relatively high ($>50 \mu\text{g L}^{-1}$) during the other study years (Fig. 5.5b). Si:SRP ratios emphasise the lower SRP values towards the end of this study (2016), compared to the early study period (2010-11; Fig. 5.5c), but Si:SRP data are not available from April 2012 to January 2016.

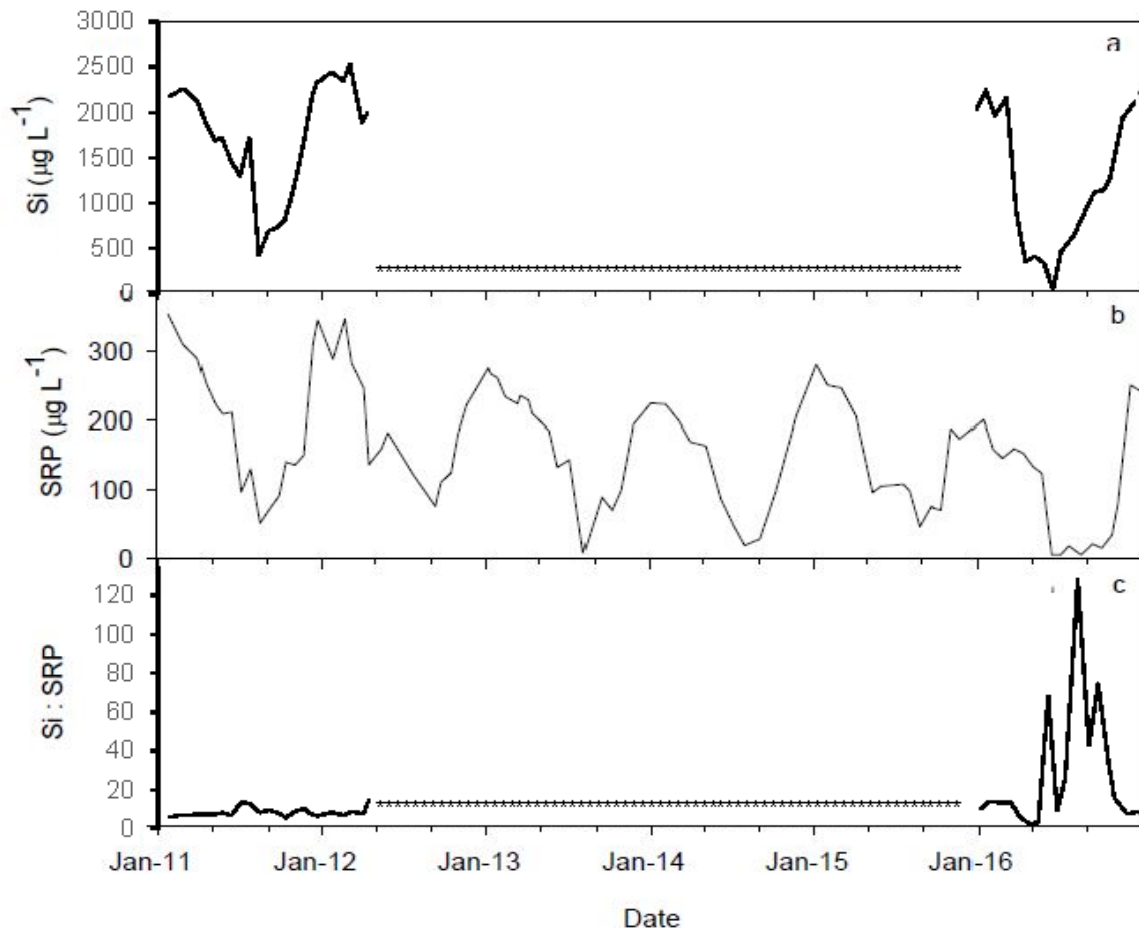


Figure 5.5. Study period nutrient concentrations at Rostherne Mere. a) Si concentrations taken from a range of sources (this study and D. B. Ryves), b) soluble reactive phosphorus (SRP), c) Si:SRP ratio. * = data unavailable.

5.4. Discussion

Phytoplankton response to the 2012 increased summer precipitation

Diatoms respond to a range of limnological factors, including hydrology, temperature, nutrients and light (Battarbee et al., 2012, Roelke et al., 2010, Wang et al., 2015, Ruhland et al., 2015). Rostherne Mere's long term limnological record (Tattersall and Coward, 1914, Livingstone and Cambray, 1978, Reynolds and Bellinger, 1992), makes it an important site of historical change over the last century, demonstrating the influence of anthropogenic nutrient enrichment on deep UK lakes. The lake has responded to rising nutrient concentrations with increasing primary production, until a reduction began following catchment management intervention in the 1990s (see chapter 3; Radbourne et al., 2017). During this time of nutrient alteration there has been a marked change in phytoplankton assemblages, with a move towards more eutrophic indicator algal species (Belcher and Storey, 1968, Reynolds and Bellinger, 1992).

Today, Rostherne Mere is still hypertrophic with high organic (autochthonous) production and organic carbon flux (see chapter 3; Radbourne et al., 2017). However, even over the 6 years of this study, there is clearly substantial inter-annual variability, with an OC trap collection range of 2.0 to 4.3 g m⁻² d⁻¹ (Table 5.2.). The most noticeable change in sedimentation is between 2012 and 2013, with 2012 producing a very low OC and diatom flux compared to other study years, followed in 2013 by the highest flux across all 6 years (Table 5.2.). The reduced trap flux in 2012 is also seen in the diatom collections (Fig. 5.2a), with the only prominent flux being *S. parvus* in early spring (Fig. 5.2d), as the regular dominant mid-spring flux of *A. formosa* (Fig. 5.2b) and the autumn trap fluxes (Fig. 5.2a) were negligible.

The reduced sediment trap capture during 2012 corresponds to a period of meteorological perturbation. Beginning from April and continuing throughout the summer of 2012, the United Kingdom witnessed historically high precipitation rates (Parry et al., 2013). Regionally around Rostherne Mere, this resulted in much higher annual precipitation values (945 mm), compared to the study period (697 mm) and 30-year mean values (669 mm), with much of this falling from April (Fig. 5.3b). Local river flow (at Bollington Mill) showed the precipitation events from April led to much higher discharge (annual average flow: during 2012 = 5.6 m⁻³ s⁻¹, mean of other study years

= $3.6 \text{ m}^{-3} \text{ s}^{-1}$; Fig. 5.1.). The corresponding reduction of summer WRT (WRT_m) and OC flux to the traps (i.e. from April 2012), and disruption of the usual spring diatom succession, imply that the increased flushing rate may have caused low phytoplankton biomass, as seen in other studies analysing the impact of hydrology and specifically floods on lake production (Tolotti et al., 2010, Cross et al., 2014). As well as reducing diatom populations by wash-out, summer cyanobacterial standing crops would be reduced because they require not only high nutrient concentrations but also calm water with low flushing rates (Huszar and Reynolds, 1997, Godlewska et al., 2003, Elliott, 2010), with cyanobacterial blooms observed to terminate following large inflow events (Roelke et al., 2010). Increased turbulence (resulting in more diatom valve breakage, linked to greater dissolution; Ryves et al., 2006) and dominance of finer, susceptible taxa such as *S. parvus* (Fig. 5.2d, promoting dissolution within the water column and trap seston; Ryves et al., 2003, Ryves et al., 2013) may also explain the poorer preservation within both upper and lower traps in 2012 (Table 5.2.). However, although phytoplankton loss through increased turbulence, flushing and poorer preservation can partly explain the low organic matter and diatom flux during summer 2012, it does not explain the almost complete absence of *A. formosa* (Fig. 5.2b) during this time, implying that the usual conditions that promote the spring *A. formosa* bloom were not present.

Other studies have found that high levels of grazing have been key in the reduction of phytoplankton crops (Meis et al., 2009, Rose et al., 2017), with diatom bloom collapse from grazing stress important in low P conditions (Huber et al., 2008). Although grazing stress is unknown for 2012, the relatively high SRP values (Fig. 5.5b) suggest this is an unlikely cause of the low diatom flux here. On the other hand, bloom collapse in high P conditions is closely related to Si depletion (Huber et al., 2008), but unfortunately Si data in summer 2012 were not available at Rostherne Mere. However, with the consistent annual replenishment of Si (Fig. 5.5a), a decreased diatom biovolume production resulting in lower Si utilisation (Table 5.2.) and the greater Si replenishment from increased catchment inflow rates as a result of flooding (Loucaides et al., 2007, Chen et al., 2014), it is unlikely Si depletion can explain the 2012 low diatom flux in this study.

Increased summer flushing rates have been linked to altered nutrient dynamics in freshwater systems, with SRP loads from internal loading being diluted earlier in the

year with increased flushing rate (Barker et al., 2005, Cross et al., 2014). Therefore, with increased flushing rate at Rostherne Mere during summer 2012, nutrient concentrations would rapidly decline compared to other years. However, nutrient concentrations at Rostherne Mere during 2012 remain at higher levels throughout the year (Fig. 5.5.), with a strong stratification limiting nutrient entrainment from the hypolimnion in all study years (Fig. 5.4.), even during times of increased storminess and rainfall in 2012 that has previously been related to partial stratification breakdown (Sriyasak et al., 2015). Nutrient concentrations in 2012 reduced to the lowest at stratification overturn of $76 \mu\text{g SRP L}^{-1}$, with other overturn low values between $5 - 51 \mu\text{g SRP L}^{-1}$ (study mean $34 \mu\text{g SRP L}^{-1}$; Fig. 5.5b). This smaller SRP reduction, with a higher minerogenic flux, suggests lower phytoplankton utilisation explains the lower flux of organic matter (Table 5.2.). This is compounded by higher summer flushing rate of nutrients also reducing SRP concentrations in 2012 compared to other study years, due to inflowing water having lower nutrient concentrations compared to the in-lake values (April to June epilimnion SRP concentration $\sim 120 \mu\text{g L}^{-1}$, inflow concentration $\sim 15 \mu\text{g L}^{-1}$; see chapter 4).

The low nutrient utilisation during 2012 is here also suggested to be partly as an influence of light limitation. The high level of precipitation during the summer would have altered light availability through increased cloudiness, with increased cloud-cover reducing solar irradiance by 1/3 (Ritchie, 2010), this having the potential to reduce annual primary production considerably (Ritchie and Larkum, 2012). Additionally, inflowing turbid flood water throughout the summer may also have reduced light available for photosynthesis (Squires and Lesack, 2003, Sthapit et al., 2008, Mihaljevic and Stevic, 2011). This is supported by a higher minerogenic flux to the sediment traps in 2012 (Table 5.2.), a signal of increased catchment input of turbid and sediment-laden water (Aryal et al., 2014).

Phenological response to variations in seasonal temperature and stratification onset

Stratification onset at Rostherne Mere between 2013 to 2015 was later than other study period years (Table 5.4.), especially in 2013 and 2015 when the March epilimnion temperatures were below the study period average (Fig. 5.3c). A change in stratification timing is known to adjust diatom phenology, and has been linked to the inter-annual variation and the longer-term shifts in climate under global change

(Walther et al., 2002, Menzel et al., 2006, Thackeray et al., 2008). There is a clear relationship between temperature, stratification and diatom phenology, because the late winter and early spring temperatures that drive the thermal density differential required to stratify the lake, is also the catalyst required to energize the spring diatom bloom replication rate (Reynolds, 2006). Therefore, the low thermal energy in a cold epilimnion that leads to a later stratification, will also delay spring diatom growth and alter diatom phenology. Later stratification onset at Rostherne Mere in 2013 and 2015 (Table 5.4.; Fig. 5.4.), coincides with later development of the spring diatom bloom (~April; Fig. 5.2.) compared to other study years (~March; Fig. 5.2.) with early warm spring epilimnion temperatures (Fig. 5.4c). Wind induced turbulence can have an impact on stratification timing if the shear stress is greater than the resistance to thermal mixing (Monismith, 1985). Here, due to the sheltered position of the lake (evident in the near half reduction in on-lake wind speeds compared to local data; see Methods) and the strong RTRM (Fig. 5.4a and 5.4b), wind is only likely to be a significant factor on stratification timing when the thermal resistance to mixing is low. Over the last 5 decades, there has been a significant change in the duration of stratification at Rostherne Mere due to a later overturn, rather than a change to onset, which is linked to changing air temperature (see chapter 4). On an inter-annual timescale, however, algal production and community structure respond to weather extreme years, with drivers such as variation in summer chl-a concentrations related to precipitation (Carvalho et al., 2012) and phytoplankton phenological timing influenced by alterations in thermal stratification (Thackeray et al., 2008).

The phenological shifts of the diatom community found in this study are more extreme than have previously been observed, with evidence of *S. parvus* not just changing timing of its bloom by a matter of days or weeks, but completely switching from blooming in spring to autumn. Due to its small size (hence rapid reproduction) and competitive advantage at low Si:SRP ratios, *S. parvus* is regularly a pioneer spring-blooming diatom in nutrient enriched lakes (Bigler et al., 2007, Kirilova et al., 2008, Berthon et al., 2014), dominating spring trap collections at Rostherne Mere in 2011 and 2012 (Fig. 5.2d) before other species outcompete it (i.e. *A. formosa* in 2011; Fig. 5.2b). However, a shift in stratification onset at Rostherne Mere in 2013, caused a modification in the timing of the spring bloom of *S. parvus* to the end of April (Fig.

5.2d), this the same time as other taxa leading to subsequent competition reducing the percentage dominance, despite the total production remaining similar (Fig. 5.2.).

The following two years (2014 and 2015), when spring thermal energy input is low, *S. parvus* is not present in spring, yet appears in autumn with other small centric diatoms, such as *Cyclotella dubius* and *C. tholiformis* (Fig. 5.2.). Further evidence that *S. parvus* is linked to spring thermal energy regime (i.e. stratification onset) is seen in 2016 when the spring epilimnion temperature was much warmer (March epilimnion temperature of 6.4 °C) and stratification was earlier (11th March, day 71; Table 5.4.), and *S. parvus* reappears as part of the early spring assemblage, returning back to the usual spring bloom pattern though with a low flux (Fig. 5.2d). As far as we are aware the seasonal switch of *S. parvus* has not been witnessed in high-resolution sediment trap monitoring or lake phytoplankton monitoring records before.

The noteworthy seasonal switch observed for *S. parvus*, along with other changes in diatom phenology observed in Rostherne Mere during this study, highlights the importance of inter-annual climatic variability on the ecology of deeper lake systems. Later stratification onset at Rostherne Mere has been linked with changes in diatom assemblage in past decades, with *A. formosa* blooming later in spring 1972 (see Reynolds and Bellinger, 1992). While inter-annual climatic variability is an important driver of inter-annual variability in freshwater lakes such as Rostherne Mere, progressive changes in climate will drive long-term limnological processes (such as stratification and nutrient cycling) and algal community dynamics that may not resemble earlier states and may lead to whole-system ecological transitions.

Implications of perturbations for longer term lake change

The direct impact of a short-term (i.e. seasonal) meteorological perturbation does not just impact the lake system for the duration of the perturbation, but can cause longer term shifts in lake ecology, primarily driven by alterations to the nutrient cycling and availability (Znachor et al., 2008, Ruhland et al., 2015, Bertani et al., 2016). Following the much reduced OC and diatom flux in Rostherne Mere during 2012, especially the late-summer to winter period, due to wetter conditions, the OC and diatom (valve and biovolume) fluxes increased during 2013 and 2014 (Table 5.2.). The 2012 autumnal SRP values are higher than other years, highlighting underutilisation during that period, with the winter replenishment of SRP not as substantial leading into 2013 (Fig.

5.5b). The reduced SRP may be an influence of faster flushing rates washing out the available SRP during the 2012-13 winter, as shown by increasing discharge at downstream Bollington Mill (Fig. 5.1a). On the other hand, the availability of Si at the start of 2013 is likely to have been increased as it is delivered by the higher inflow (Fig. 1a) with less drawdown by diatoms in autumn 2012 (Fig. 5.2a), despite the reduced Si replenishment from diatom dissolution following a smaller diatom crop in 2012. Therefore, the Si:SRP ratio in spring 2013 would probably have been high, as is evident in the higher diatom biovolume (and so Si) flux (Table 5.2), with the increased importance of Si-rich taxa, such as *S. neoastrea* (Fig. 5.2c, Table 5.1.; Gibson et al., 2000) and *A. granulata* (Fig. 5.2e, Table 5.1.).

Additionally to the change in nutrient availability during 2013, later stratification onset in 2013-15 shifted the phenology of the spring diatom bloom (see above), leading to a changes in nutrient uptake. A later spring diatom bloom would result in a shorter time for spring nutrient utilisation, as well as favouring other taxa with different nutrient uptake strategies. For example, the competitive advantage of *S. parvus*, a low energy early spring taxon, would be lost, thus the early spring nutrient utilisation would be reduced, leading to an altered nutrient environment for the later spring blooms of *A. formosa* and *S. neoastrea*, in this case enhancing their growth potential (see above). The changes in the spring nutrient uptake at Rostherne Mere appear to encourage a greater autumnal diatom crops with larger fluxes in autumn during 2013-15, whereas there were larger fluxes in 2011-12 and 2016 when stratification onset was earlier (Fig. 5.2a).

Furthermore, the changes in the diatom assemblage during the study were not limited to the persistence of the same diatom taxa. From 2013 to 2016, there is evidence of a species shift with decreased abundance of *A. granulata* (Fig. 5.2e) and an increase in *Cyclotella* spp. (Fig. 5.2f and 5.2g). If these gradual changes in dominant species are climate-driven, they may indicate a long-term shift to a different diatom community as perturbations cascade through the system. Battarbee et al. (2012) hypothesised that the future trajectory of primary production and nutrient load may take a range of pathways, probably not returning to a previous ecological baseline with nutrient load recovery, yet likely to undergo a critical transition to a new (quasi-) permanent state.

5.5. Conclusions

Previously, nutrient loading has been seen as a major driver of ecological change in freshwater systems, along both eutrophication and oligotrophication pathways. Although primary production at Rostherne Mere's has fallen over the last ~20 years as P loading has reduced (see chapter 3; Radbourne et al., 2017), the interactions of multiple ecosystem drivers (here climate and nutrients) can complicate the oligotrophication trajectory on seasonal, annual and multi-annual timescales. There is increasing evidence of the dynamic response of phytoplankton communities to climate change through the alteration of physical lake parameters, such as thermal stratification, flushing rate and light availability, having a direct impact on fundamental aspects of aquatic ecosystem functioning and altering algal communities, bloom phenology and primary production. These changes in the physical system may drive great inter-annual variability (as seen in this sediment trap record), or it may cause the algal community to reach a tipping point, crossing a critical transition to a potentially irreversible new phase, resulting in cascading impacts through the ecosystem.

The future implications of climate driven change are expected only to increase in importance if the future projections of UK climatic warming, being +3.4 °C from 2020 to 2100 (UKCP09 projections; Murphy et al., 2009), and the implied potential for increased frequency and intensity of meteorological perturbations, come to pass. Interaction between climatic and other stressors on freshwater systems will lead to more frequent seasonal and inter-annual fluctuations and state changes as aquatic ecosystems respond to the changing limnological environment. Therefore, future research design for assessment of current ecological status in freshwaters must consider potential short-term fluctuations driven by climate variation and longer-term perturbations, with priority given to developing and maintaining longer term data sets and studies.

6. The impacts of changing nutrient load and climate on a deep, eutrophic, monomictic lake

6.1. Introduction

Nutrient availability is a major factor affecting lake ecosystem functioning including productivity, the development of potentially toxic algal blooms and oxygen depletion (Sas, 1989). Anthropogenic nutrient enrichment has increased nutrient loads, causing many lakes to become eutrophic (Smith et al., 2006). Climate also has a major effect on lakes via water temperature and stratification (Hutchinson and Löffler, 1956) and climate change has increasingly become recognised as having a substantial impact on lake structure and function globally (Tranvik et al., 2009, Williamson et al., 2009b, Paerl and Huisman, 2008). Long-term incremental increase of air temperature influences lake thermal structure (Gauthier et al., 2014, Liu et al., 2014) and the timing of stratification (Meis et al., 2009, Izmet'eva et al., 2016). Furthermore, the shorter-term impact of heatwaves, droughts and flooding can alter the hydrological balance and ecological structure in many lakes (Bakker and Hilt, 2016, Bertani et al., 2016, Wigdahl-Perry et al., 2016). Thus, if future projections of UK climatic warming are accurate, with annual average temperatures rising by +1.4 °C from 2020 to 2060 and +3.4 °C from 2020 to 2100 (UKCP09 projections; Murphy et al., 2009), there are likely to be substantial effects on lakes across the UK. However, the precise direction and magnitude of change is uncertain since multiple stressors may interact in synergistic, antagonistic or additive ways (Coors and De Meester, 2008). Furthermore, lakes are differentially sensitive to system stressors (i.e. George et al., 2004) further complicating the assessment of how an individual lake will respond to environmental change or management intervention.

Rostherne Mere, Cheshire, UK is a prime example of a eutrophic lake that has undergone a significant change in trophic status over the last century caused by the direct impact of human activity (Moss et al., 2005). Like many such lakes (Schindler, 2006, Zamparas and Zacharias, 2014), Rostherne Mere has recently undergone catchment-scale management intervention to limit nutrient load and reduce lake nutrient concentrations. While reducing the external phosphorus load improved ecological condition in some lakes (Jeppesen et al., 2005, Sondergaard et al., 2005),

many have only witnessed a slow recovery as a result of internal loading of soluble reactive phosphorus (SRP) derived from historic SRP inputs stored within the upper sediment (Schindler, 2006, Jarvie et al., 2013a). Rostherne Mere is a small but deep lake permitting a particularly long and strong summer stratification (see chapter 3; Radbourne et al., 2017). In conjunction with high productivity, this drives rapid oxygen depletion at depth following spring stratification (Scott, 2014), favouring the release of large quantities of remobilised P from the sediment into the hypolimnion, potentially slowing the rate of recovery and extending the requirement for management intervention.

This study utilises observed catchment and lake monitoring data from 2016 to assess contemporary nutrient dynamics at Rostherne Mere. These data are used in the biophysical PROTECH model (Phytoplankton Responses To Environmental CHange; Reynolds et al., 2001, Elliott et al., 2010) to simulate a range of future nutrient (internal SRP load and external SRP load) and climate (air temperature) scenarios (UKCP09 projections; Murphy et al., 2009) to determine the main drivers of recovery and disentangle the combined importance of nutrient loads and changing climate on key biophysical lake properties and dynamics.

6.2. Methods

Collection and analysis of field data

Between January 2016 and January 2017, water samples were collected approximately every 3 weeks from Rostherne Brook (the main inflow, draining 79% of the catchment), Blackburn's Brook (outflow) and the central lake surface (UKLEON buoy site; water depth ~26 m), with multiple water column depth samples (6, 12, 18 and 24 m) added to the 3 weekly collection programme from September 2016. Water samples were shipped to an external certified laboratory (National Laboratory Service, UK) for orthophosphate (soluble reactive phosphorus; SRP), total phosphorus (TP), dissolved inorganic nitrogen (DIN) and dissolved silicate (DSi) nutrient analysis. Additionally, an integrated water column sample (0–8 m) from the central lake location was collected for live phytoplankton identification and chlorophyll *a* (chl-*a*) analysis. Live phytoplankton were analysed after concentrating a 1 L sample using a sequence of settling procedures, using the gridded cell (Sedgwick-Rafter cell) total abundance

count method (Brierley et al., 2007). Phytoplankton were counted using a 400x magnification, counting total abundance within grid cells for upscaling to the whole sample. Number of colonies were counted for *Microcystis* spp., filaments for *Aphanizommon* spp. and cells for all other algae. Chl-*a* analysis involved a standard spectrophotometer approach, with recordings taken at wavelengths of 630, 645, 665 and 750 nm and an extraction solvent of 80% acetone (Sartory and Grobbelaar, 1984). Secchi depth at the water sampling site was recorded during each visit.

Inflow and outflow discharge was determined by calculating a linear discharge relationship between cross-sectional profiles and sectional velocities recorded for a range of stage heights over 2016. This empirical stage-discharge relationship was then applied to continuous stage heights measurements recorded using a Van Essen mini-diver data logger (www.vanessen.com), recording water pressure every 5 minutes and calibrated to a barometer located at the lake shore, to provide a high-resolution record of inflow and outflow discharge for the whole year.

The standard outflow method for water residence time (WRT) was estimated as the annual average outflow rate against the total lake volume. An adjusted method (WRT_m) was also used, calculated as the monthly average outflow rate against the monthly available mixed lake volume (i.e. during the stratified period from April to November, this is the epilimnion, but during the mixed period from December to March, this is the entire lake).

The PROTECH model

PROTECH simulates the responses of a number of phytoplankton populations distributed in a 1D vertical water column at daily time steps, but also calculates key physical limnological parameters such as thermocline development, stratification pattern, and nutrient concentrations. A full description of the model's equations and concepts has been already published (Reynolds et al., 2001, Elliott et al., 2010) but the main biological component of the model is the daily change in the chl-*a* concentration ($\Delta X/\Delta t$) attributable to each phytoplankton population:

$$\Delta X/\Delta t = (r - S - G - D) X \quad (\text{eqn. 6.1.})$$

where r is the growth rate defined as a proportional increase over 1 day, S is the loss caused by settling out from the water column, G is the loss caused by *Daphnia* grazing (it is assumed only phytoplankton <50 µm diameter are grazed) and D is the dilution loss caused by hydraulic exchange.

The growth rate (r) is further refined by:

$$r = \min \{r'_{(\theta, I)}, r'_P, r'_N, r'_{Si}\} \quad (\text{eqn. 6.2.})$$

where $r'_{(\theta, I)}$ is the growth rate at a given water temperature and light intensity and r'_P , r'_N , r'_{Si} are the growth rates determined by SRP, N and DSi concentrations below these respective threshold concentrations: < 3, 80 and 500 µg L⁻¹ (Reynolds, 2006). The r' values are phytoplankton-dependent (e.g. non-diatom taxa are not limited by silica concentrations below 500 µg L⁻¹ and nitrogen-fixing cyanobacteria are not limited by nitrogen) and, crucially, relate to the morphology of the taxon. The phytoplankton community used in the model were selected from analysis of the most abundant species observed in the lake (see chapter 4), giving a total of 7 phytoplankton taxa: *Asterionella*, *Stephanodiscus* (diatoms), *Cryptomonas* (cryptophyta), *Gomphosphaeria*, *Microcystis*, *Aphanizomenon* and *Dolichospermum* (cyanobacteria).

Water temperature and light (i.e. cloud cover and seasonal irradiance) are varied at each time-step throughout the simulated water column in response to external meteorological divers. The value of $\Delta X/\Delta t$ (eqn. 6.1.) is modified on a daily time-step for each algal taxon in each layer of the water column (layers are 0.1 m deep).

The model was run and compared to the observed data recorded from the lake during 2016 by using the coefficient of determination (R^2 and $RMSE$). After the initial simulation, as expected it became clear that an internal, hypolimnetic nutrient supply of SRP was required, as has been cited previously as an important component of P dynamics at Rostherne Mere (Carvalho et al., 1995, Moss et al., 2005). Therefore, incremental daily amounts of SRP were added to the bottom 15 m of the water column from 1st June for 90 days until the hypolimnion concentration matched those observed from the depth profiles: 7.8 µg SRP L⁻¹ d⁻¹ was found to be optimal. The model assumes the internally loaded SRP is not mixed into the surface water until stratification breaks down, a suitable simplifying assumption in a strongly stratifying

lake such as Rostherne Mere (Mackay et al., 2014). The internal load period of 90 days was fixed to ensure that the internal load only occurs during anoxic stratification (a feature of Rostherne Mere; see chapter 3; Radbourne et al., 2017) for all climate change scenarios, because anoxia promotes the sediment release of iron bound P for replenishment into the water column (Nurnberg, 1984). This P will only be redistributed throughout the water column at stratification overturn due to the strong summer stratification within the lake.

Future climate scenarios

The calibrated 2016 simulation was taken as a baseline and then re-run through a combination of progressive changes to air temperature and nutrient load. Each future projection scenario was run in daily time steps for 10 years using the 2016 driving data repeatedly, and the final year only was used for the analysis to allow the simulation time to move away from the baseline and stabilise under the new driving conditions. The different scenarios were created by application of UKCP09 future temperature change projections (with 11 model simulations), forecasting daily temperatures using years 360 days long, as used by the UKCP09 models, between 2011-2020, 2051-2060 and 2091-2100 for the 25 km² grid reference of Rostherne Mere (the UK Met Office Hadley Centre Regional Model Perturbed Physics Ensemble simulations HadRM3-PPE; Murphy et al., 2009). Temperature change was combined with decreasing SRP loads compared to 2016, through independently multiplying measured internal and external SRP loads in 2016 by 100% (i.e. no change from 2016; referred to as high), 60% (referred to as mid) and 20% (referred to as low) from the 2016 baseline. Furthermore, a single simulation of the current 2016 baseline with a 10-fold increase in external SRP concentration was modelled, from an annual average of 20 µg L⁻¹ to 200 µg L⁻¹, designed to simulate an unmanaged catchment similar to that of pre-sewage treatment work diversion in 1991 (Carvalho et al., 1995). In total this produced 298 scenario combinations (i.e. 11 different temperature models at 3 time frames, with 3 external SRP loadings and 3 internal SRP loadings, plus 1 increased external load simulation).

Model simulation results were statistically analysed using a single factor ANOVA, testing the significance between the 11 temperature forecast models with external load change, internal load change and temperature change.

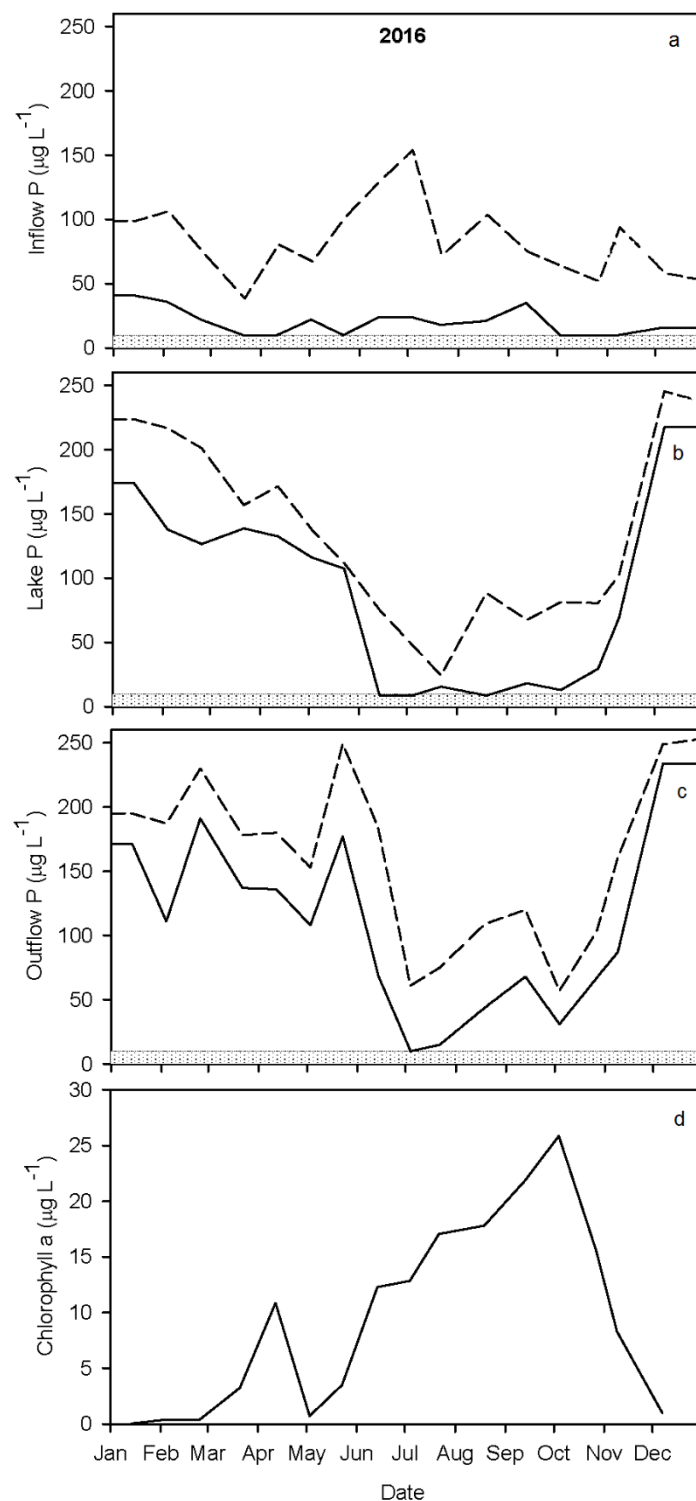


Figure 6.1. Seasonal changes in concentration of P and chlorophyll a at Rostherne Mere for 2016. a) P inflow concentration, b) P lake epilimnion concentration, c) P outflow concentration and d) epilimnion chlorophyll a concentration. For phosphorus, solid line represents SRP and dashed line TP. Analysis detection limit represented by shaded area at 10 µg L⁻¹.

6.3. Results

Seasonal changes in Rostherne Mere

The ratio of TP to SRP concentrations at Rostherne Mere was fairly constant throughout 2016 (Fig. 6.1b), thus SRP was utilised in this study because available reactive P is important for phytoplankton ecology and its use will not significantly underestimate the P budget. The concentration of SRP in Rostherne Mere was high at the start of 2016 ($>150 \mu\text{g L}^{-1}$; Fig. 6.1b), but then decreased as it became diluted with water from the inflow ($\sim 20 \mu\text{g L}^{-1}$; Fig. 6.1a) and through algal uptake (observed chl-a increase; Fig. 6.1d). By mid-June, the concentration of SRP within the lake had fallen to levels near (or below) analysis detection limits ($<10 \mu\text{g L}^{-1}$; Fig. 6.1b). Low SRP concentrations ($<18 \mu\text{g L}^{-1}$) in the epilimnion from mid-June to November (Fig. 6.1b) limit algal growth, as seen in the chl-a production reaching a maximum $25.8 \mu\text{g L}^{-1}$ (Fig. 6.1.d), with production sustained, and thus limited, by the inflow SRP concentration (mean June to November inflow SRP concentration $22 \mu\text{g L}^{-1}$; Fig. 6.1b).

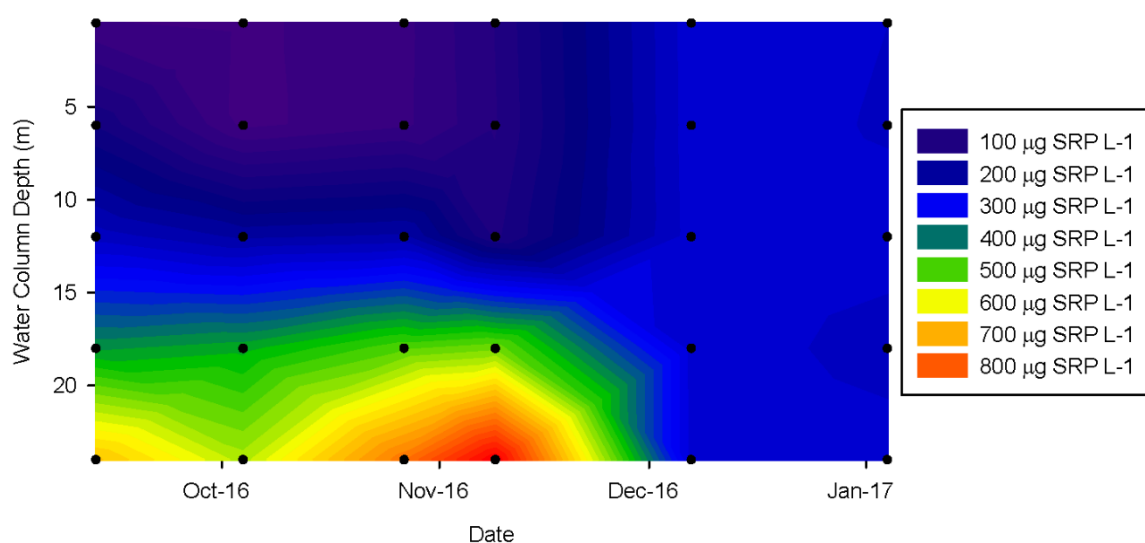


Figure 6.2. Internal concentration of SRP building in the hypolimnion during stratification and released into the whole water column upon stratification overturn. Black dots represent sampling points.

During summer, anoxic stratification in the hypolimnion establishes a high concentration of sediment-derived SRP at depth ($>800 \mu\text{g L}^{-1}$; Fig. 6.2.), which is dispersed throughout the water column at overturn in late November, returning the whole lake to the similar high SRP concentrations found at the start of the year (Fig.

6.1b). The mass balance of P during 2016 (see chapter 4) shows that Rostherne Mere was a net source of P (inflow 864 kg TP, outflow 1416 kg TP = net loss 552 kg TP; Fig. 6.1a and 6.1c), supporting the inference that the major source of this large quantity of P replenishing the water column annually is derived internally from the sediment P store, not from the managed pastureland catchment external stream inflow loads. DIN and DSi were deemed not to be important for overall chl-*a* production with concentrations being high throughout the year in both the inflow (annual mean 2.2 mg DIN L⁻¹, 7.4 mg DSi L⁻¹; minima 0.2 mg DIN L⁻¹, 0.5 mg DSi L⁻¹; data not shown) and lake (annual mean 2.9 mg DIN L⁻¹, 2.7 mg DSi L⁻¹; minima 0.2 mg DIN L⁻¹, 0.2 mg DSi L⁻¹; data not shown).

The WRT for Rostherne Mere calculated for 2016 using the standard method was 0.82 years (~10 months). The mixed lake WRT (WRT_m) that takes account of the strong stratification for 8.5 months (mid-March to end-November), which limits the available lake volume for outflow export, gave an annual estimate of 0.57 years (~7 months).

Table 6.1. Annual mean values (µg L⁻¹) for soluble reactive phosphorus (SRP) and total, cyanobacteria and diatom chlorophyll *a* (chl-*a*).

	SRP	Total Chl- <i>a</i>	Cyanobacteria Chl- <i>a</i>	Diatom Chl- <i>a</i>
2016 baseline	94.4	9.5	5.3	0.9
PROTECH validation	78.2	12.2	7.2	1.4
10x external SRP	118.0	38.3	33.7	1.3

Calibration and validation of PROTECH

The only calibration to PROTECH that was required was to include sediment released SRP into the hypolimnion between 1st June and 30th August, to reflect its build up over the period of stratification and subsequent mixing throughout the water column at overturn (see Methods). Other coefficients were left at their standard values. The resulting comparisons between observed and simulated variables for the year 2016 were good for surface water temperature ($R^2 = 0.98$, $p < 0.001$, RMSE = 0.64; Fig. 6.3a), the concentration of SRP ($R^2 = 0.76$, $p < 0.001$, RMSE = 48.7; Fig. 3b) and total chl-*a* ($R^2 = 0.93$, $p < 0.001$, RMSE = 4.68; Fig. 6.3c).

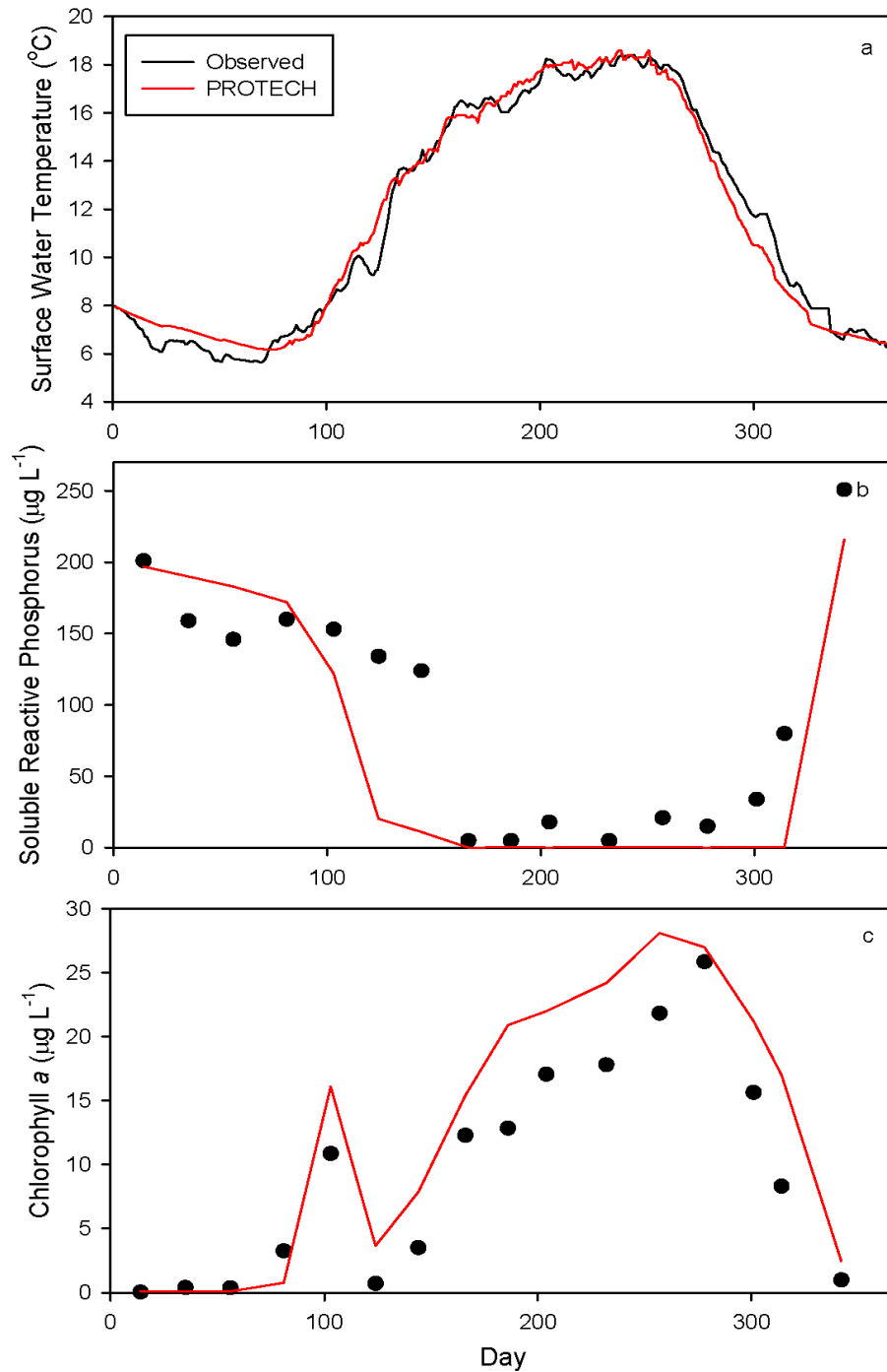


Figure 6.3. Validation plots comparing measured and modelled changes in Rostherne Mere during 2016; a) surface water temperature ($^{\circ}\text{C}$; $R^2 = 0.98$, $p < 0.001$), b) Soluble reactive phosphorus (SRP) concentrations in the epilimnion (SRP $\mu\text{g L}^{-1}$; $R^2 = 0.76$, $p < 0.001$), c) chlorophyll a epilimnion integrated sample (chl-a, $\mu\text{g L}^{-1}$; $R^2 = 0.93$, $p < 0.001$).

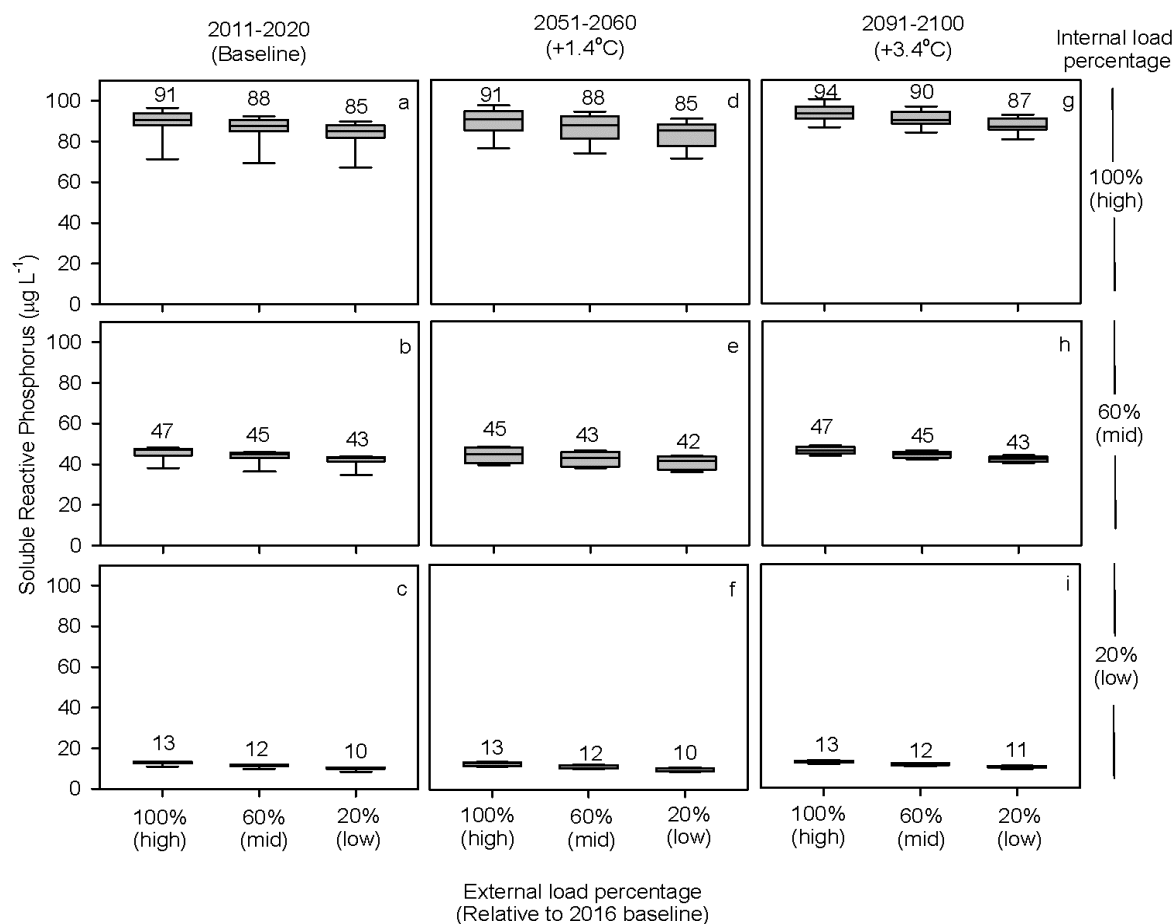


Figure 6.4. Response of annual average SRP concentration to altered external and internal phosphorus loads under three climate scenarios. Final modelled year average for each time frame is divided into an internal load percentage and external load percentage with a box and whisker plot representing the quartile range, 5th/95th percentiles and median values for the 11 UKCP09 climate model projections. Median values annotated above each box.

Response of SRP concentration to future change

Model simulations of possible changes to future internal and external SRP load, along with increases in air temperature over time, altered annual mean lake SRP concentrations. Reduction of the internal legacy SRP load alone had a greater effect on SRP concentration in the lake than changes in external load from inflowing streams (Fig. 6.4.). A reduction of internal loading from high to mid (60% of 2016 value) caused SRP concentration to change by -48.9% (Table 6.2.), while a reduction of internal load from high to low (20% of 2016 value) caused SRP concentration to change by -85.6% (Table 6.2.; external load high, i.e. no change from 2016 baseline). All reductions of

Table 6.2. Modelled annual mean values ($\mu\text{g L}^{-1}$) for soluble reactive phosphorus (SRP), chlorophyll *a* (chl-*a*) and the ratio between Chl-*a*:SRP for different internal and external SRP loads and climate scenarios. Values based on the final year annual averages for 11 temperature model forecasts.

Internal load	High external load			Mid external load			Low external load		
	SRP	Chl- <i>a</i>	Ratio	SRP	Chl- <i>a</i>	Ratio	SRP	Chl- <i>a</i>	Ratio
2011-2020									
High	89.0	20.0	0.22	86.0	18.1	0.21	83.0	16.0	0.19
Mid	45.5	9.8	0.22	43.5	8.3	0.19	41.5	6.3	0.15
Low	12.8	7.0	0.55	11.5	5.7	0.50	10.2	4.6	0.45
2051-2060									
High	89.6	22.6	0.25	86.7	21.2	0.24	83.5	19.2	0.23
Mid	44.8	10.6	0.24	43.0	9.1	0.21	40.9	7.4	0.18
Low	12.7	7.2	0.57	11.4	5.7	0.50	10.0	4.7	0.47
2091-2100									
High	93.6	21.8	0.23	90.9	20.0	0.22	87.6	18.2	0.21
Mid	46.7	9.5	0.20	44.6	7.6	0.17	42.4	5.2	0.12
Low	12.9	6.6	0.51	11.7	5.3	0.45	10.4	4.2	0.40

internal loads under all future warming scenarios are statistically significant (Table 6.3.). A reduction in external load in conjunction with a reduction in internal load amplified change, with an additional 1.3% (total reduction -50.2%; Table 6.2.) and 2.2% (total reduction 87.8%; Table 6.2.) change in SRP load from high to mid and high to low internal load reduction, respectively. Additionally, an increase in air temperature (i.e. future climatic warming scenarios) combined with a reduction in internal load reduced the SRP concentrations further (external load high in 2100: -50.1% difference between high to mid internal load and -86.2% between high to low internal load; Table 6.2.), which was again amplified in conjunction with a reduction of external load (external load low in 2100: -51.6% difference between high to mid internal load and -88.1% between high to low internal load; Table 6.2.).

Altering external load alone (i.e. maintaining current baseline of high internal load) had a smaller impact on SRP change compared to internal load change, with a -3.4% reduction between high and mid external load (Table 6.2.), and -6.4% from high to low

Table 6.3. Significance of external load change, internal load change and temperature change on the final modelled year annual soluble reactive phosphorus (SRP) for 11 future temperature models. *F*-values (df 2,30) and significance from single factor ANOVA (n=33) are presented.

Significance of external load change			
Internal load	Future time frame		
	2011-2020	2051-2060	2091-2100
High	1.53 ns	2.36*	29.46***
Mid	3.70 ns	3.79*	26.32***
Low	5.56**	17.28***	47.52***
Significance of internal load change			
External load	Future time frame		
	2011-2020	2051-2060	2091-2100
High	617.51***	669.4***	679.89***
Mid	851.28***	854.34***	885.94***
Low	2275.43***	2509.7***	2509.70***
Significance of temperature change			
Internal load	External load		
	High	Mid	Low
High	1.63 ns	1.95 ns	1.81 ns
Mid	1.08 ns	0.94 ns	0.81 ns
Low	0.26 ns	0.47 ns	0.58 ns

Note: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$; ns $p > 0.05$

(Table 6.2.), these simulations not being statistically significant (Table 6.3.). However, the impact of the external load increased with a reduction in the internal load (under low internal load: -10.2% difference between high to mid external load and -20.3% between high to low external load; Table 6.2.), with external load change becoming increasingly statistically significant under low internal nutrient loading and future warming scenarios (Table 6.3.). Increasing temperature alone (i.e. nutrient loads remain the same over time) did not have a statistically significant effect on SRP concentration (Table 6.3.), altering it only slightly, with a $\pm < 2\%$ change between 2020 and 2060 and a $< 6\%$ increase between 2020 and 2100 (Table 6.2.).

Response of chl-a concentration to future change in climate and nutrient load

The concentration of chl-a responded to the alterations in SRP concentration (Fig. 6.5.). With external loading at current (high) levels, a reduction in internal loading led to the greatest chl-a change, with a -51.0% (high to mid internal load) and -65.0% (high

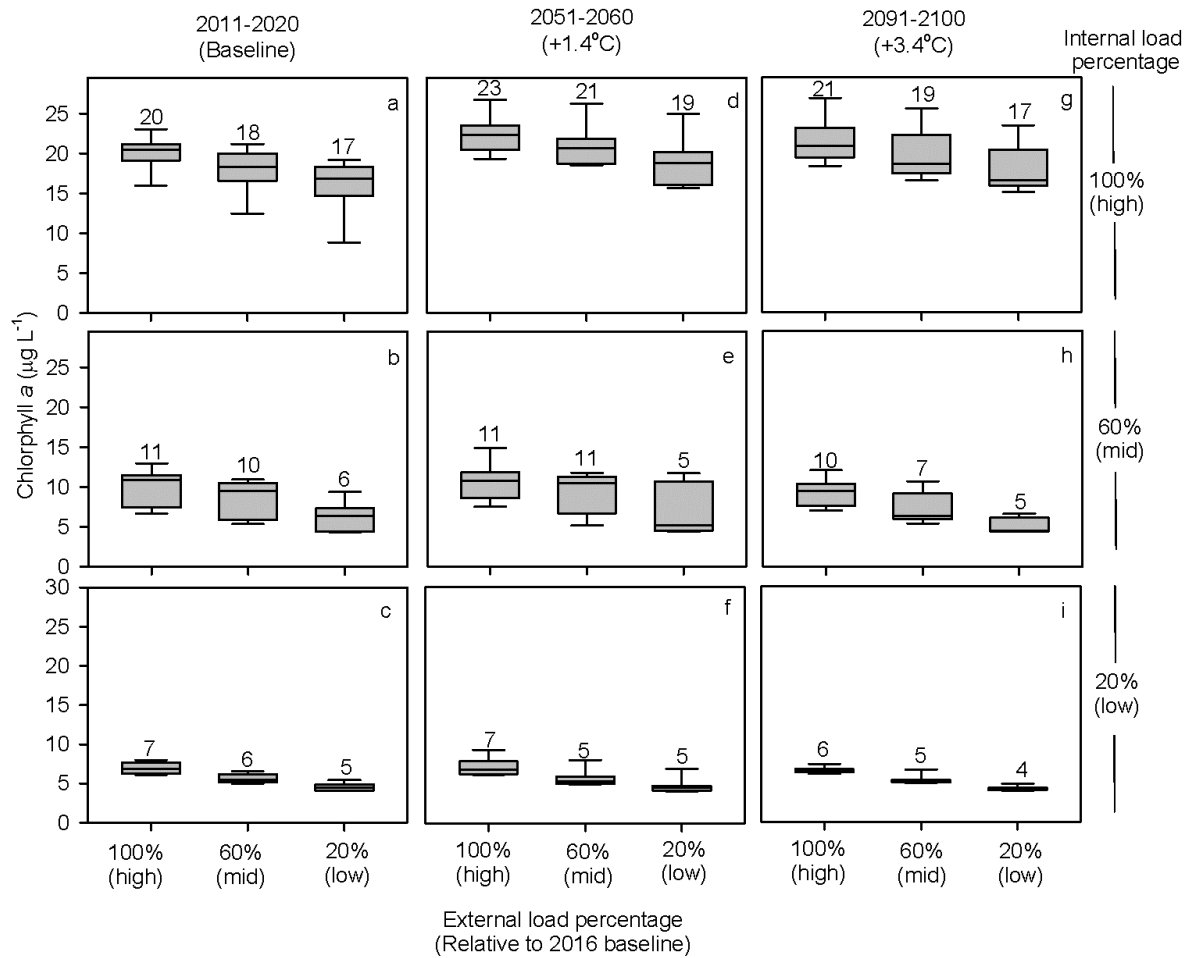


Figure 6.5. Response of annual average chl-a concentration to altered external and internal phosphorus loads under three climate scenarios. Final modelled year average for each time frame is divided into an internal load percentage and external load percentage with a box and whisker plot representing the quartile range, 5th/95th percentiles and median values for the 11 UKCP09 climate model projections. Median values annotated above each box.

to low internal load) reduction (Table 6.2.). All scenarios of internal load change were statistically significant (Table 6.4.). Like SRP, the chl-a reduction is amplified by a reduced external load or increased temperature (Table 6.2.). A combination of reduced internal loads, reduced external loads and increased temperature produced the greatest chl-a reductions (Table 6.2.). External load change in the absence of temperature change had a smaller impact, again this influence is amplified in conjunction with reducing internal load (Table 6.2.). The impact of changing external load on chl-a was statistically significant in all scenarios, with increasing significance in future temperature scenarios and reduced internal loads (Table 6.4.).

In future scenarios where nutrient loads remained constant but air temperature alone increased, chl-*a* concentrations increased by 0 to 20% between 2020 and 2060, with the biggest change in high nutrient loading scenarios and the smallest change in low nutrient loading scenarios (Table 6.2.). However, from 2060 to 2100, all nutrient scenarios suggested a decline in chl-*a* concentrations (Table 6.2.) by a range of -3.5% to -27.8%, with the largest reduction in the mid and low internal load scenarios and lower external load scenarios (Table 6.2.). Statistical significance of temperature change was only evident in the high nutrient load scenarios (Table 6.4.).

The additional simulation of future change with a 10-fold external SRP concentration increase showed an increase in SRP and chl-*a*, with the predominant increase found in the cyanobacterial species abundance (Table 6.1.).

Table 6.4. Significance of external load change, internal load change and temperature change on the final modelled year annual chlorophyll *a* (chl-*a*) for 11 future temperature models. *F*-values (df 2,30) and significance from single factor ANOVA (n=33) are presented.

Significance of external load change			
Internal load	Future time frame		
	2011-2020	2051-2060	2091-2100
High	5.71**	7.02***	47.42***
Mid	4.70*	3.63*	15.79***
Low	4.19*	19.85***	84.44***
Significance of internal load change			
External load	Future time frame		
	2011-2020	2051-2060	2091-2100
High	144.75***	103.98***	85.62***
Mid	180.50***	145.82***	95.39***
Low	202.10***	151.37***	216.16***
Significance of temperature change			
Internal load	External load		
	High	Mid	Low
High	3.40*	3.41*	2.99 ns
Mid	0.81 ns	1.09 ns	2.91 ns
Low	1.84 ns	0.87 ns	2.03 ns

Note: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$; ns $p > 0.05$

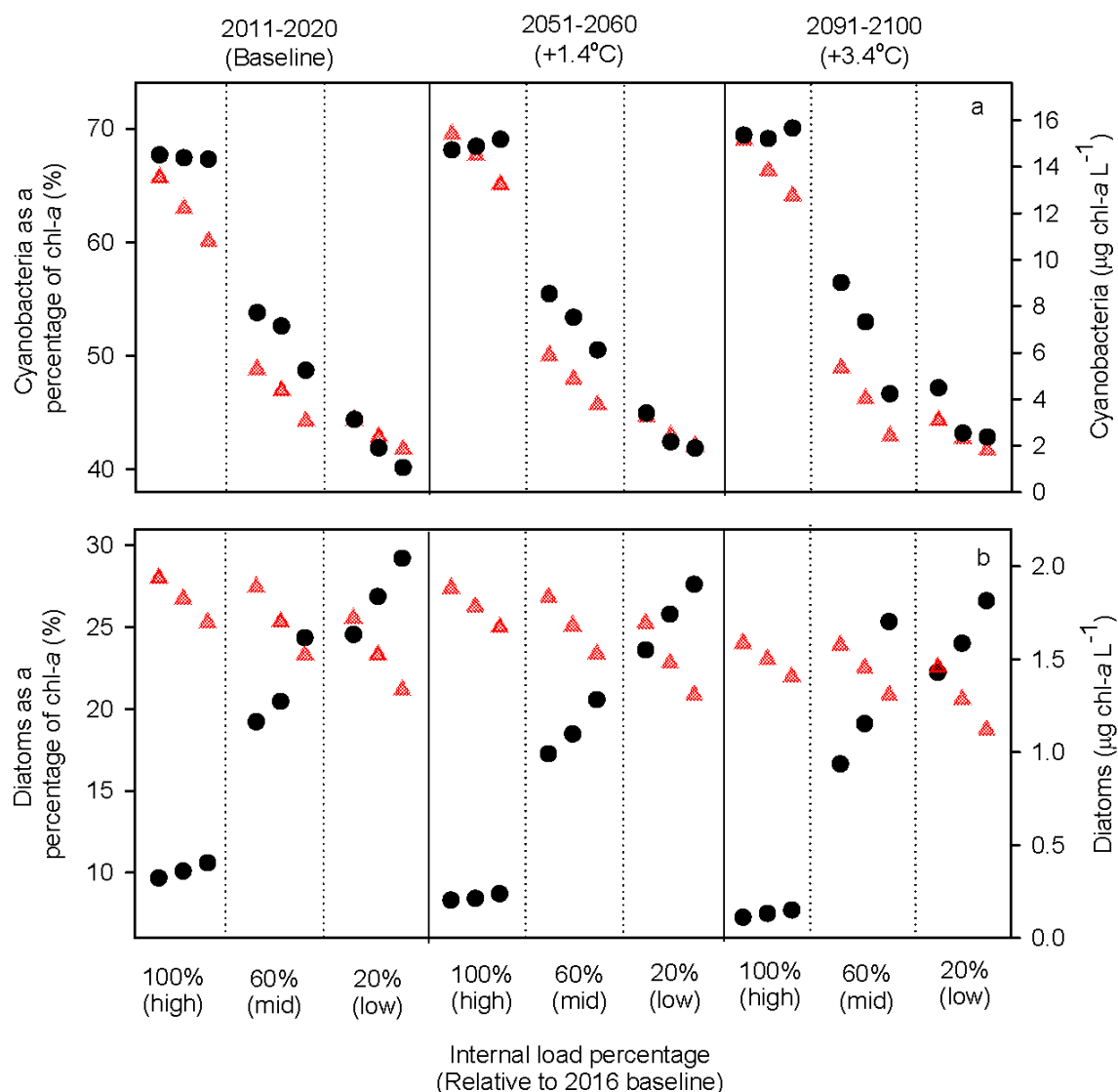


Figure 6.6. Annual average modelled phytoplankton blooms in future nutrient and climate scenarios. a) Cyanobacterial bloom assemblage size (red triangles; $\mu\text{g chl-a L}^{-1}$) and bloom dominance as a percentage of modelled chl-a values (black dots; %). b) Diatom bloom assemblage size (red triangles; $\mu\text{g chl-a L}^{-1}$) and bloom dominance as a percentage of modelled chl-a values (black dots; %). The three symbols in each segment represent high, mid and low external nutrient load scenarios (from left to right). Note that the sum of cyanobacteria and diatoms do not equal 100% as do not include cryptophytes, which showed little response so were not graphically represented.

Response of phytoplankton to future change in climate and nutrient load

Annual modelled phytoplankton assemblages differed between future scenarios (Fig. 6.6a and 6.6b). Cyanobacterial dominance showed a substantial decrease in bloom size and proportional chl-a dominance between the high internal load and the mid and

low internal loads for all future scenarios (Fig. 6.6a). External load reduction had a greater influence by reducing cyanobacterial dominance in lower internal load scenarios, while temperature increased the cyanobacterial dominance in future warmer climates (Fig. 6.6a). The 10x increased external load scenario showed an increase in cyanobacterial dominance (88% of total chl-a; Table 6.1.), with a much larger bloom evident.

Annual modelled diatom abundance (in terms of chl-a) showed little change under all future change scenarios (Fig. 6.6b). Due to the limited response in chl-a production, the relative contribution to total algal chl-a increased with a decreasing total chl-a (Fig. 6.5.) and cyanobacterial bloom size (Fig. 6.6a).

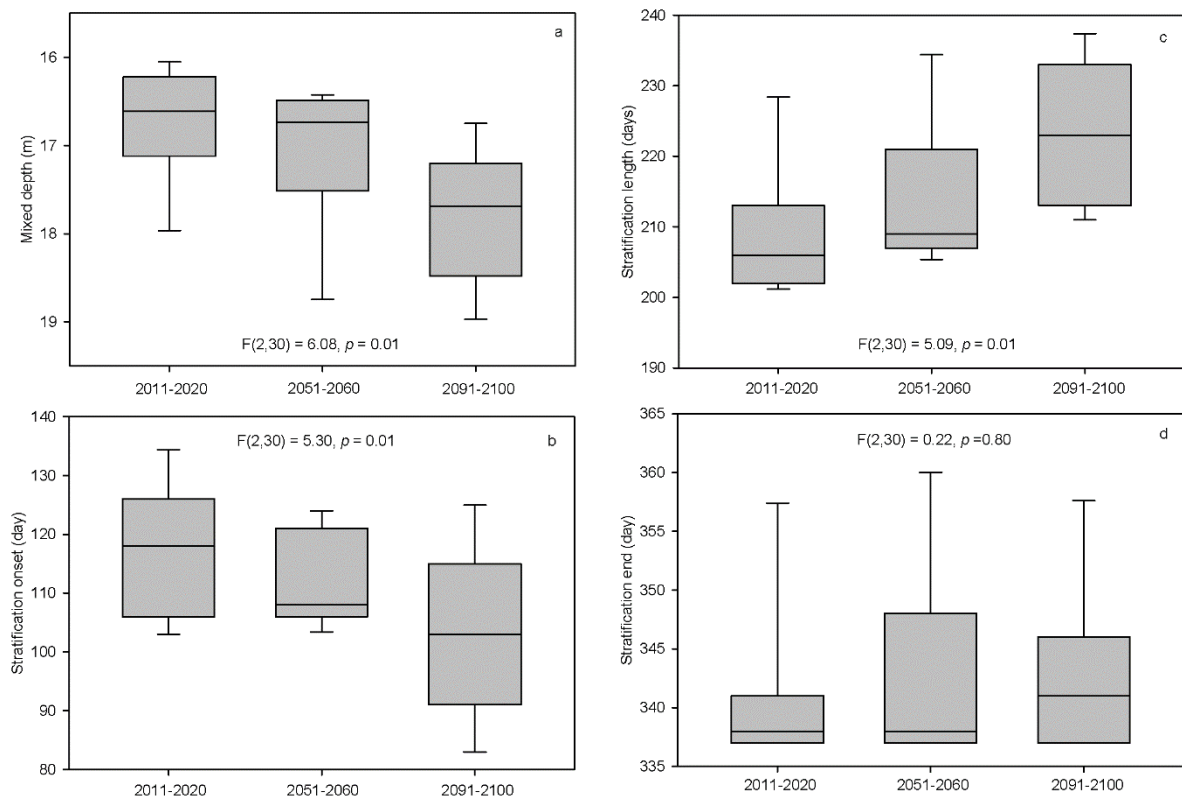


Figure 6.7. Response of annual average stratification patterns to future climate change. Box and whisker plots summarise the quartile range, 5th/95th percentiles and median of the 11 UKCP09 climate model projections for three future time frames and the impact on; a) average stratified mixed depth (i.e. thermocline depth), b) stratification length, c) time of stratification onset, d) time of stratification end (overturn). Single factor ANOVA *f*-values and significance included as annotation for each plot.

Response of lake thermal structure and stratification to future climate change

Future temperature changes compared to the 2020 baseline (i.e. final year of 2011-2020 future temperature scenario), represented an annual average increase of air temperature of 1.4 °C by 2060 and 3.4 °C by 2100. Increases in temperature altered the water column mixing and stratification patterns. Compared to the baseline climate, the annual average mixing depth increased by +0.48 m by 2060 and by +1.12 m by 2100 (Fig. 6.7a), a statistically significant result ($F(2,30) = 6.08, p < 0.01$). Consequently, the WRT_m increased from 0.57 years (using 2016 as baseline) to 0.58 years by 2060 and 0.60 years by 2100, although the changes was not statistically significant.

The increase in air temperature also led to a statistically significant earlier onset of stratification (Fig. 6.7b; $F(2,30) = 5.30, p < 0.01$). This was 6 days earlier by 2060 and 14 days earlier by 2100. Thus, overall stratification duration increased significantly (Fig. 6.7c; $F(2,30) = 5.09, p < 0.01$), because the timing of the breakdown of stratification was unaffected by the future climate scenarios (Fig. 6.7d; statistically not significant difference $F(2,30) = 0.22, p < 0.80$). Longer periods of stratification changed the WRT_m from 0.57 years (using 2016 as baseline) to 0.56 years by 2060 and 0.55 years by 2100. However, the combination of deeper mixing (lengthening WRT_m) and longer stratification (shorter WRT_m) offset each other so that WRT_m was 0.58 years in both 2060 and 2100.

A small number of individual model scenarios of climatic warming suggested stratification overturn may not occur until early January the following year (shown here as the final day of the modelled year, day 360; Fig. 6.7d). These scenarios forecast the late stratification end time and in turn lead to a slightly later stratification onset the following year, explaining the range of stratifications projected by the 11 climate model scenarios and the benefit of using the average of these models.

6.4. Discussion

Internal legacy SRP limiting future recovery

Many lakes have been the focus of management intervention in an attempt to reduce previously high nutrient loads in order to improve ecological function (Schindler, 2006). However, nutrient recovery in some lakes has been slowed by the influence of internal sediment SRP release, annually replenishing the lake water column with large quantities of SRP (Sondergaard et al., 2005, Schindler, 2006, Jarvie et al., 2013a). Rostherne Mere is an excellent case in point; a long history of anthropogenic nutrient loading produced hypereutrophic conditions, with the subsequent management interventions only producing a slight recovery in lake nutrient concentrations (Moss et al., 2005), despite a large reduction in external P loads in the predominantly pastureland catchment of Rostherne Mere (Carvalho et al., 1995). However, the reduced P inputs did not lead to a similar reduction of P export, resulting in the lake becoming a large net source of P following sewage treatment works diversion, this net export is sustained to the present day with a net 552 kg TP exported during 2016. Chapter 3 (Radbourne et al., 2017) highlighted the efficient sedimentation and burial of algal production in Rostherne Mere, which delivers large quantities of P rich organic carbon to the sediment surface, some of which will be mineralised, releasing the bound P for algal utilisation and lake concentration replenishment. However, the quantities of P replenished from mineralising algae in the water column cannot explain annual replenishment alone, highlighting the important role of internally loaded P from lake sediments during anoxic stratification (Nurnberg, 1984), producing high concentrations of SRP in the hypolimnion during stratification ($>800 \mu\text{g L}^{-1}$), which at stratification overturn, annually replenishes the water column P concentrations, explaining the slow long-term recovery trajectory of Rostherne Mere over the last 25 years (Moss et al., 2005).

This study also supports this finding, clearly showing that the main driver of substantial change at Rostherne Mere would be the reduction of the large internal SRP load. For example, a reduction of the internal loads by 40% resulted in a 48.9% reduction in SRP and a 51% reduction in chl-a concentrations, compared to the same reduction in external load causing a reduction of just 3.4% in SRP and 9.5% in chl-a concentrations. The substantial difference between the importance of internal loads and external loads is explained by the relative load size change, with a much larger reduction in internal loading (baseline $\sim 200 \mu\text{g L}^{-1}$) compared to external loading (baseline $\sim 20 \mu\text{g L}^{-1}$).

A reduction in in-lake nutrient concentrations, following management intervention reducing external nutrient loading, can be delayed by the internal replenishment of sediment legacy SRP, especially in deep stratifying lakes (Sondergaard et al., 2005). Previous studies at Rostherne Mere have also suggested a delay in the recovery trajectory, since management intervention in 1991, is likely to be caused by the influence of internally loaded SRP (Carvalho et al., 1995, Moss et al., 2005). Comparison of observed data at Rostherne Mere supports this assessment with long term recovery delayed by the internal legacy SRP load building a substantial hypolimnetic SRP concentration during stratification, which, with autumn overturn, replenishes the whole lake SRP pool and persists into the next spring. It has been suggested that over time the internal legacy SRP can be controlled and reduced through the reduction of external SRP loads, eventually exhausting the standing internal legacy SRP store, yet a full lake response may take decades or longer (Jarvie et al., 2013a) depending upon the lake morphometry and store size (Sondergaard et al., 2005). This study was based on the 2016 baseline internal SRP release. However, in future warmer scenarios it can be assumed that changes in stratification patterns (i.e. deeper and/or longer stratification) will lengthen periods of anoxia for increased internal SRP release (Hecky et al., 2010, Jarvie et al., 2013b). Therefore, it is possible that with future warming the internal load contribution may increase through longer periods of anoxia promoting P release, however, this may be offset or surpassed by the gradual decrease in P available for remobilisation as the sediment source exhausts.

Contribution of internal and external loads to the concentration of Chl-a

In the past, management interventions to reduce nutrient concentrations in lakes have mainly focused on reducing the external loads of SRP from the catchment (Sas, 1989). However, with the impact of large internal sediment SRP loads slowing the recovery trajectories of many lakes (Sondergaard et al., 2005), the current and future focus of lake management strategies is turning to other approaches such as chemically limiting the internal sediment contribution (i.e. phosphate inactivation agents; Meis et al., 2013, Zamparas and Zacharias, 2014, Hupfer et al., 2016), as it will have the greatest influence in reducing the in-lake SRP concentrations, as seen in this study.

However, here I find the reduction of chl-a concentrations to be non-linear to the reduction of SRP concentrations. The model simulations show that there is a greater proportional reduction in SRP to chl-a with a reduction of internal load (Table 6.2.), with scenarios of high internal and high external load having a chl-a:SRP ratio of 0.22, compared to scenarios of low internal and high external load having a chl-a:SRP ratio of 0.55, a substantial increase in ratio. Only reducing the external load (i.e. internal load and climate unchanged) results in a slight chl-a:SRP ratio reduction, which suggests external load is a key driver in chl-a production despite its small impact on SRP load. Similar non-linear patterns between chl-a and SRP are evident in all nutrient scenarios. Statistical analysis confirms the importance of the external load for chl-a concentrations, which is statistically significant for all nutrient scenarios, while external load reduction is only significant for SRP when internal loading is low, predominantly due to the increasing relative ratio of load size (i.e. the external load has a greater proportion of the total nutrient input), or with future temperature influence.

The high nutrient scenarios that have a proportionally low chl-a concentration may be explained by the influence of light limitation through algal self-shading, which has been previously cited as a potential factor limiting growth at Rostherne Mere (Reynolds and Bellinger, 1992, Carvalho, 1993). However, although light limitation could have some impact on the production capacity at Rostherne Mere (in the high nutrient scenarios), it does not explain the proportionally high importance of the external load on chl-a compared to SRP. The luxury uptake of SRP by phytoplankton could also go some way to explain the variation in the chl-a to SRP ratios, though it may only sustain growth for ~2 weeks (Eixler et al., 2006, Powell et al., 2009). However, although this may affect observations at Rostherne Mere, the PROTECH model does not include the function to model luxury uptake and as such cannot be the reason behind the variation in this study.

Here I propose the reason for the non-linear responses in chl-a:SRP ratio from changes in external load at Rostherne Mere is caused by seasonal nutrient availability and subsequent importance of timing of the nutrient replenishment from external inflow. Rostherne Mere begins the year with a high SRP concentration following the large internally replenished SRP load during the winter mixing, which always occurs after the end of the previous year growing season. The high in-lake concentrations decline with dilution by inflow of stream water with a low SRP concentration and

phytoplankton utilisation, so that by mid-June SRP concentrations are representative of the inflow. Therefore, from this point SRP will be replenished predominantly from the inflow, because internally-generated SRP replenishment from the decomposition of dead, moribund and senescent phytoplankton in the water column (see chapter 3; Radbourne et al., 2017) and hypolimnion entrainment are both very low. Thus, a reduction in the external SRP load, although having a minor impact for much of the year (e.g. November to mid-June) due to the high SRP load from the internal legacy store, will have a greater importance in replenishing the SRP later in the year, driving late-summer phytoplankton blooms and subsequent chl-*a* concentrations.

Furthermore, the future scenario of a 10-fold increase in external SRP concentration, designed to simulate an unmanaged catchment, showed a substantial increase in SRP and chl-*a*, driven by a rise in summer blooms (33.7 $\mu\text{g chl-}a \text{ L}^{-1}$; model validation baseline 7.2 $\mu\text{g chl-}a \text{ L}^{-1}$). The substantial rise in the summer cyanobacterial blooms with an increase in the external SRP concentration under current conditions, confirms the role of the external load in replenishing the late summer SRP, highlighting the importance of the external load management in lakes such as Rostherne Mere. Additionally, whilst not modelled here, the UKCP09 model projections suggest with future climate change there will be an increase in precipitation (Murphy et al., 2009). Thus, with increasing precipitation it can be assumed external SRP (and TP) load would increase through the higher inflow flow rate (Andersen et al., 2006, Jeppesen et al., 2011). Therefore, the potential increasing external load driven by future climate change highlights the necessity for continued external load management. Despite the relatively small influence at the annual scale of external SRP loads on the in-lake SRP concentration in current high internal load scenarios, the importance of external load management should not be underestimated because it disproportionally supports chl-*a* production, especially in the late summer. Thus, management of the external SRP load is still of great importance, even though reducing the internal load is the main driver of a reduction of annual concentrations of SRP and chl-*a*.

The effect of climatic warming on the concentration of Chl-a

Increased air temperature between 2020 and 2060 led to a slight increase in chl-*a* concentration, without nutrient load adjustment, as is seen in other studies (Elliott et al., 2016, Izmet'eva et al., 2016). The increase was smaller in low nutrient

concentration scenarios, as found elsewhere (Tadonleke, 2010). Statistical analysis confirmed the modest impact of temperature increase on chl-a, with only the two highest nutrient concentration scenarios statistical significance found in being significantly different. However, chl-a concentrations at higher temperatures corresponding to the 2100 time period were lower than those forecast for 2060, resulting in an overall reduction in chl-a from the 2020 forecast, apart from under the high internal load scenario. This reduction in chl-a with continued warming at mid and low internal SRP loads is counter to other modelling studies simulating warming, that reported a step change increase with higher warming scenarios in similar lake systems (Tadonleke, 2010, Elliott et al., 2016). I attribute this response in Rostherne Mere to the effect of increased temperature on stratification patterns that affects the cycling and availability of nutrients (discussed later).

Phytoplankton assemblage change driven by climate and nutrient loads

Modelled cyanobacterial blooms showed a similar response to change as chl-a under future change scenarios, with internal load driving the major adjustment in cyanobacterial chl-a, external load having a greater influence in low internal load scenarios and temperature increasing cyanobacterial chl-a. However, in lower internal load scenarios, cyanobacterial blooms were substantially reduced in proportion to total chl-a, highlighting the importance of the internal load on lake algal ecology. A decrease in external load had less effect on cyanobacterial blooms than a reduction in internal load, yet had the potential to play a significant role in cyanobacterial production under lower internal loads or if management controls were to be removed (i.e. 10x external load scenario), confirming the importance of continued management control of external nutrient loads on the algal community.

Temperature increase led to an increase in cyanobacterial dominance, as has been seen in other studies (Paerl et al., 2011, Elliott, 2012a, Kosten et al., 2012). The cyanobacterial decrease under future climates followed a pattern that was similar to chl-a (see above). However, diatoms did not show a proportional change in chl-a. With blooms forming in spring, diatoms utilise the higher levels of SRP (and dissolved Si) available early in the year produced by the internal load released into the whole water column on destratification at the end of the previous year. Therefore, the diatoms are not significantly nutrient limited in any future change scenario, and are largely

unaffected by reduced internal and external nutrient loads. The relatively small response of diatom chl-*a* to changing nutrient loads, compared with the reduction seen in the cyanobacterial blooms, results in diatoms contributing more of the algal chl-*a* as cyanobacterial blooms decline under lower nutrient load scenarios.

Climatic warming alters stratification depth, length and timing

The large range of SRP concentrations in Rostherne Mere across the annual cycle is predominantly driven by the long stratification (0.71 years) and rapid flushing rate (0.82 years WRT method; 0.57 years WRT_m method). Strong stratification allows anoxia to develop at depth, promoting SRP release and minimising the entrainment of SRP into the surface layer during the growing season. A long-stratified period results in a late breakdown and subsequent release of SRP into the upper water column after the end of the growing season. During winter mixing, the flushing rate decreases due to a larger volume available to flush (see WRT_m), despite higher discharge, therefore concentrations of SRP persist until spring when increased flushing rate from stratification onset and an improved light climate for biological uptake reduce the available SRP in the epilimnion. Therefore, a change in the development of stratification at Rostherne Mere could influence the cycling and availability of nutrients.

A warmer climate has been shown to increase the mixed depth, with higher air temperatures altering the thermal dynamics in the epilimnion (Gauthier et al., 2014, Liu et al., 2014). Here, the increase in mixed depth in Rostherne Mere (represented by the average thermocline depth during stratification) was also statistically significant under future scenarios of a warmer climate. A deeper mixed layer increases the available water column susceptible to flushing and hence increases the retention time. An increase in WRT_m would lead to an increase in nutrient availability, as epilimnion flushing will take longer to reduce high concentrations of early spring. Yet, the increase in WRT_m is small and the increase in mixing depth would be unlikely to have a large influence on the algal populations.

The duration of stratification can be increased in a warmer climate, as found by others (Liu et al., 2014, Izmet'seva et al., 2016) and here. A longer stratification time would lead to a faster flushing rate with the mean average lake volume available for flushing (i.e. epilimnion) being smaller for longer in the year. Here, the impact of the future projected increase in stratification length led to a slight decrease in WRT_m that would

lead to less nutrient availability, thus smaller phytoplankton blooms. However, the decrease is again minor and is likely not to be significant in isolation. The combination of deeper stratification lengthening the WRT_m and a longer stratification shortening the WRT_m , in the case of Rostherne Mere, is forecast to result in a net offset and so will have a minimal effect.

The earlier onset of stratification could lead to the utilisation of available nutrients earlier in the year, with the access to nutrients in the hypolimnion restricted for longer. Therefore, nutrient concentration reduction through dilution and uptake may lead to changed timing of nutrient availability, possibly reducing the nutrient store earlier in the year before summer cyanobacterial blooms dominate, resulting in a reduction of bloom size. Evidence of such reductions is seen in the lower chl-a concentrations in 2100 scenarios compared to the 2060 scenarios. Earlier stratification onset in 2100 leads to earlier nutrient limitation and thus lower productivity for a larger part of the summer period. Furthermore, the net reduction of chl-a from 2020 to 2100 in low internal load scenarios highlights the importance of the legacy (sediment) SRP replenishment for sustaining the baseline chl-a production. Therefore, with low internal load replenishment and reductions of external load, the limitation effect is amplified (i.e. lower chl-a production) due to the role of external load in sustaining the summer production.

Contextualising the scenario space

The likelihood of the future scenarios assessed in this study becoming a reality for Rostherne Mere is difficult to quantify as it relies on the actions of many different stakeholders and environmental conditions. Therefore, I have presented a full range of possibilities from the current nutrient load to a much-reduced state following potentially far greater management intervention. The most likely scenarios are the future temperature projections due to the 11 detailed models utilised from the UKCP09 data sets (Murphy et al., 2009). The external load at Rostherne Mere following sewage treatment works diversion in 1991 reduced rapidly (Carvalho et al., 1995) and has since been relatively stable (Moss et al., 2005) and therefore may be expected to remain stable at the current high scenario into the future. However, additional management intervention has the potential to reduce further the external load, yet the likelihood of this happening will be dependent upon the future management priorities

and budgetary availability. As Rostherne Mere is a SSSI and Ramsar site it has the potential to be a priority for future further intervention, but the nature and scale of any intervention, and the impact this could have upon the external load, is uncertain. The likelihood of the internal load scenarios is also unclear. A gradual exhaustion of the sediment P source should be expected due to the large net annual P export (552 kg TP in 2016). However, although the sediment P-source is not infinite, the long history of nutrient enrichment, together with the high sedimentation and burial rate (see chapter 3; Radbourne et al. (2017), implies it could be very large and may take decades or even centuries to exhaust gradually (Reddy et al., 2011, Sharpley et al., 2013). Furthermore, management intervention may also play a role in the internal load contribution with the increased popularity of phosphate inactivation agents (i.e. aluminium addition, Meis et al., 2013, Zamparas and Zacharias, 2014). However, like the argument for additional external load management above, these management interventions are costly processes with mixed longevity of results and uncertain wider, longer-term ecological impacts (Jensen et al., 2015, Huser et al., 2016a). Rostherne Mere has previously been considered as a test site for regional phosphate inactivation agent treatment, yet was decided to be too costly to try at this time (Genevieve Madgwick, Natural England, pers. comms.), yet clearly future management priorities and budgetary availability are difficult to predict.

6.5. Conclusion

Rostherne Mere's trophic trajectory towards recovery, monitored since 1991, has been limited by the large annual internal loading of SRP from the profundal sediment. Future scenarios of changes in internal SRP load, external SRP load and air temperature over the rest of the 21st century show that this legacy sediment SRP loading will control the extent of lake recovery, with alterations in internal load leading to the greatest change in concentration of SRP, chl-*a* and cyanobacterial populations. However, internal load reductions are realistically unlikely to occur on the large scale modelled in this study within the next century. Conversely, external SRP loading may have the potential to be reduced by management within a much shorter timeframe (i.e. <10 years). Therefore, external SRP loading, although having a relatively small influence on future SRP scenarios, does have an important role in the future chl-*a* production at

Rostherne Mere, due to the replenishment of SRP throughout the summer, sustaining the summer cyanobacterial blooms. The summer reduction in SRP is brought about by the combination of a long stratification time and fast flushing rates, leading to the mixed epilimnion being diluted by the managed external contribution. Climate appears to have the smallest direct influence on the future of nutrient utilisation and change at Rostherne Mere. However, the indirect impact of changing stratification patterns (i.e. mixing depth, length and onset timing) and potential for increased internal loading contributions, could decrease the available nutrients in the epilimnion in late summer and autumn, yet increase the internal load contribution for winter replenishment, subsequently adjusting the rate and trajectory of future recovery and potentially altering algal community structure.

7. Thesis Synthesis

7.1. Disentangling nutrients and climate

The findings in this research aim to disentangle nutrients and climate as drivers of change in a deep eutrophic freshwater system by looking at the past, present and possible future trajectories of change. Historically Rostherne Mere has been impacted by anthropogenic nutrient enrichment from a sewage treatment works upstream of the lake. The substantial rise in nutrient concentrations over the 20th century increased phytoplankton production, thus increasing total sedimentation. This reflected in an increase in the organic carbon burial rate (see chapter 3). Furthermore, with a rise in trophic status, it has previously been reported that there was an alteration in the phytoplankton dominance, with a move towards a dominance of cyanobacteria (Reynolds & Bellinger, 1992), which remains dominant in summer to present (see chapter 4).

Diatom assemblages are shown in this research to be rapidly adjusting to changes in their environment (chapter 5). Climatic extremes and changes in nutrient availability (through gradual nutrient reduction or shifts driven by climatic perturbation altering cycling patterns) will influence the diatom species dominance and overall production size. Therefore, with diatoms responding to changes in the environment and these changes having an impact on the OC burial potential of a lake, the feedback of climate and nutrient change is further reaching than just an environmental proxy of ecological change, yet extends to wider implications of broad scale ecosystem services. For example, in 2012 the low sediment and diatom yield in the sediment traps following a poor growing season from extreme summer weather conditions would have led to a much reduced OC burial for that year. This reduced burial signal will likely be gradually lost in the sediment archive, especially with 2013 producing a larger than average sediment yield (see chapter 5), yet, it does go some way to highlight the importance of climate variability upon not only phytoplankton assemblages, but also other areas such as OC burial. Appendix 3 provides additional data from a sediment core that has been assessed for diatom assemblages. It shows diatom abundances had increased during the early part of the 20th century in line with that evident in the phosphorus concentrations and OC burial rate (see Appendix 3 fig. 3), with the increase in diatoms during this time having greatly contributed to the increasing OC burial rate (chapter 3).

Towards the height of nutrient concentrations the diatoms in the core suggest a downturn in the total diatom accumulations (see Appendix 3 fig. 3), likely as an impact of being outcompeted by cyanobacterial blooms (see chapter 4) in these very high P concentrations and maybe as an influence of Si limitation (see Appendix 3). Interestingly during this time the dip in diatom accumulations corresponds to a lower OC burial rate data point (see Appendix 3 fig. 3). Potentially, this lower OC burial rate during the peak nutrient concentrations is a function of the switch to a predominantly cyanobacteria dominated system with less diatom production, as cyanobacteria are a more labile (soft) algae that can be mineralised more easily than the more stable (hard) siliceous walled diatom frustule. Therefore, with an increased cyanobacterial dominance, a higher proportion of the total production may be mineralised compared to a diatom dominated system, leading to a reduction in the total OC sedimented for burial. This link between OC burial rates and a shift in dominant phytoplankton type is an interesting hypothesis that requires further research exploration.

Following management intervention for nutrient reduction, by re-directing the sewage treatment works in 1991 and implementing agricultural catchment nutrient plans (Carvalho, *et al.* 1995), the early signs towards a reversal in the trajectory of change is evident. The reduced catchment nutrient loads and lake concentrations (chapter 4), has reduced OC burial rates (chapter 3) and total diatom production (Appendix 3 fig. 3). Importantly, with the reduction in external nutrient concentrations the in-lake stores of nutrients (i.e. internal P loading) and the seasonal catchment hydrology (i.e. flushing rate) have become key drivers of current change (chapter 4). The annual internal P loading, replenishing the water column each winter, sustains the high trophic status of the lake (chapter 4). However, flushing rates are shown to have an impact on the seasonal ecology, with the rapid flushing of the epilimnion reducing the available nutrient concentrations by mid-summer (chapter 4), having the potential to limit algal growth. The pace at which the epilimnion flushes is driven by the meteorological conditions, with increased rainfall leading to faster flushing rates, as was seen in 2012 where unusually high summer rainfall reduced the number of diatoms in the sediment trap collections (chapter 5). It can be noted here, some cyanobacteria, have been shown to have the ability to mobilise between the nutrient-poor yet warm and light epilimnion and the nutrient-rich yet cold and dark hypolimnion, to sustain growth that may otherwise be limited in conditions like those seen at Rostherne Mere (Head *et al.*

1999), therefore they may not be impacted as greatly by this nutrient flushing driver as other phytoplankton might be.

Looking forward to possible future scenarios of change at Rostherne Mere (chapter 6), there is a clear importance in the nutrient load management, with the internal load projected to be the main driver of possible change and the external nutrient load together with flushing rates a key for the late-summer phytoplankton growth (corresponding to results in the current lake assessment, see chapter 4). Future gradual changes in climate scenarios will alter the catchment and lake hydrology, adjust stratification timings and ultimately impact the nutrient cycling and availability for the phytoplankton, these all of great importance for the lake ecological balance, through the changing impacts of nutrient replenishment and flushing rates (chapter 4) and extreme variability causing short-term shifts in state (chapter 5).

Lake restoration efforts (i.e. nutrient reduction) and climate are shown to work in both additive and antagonistic ways. A warmer and wetter future climate will lead to increased flushing and longer stratification (chapter 6), that produces a higher net export and lower epilimnion concentration of nutrients in a well-managed catchment (chapter 4), thus a greater lake recovery. Yet, a reduction in nutrients (chapter 3) and climatic extreme events (chapter 5) leads to less phytoplankton production and sedimentation, therefore less OC burial.

Overall, this study highlights that environmental change (recovery and climate) drives freshwater systems (through direct nutrient change and indirect flushing impacts). These changes in the freshwater system lead to shifts in the dominance of phytoplankton types (i.e. cyanobacteria vs diatoms), that can cause cascading impacts across the system, such as changes in OC burial rates through changes in the total production size and / or the variation in the lability of the dominant phytoplankton type (i.e. more stable siliceous diatoms vs labile cyanobacteria).

7.2. Management implications

This study has found the past, present and future of Rostherne Mere is predominantly driven by nutrient loads as a long-term implication of recent (i.e. last ~100 years) historical anthropogenic enrichment. The long-term impact of this nutrient enrichment has implications for management intervention and recovery target setting, because not only can the recovery process be delayed by large quantities of legacy P stored in

the sediment and released annually via internal loading (see chapter 4), subsequently being aesthetically and financially costly (Pretty et al., 2003), yet can lead to a new (meta)stable state being reached, not returning to a previous baseline target state (see chapter 5). Management target setting in impacted lakes is a difficult task with many issues surrounding the definition of a reference point for recovery targets (Bennion et al., 2011, Poikane et al., 2014) as many lakes have been impacted for decades to centuries or even longer by anthropogenic activity (Lotter, 1998, McGowan et al., 2012, Mills et al., 2014). Additionally many lake recovery trajectories differ from a simple linear return to a past state (Battarbee et al., 2012). Furthermore, in lakes such as Rostherne Mere that have a large range of annual nutrient concentrations, a consideration of the management classification assessment should be made, as currently it does not take into account the seasonal variation possible in each individual catchment. For example, this study highlighted that Rostherne Mere for part of the year has low P concentrations (summer; see chapter 4), implying that managed recovery has been a relative success, however, due to the high average annual concentrations (boosted by winter high concentrations; see chapter 4) Rostherne's current management status is highly undesirable.

The implication of climate change for management target setting adds a further issue for effective and realistic targets. The future projections for a changing climate will not only directly impact the lake through altering the physical limnological regime over a short (see chapter 5) and longer-term (see chapter 6), yet it will also indirectly impact the cycling and availability of the nutrient loads (see chapter 6), diverting the anticipated managed recovery trajectory along a new path. Therefore, this study highlights the growing requirement for management practitioners to consider the policy for setting and reviewing recovery targets in impacted systems, defining more realistic metrics and processes to inform future decision making (Carvalho et al., 2013, Poikane et al., 2014). Furthermore, beyond the changes in the water body itself, future changes in catchment land use will also be of upmost importance for change, requiring assessment to support the implementation of freshwater management policies (Hering et al., 2015). For example, climate change can lead to natural changes in vegetation and crop selection, or anthropogenic infrastructure developments can alter the hydrology and nutrient transfer within the catchment, as has been seen recently within the Rostherne Mere catchment from the building of a new major road system,

disturbing the subsoils and leading to increased allochthonous sediment transfer (Keaveney et al., in progress), and altering the north catchment hydrology and nutrient use on the land with a change from agriculture to hard standing road.

Additionally, this research highlights the increasing requirement for lake managers to consider the wider implications of nutrient recovery schemes, as lakes have the great capacity to bury vast quantities of carbon within their sediments over geological timescales (i.e. 10^3 to 10^5 years; see chapter 3). Therefore, in lake systems that have a propensity to bury autochthonous carbon and may be difficult to recover to desirable target levels, a cost-benefit analysis might take advantage of this by enhancing some ecosystem services (i.e. carbon sequestration) while also providing a financial saving for management intervention, introducing the option of selective lake recovery management. However, at a lake with protected status, like Rostherne Mere (SSSI, NNR, Ramsar), other ecosystem services will likely take priority for management target setting.

Finally, this study highlights the importance of combining short-term and long-term limnological techniques for the assessment and future projections of change. The observed inter-annual variability highlights the importance of long-term monitoring, with Rostherne Mere's rich history of scientific interest making it one of the most important freshwater bodies in the UK and beyond. Therefore, continued monitoring and assessment of the proxies of change will provide an excellent opportunity for continued understanding of freshwater bodies and their catchments under changing anthropogenic and climatic impact.

8. References

- ADLER, S., HUEBENER, T., DRESSLER, M., LOTTER, A. F. & ANDERSON, N. J. 2010. A comparison of relative abundance versus class data in diatom-based quantitative reconstructions. *Journal of environmental management*, 91, 1380-1388.
- ALIN, S. R. & JOHNSON, T. C. 2007a. Carbon cycling in large lakes of the world: A synthesis of production, burial, and lake-atmosphere exchange estimates. *Global Biogeochemical Cycles*, 21.
- ALIN, S. R. & JOHNSON, T. C. 2007b. Carbon cycling in large lakes of the world: A synthesis of production, burial, and lake-atmosphere exchange estimates. *Global Biogeochemical Cycles*, 21, 1-12.
- ANDERSEN, H. E., KRONVANG, B., LARSEN, S. E., HOFFMANN, C. C., JENSEN, T. S. & RASMUSSEN, E. K. 2006. Climate-change impacts on hydrology and nutrients in a Danish lowland river basin. *Science of the Total Environment*, 365, 223-237.
- ANDERSON, N. J. 1990. Variability of diatom concentrations and accumulation rates in sediments of a small lake basin. *Limnology and Oceanography*, 35, 497-508.
- ANDERSON, N. J. & BATTARBEE, R. W. 1994. Aquatic community persistence and variability: A palaeoecological perspective. In: GILLER, P. A., HILDREW, A. & RAFELLI, D. (eds.) *Aquatic Ecology: Scale, Pattern and Process*. Oxford: Blackwell Scientific Press.
- ANDERSON, N. J., BENNION, H. & LOTTER, A. F. 2014. Lake eutrophication and its implications for organic carbon sequestration in Europe. *Global Change Biology*, 20, 2741-2751.
- ANDERSON, N. J., DIETZ, R. D. & ENGSTROM, D. R. 2013. Land-use change, not climate, controls organic carbon burial in lakes. *Proceedings of the Royal Society B-Biological Sciences*, 280, 1-7.
- APOTHELOZ-PERRET-GENTIL, L., CORDONIER, A., STRAUB, F., ISELI, J. & ESLING, P. 2017. Taxonomy-free molecular diatom index for high-throughput eDNA biomonitoring. *Molecular Ecology Resources*, 17, 1231-1242.
- APPLEBY, P. G. 2001. Chronostratigraphic techniques in recent sediments. In: LAST, W. M. & SMOL, J. P. (eds.) *Tracking Environmental Change Using Lake Sediments. Volume 1: Basin Analysis, Coring, and Chronological Techniques*. Dordrecht: Kluwer Academic Publishers.
- ARYAL, R., GRINHAM, A. & BEECHAM, S. 2014. Tracking Inflows in Lake Wivenhoe during a Major Flood Using Optical Spectroscopy. *Water*, 6, 2339-2352.
- AUSTIN, J. A. & ALLEN, J. 2011. Sensitivity of summer Lake Superior thermal structure to meteorological forcing. *Limnology and Oceanography*, 56, 1141-1154.
- BAKKER, E. S. & HILT, S. 2016. Impact of water-level fluctuations on cyanobacterial blooms: options for management. *Aquatic Ecology*, 50, 485-498.
- BARKER, P. A., PATES, J. M., PAYNE, R. J. & HEALEY, R. M. 2005. Changing nutrient levels in grasmere, English lake district, during recent centuries. *Freshwater Biology*, 50, 1971-1981.

- BARRY, C. D., RENOU-WILSON, F., WILSON, D., MULLER, C. & FOY, R. H. 2016. Magnitude, form and bioavailability of fluvial carbon exports from Irish organic soils under pasture. *Aquatic Sciences*, 78, 541-560.
- BATTARBEE, R. W. 1977. Observations on the recent history of Lough Neagh Northern Ireland and its drainage basin. *Philosophical Transactions of the Royal Society of London B Biological Sciences*, 281, 303-346.
- BATTARBEE, R. W., ANDERSON, N. J., BENNION, H. & SIMPSON, G. L. 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, 2091-2106.
- BATTARBEE, R. W., JONES, V. J., FLOWER, R. J., CAMERON, N. G., BENNION, H., CARVALHO, L. & JUGGINS, S. 2001. Diatoms. In: SMOL, J. P., BIRKS, H. J. B., LAST, W. M., BRADLEY, R. S. & ALVERSON, K. (eds.) *Tracking Environmental Change Using Lake Sediments: Terrestrial, Algal, and Siliceous Indicators*. Dordrecht: Springer Netherlands.
- BATTARBEE, R. W. & KNEEN, M. J. 1982. The use of electronically counted microspheres in absolute diatom analysis. *Limnology and Oceanography*, 27, 184-188.
- BECK, K. K., MEDEIROS, A. S. & FINKELSTEIN, S. A. 2016. Drivers of Change in a 7300-Year Holocene Diatom Record from the Hemi-Boreal Region of Ontario, Canada. *Plos One*, 11, 20.
- BELCHER, J. H. & STOREY, J. E. 1968. The phytoplankton of Rostherne and Mere Meres, Cheshire. Hull: Naturalist.
- BENNION, H., BATTARBEE, R. W., SAYER, C. D., SIMPSON, G. L. & DAVIDSON, T. A. 2011. Defining reference conditions and restoration targets for lake ecosystems using palaeolimnology: a synthesis. *Journal of Paleolimnology*, 45, 533-544.
- BERTANI, I., PRIMICERIO, R. & ROSSETTI, G. 2016. Extreme Climatic Event Triggers a Lake Regime Shift that Propagates Across Multiple Trophic Levels. *Ecosystems*, 19, 16-31.
- BERTHON, V., ALRIC, B., RIMET, F. & PERGA, M. E. 2014. Sensitivity and responses of diatoms to climate warming in lakes heavily influenced by humans. *Freshwater Biology*, 59, 1755-1767.
- BIGLER, C., VON GUNTEN, L., LOTTER, A. F., HAUSMANN, S., BLASS, A., OHLENDORF, C. & STURM, M. 2007. Quantifying human-induced eutrophication in Swiss mountain lakes since AD 1800 using diatoms. *Holocene*, 17, 1141-1154.
- BLOESCH, J. 1994. A Review of Methods used to Measure Sediment Resuspension. *Hydrobiologia*, 284, 13-18.
- BLOESCH, J. & BURNS, N. M. 1980. A Critical-Review of Sedimentation Trap Technique. *Schweizerische Zeitschrift Fur Hydrologie-Swiss Journal of Hydrology*, 42, 15-55.
- BRIERLEY, B., CARVALHO, L., DAVIES, S. & KROKOWSKI, J. 2007. Guidance on the quantitative analysis of phytoplankton in Freshwater Samples. Report to SNIFFER (Project WFD80), Edinburgh, December 2007.
- BROOKS, A. S. & ZASTROW, J. C. 2002. The potential influence of climate change on offshore primary production in Lake Michigan. *Journal of Great Lakes Research*, 28, 597-607.
- BROTHERS, S. M., HILT, S., ATTERMAYER, K., GROSSART, H. P., KOSTEN, S., LISCHKE, B., MEHNER, T., MEYER, N., SCHARNWEBER, K. & KOHLER, J.

2013. A regime shift from macrophyte to phytoplankton dominance enhances carbon burial in a shallow, eutrophic lake. *Ecosphere*, 4, 1-17.
- BUFFAM, I., TURNER, M. G., DESAI, A. R., HANSON, P. C., RUSAK, J. A., LOTTIG, N. R., STANLEY, E. H. & CARPENTER, S. R. 2011. Integrating aquatic and terrestrial components to construct a complete carbon budget for a north temperate lake district. *Global Change Biology*, 17, 1193-1211.
- BUQUET, D., ANSCHUTZ, P., CHARBONNIER, C., RAPIN, A., SINAYS, R., CANREDON, A., BUJAN, S. & POIRIER, D. 2017. Nutrient sequestration in Aquitaine lakes (SW France) limits nutrient flux to the coastal zone. *Journal of Sea Research*.
- BURDIGE, D. J. 2007. Preservation of Organic Matter in Marine Sediments: Controls, Mechanisms, and an Imbalance in Sediment Organic Carbon Budgets? *Chemical Reviews*, 107, 467-485.
- BUTZER, K. 2015. Anthropocene as an evolving paradigm. *Holocene*, 25, 1539-1541.
- CALVERT, S. E., KARLIN, R. E., TOOLIN, L. J., DONAHUE, D. J., SOUTHON, J. R. & VOGEL, J. S. 1991. Low organic-carbon accumulation rates in Black-Sea sediments. *Nature*, 350, 692-695.
- CAPON, S. J., LYNCH, A. J. J., BOND, N., CHESSMAN, B. C., DAVIS, J., DAVIDSON, N., FINLAYSON, M., GELL, P. A., HOHNBERG, D., HUMPHREY, C., KINGSFORD, R. T., NIELSEN, D., THOMSON, J. R., WARD, K. & MAC NALLY, R. 2015. Regime shifts, thresholds and multiple stable states in freshwater ecosystems; a critical appraisal of the evidence. *Science of the Total Environment*, 534, 122-130.
- CARLSON, R. E. 1977. Trophic State Index for Lakes. *Limnology and Oceanography*, 22, 361-369.
- CARNERO-BRAVO, V., MERINO-IBARRA, M., RUIZ-FERNANDEZ, A. C., SANCHEZ-CABEZA, J. A. & GHALEB, B. 2015. Sedimentary record of water column trophic conditions and sediment carbon fluxes in a tropical water reservoir (Valle de Bravo, Mexico). *Environmental Science and Pollution Research*, 22, 4680-4694.
- CARPENTER, S. R. 2005. Eutrophication of aquatic ecosystems: Bistability and soil phosphorus. *Proceedings of the National Academy of Sciences of the United States of America*, 102, 10002-10005.
- CARPENTER, S. R., LUDWIG, D. & BROCK, W. A. 1999. Management of eutrophication for lakes subject to potentially irreversible change. *Ecological Applications*, 9, 751-771.
- CARVALHO, L. 1993. *Experimental limnology on four Cheshire Meres*. PhD, Liverpool University.
- CARVALHO, L., BEKLIOGLU, M. & 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, 399-410.
- CARVALHO, L., MILLER, C., SPEARS, B. M., GUNN, I. D. M., BENNION, H., KIRIKA, A. & MAY, L. 2012. Water quality of Loch Leven: responses to enrichment, restoration and climate change. *Hydrobiologia*, 681, 35-47.
- CARVALHO, L., POIKANE, S., SOLHEIM, A. L., PHILLIPS, G., BORICS, G., CATALAN, J., DE HOYOS, C., DRAKARE, S., DUDLEY, B. J., JARVINEN, M., LAPLACE-TREYTURE, C., MAILEHT, K., MCDONALD, C., MISCHKE, U., MOE, J., NOGES, P., NOGES, T., OTT, I., PASZTALENIEC, A.,

- SKJELBRED, B. & THACKERAY, S. J. 2013. Strength and uncertainty of phytoplankton metrics for assessing eutrophication impacts in lakes. *Hydrobiologia*, 704, 127-140.
- CATALAN, N., MARCE, R., KOTHAWALA, D. N. & TRANVIK, L. J. 2016. Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geosci*, 9, 501-504.
- CATTANEO, A., GALANTI, G., GENTINETTA, S. & SUSANA, A. 1998. Epiphytic algae and macroinvertebrates on submerged and floating-leaved macrophytes in an Italian lake. *Freshwater Biology*, 39, 725-740.
- CHARLTON, M. N. & LEAN, D. R. S. 1987. SEDIMENTATION, RESUSPENSION, AND OXYGEN DEPLETION IN LAKE ERIE (1979). *Journal of Great Lakes Research*, 13, 709-723.
- CHEN, G. & RYNEARSON, T. A. 2016. Genetically distinct populations of a diatom co-exist during the North Atlantic spring bloom. *Limnology and Oceanography*, 61, 2165-2179.
- CHEN, N. W., WU, Y. Q., WU, J. Z., YAN, X. L. & HONG, H. S. 2014. Natural and human influences on dissolved silica export from watershed to coast in Southeast China. *Journal of Geophysical Research-Biogeosciences*, 119, 95-109.
- CLOW, D. W., STACKPOOLE, S. M., VERDIN, K. L., BUTMAN, D. E., ZHU, Z. L., KRABBENHOFT, D. P. & STRIEGL, R. G. 2015. Organic Carbon Burial in Lakes and Reservoirs of the Conterminous United States. *Environmental Science & Technology*, 49, 7614-7622.
- COLE, J. J., PRAIRIE, Y. T., CARACO, N. F., MCDOWELL, W. H., TRANVIK, L. J., STRIEGL, R. G., DUARTE, C. M., KORTELAJINEN, P., DOWNING, J. A., MIDDELBURG, J. J. & MELACK, J. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10, 171-184.
- COMMISSION, E. 2012. Danish European Water Framework Directive: River Basin Management Plans. In: COMMISSION, E. (ed.) *Implementation of the Water Framework Directive*. European commission, Brussels: European commission.
- COORS, A. & DE MEESTER, L. 2008. Synergistic, antagonistic and additive effects of multiple stressors: predation threat, parasitism and pesticide exposure in *Daphnia magna*. *Journal of Applied Ecology*, 45, 1820-1828.
- CORY, R. M., WARD, C. P., CRUMP, B. C. & KLING, G. W. 2014. Sunlight controls water column processing of carbon in arctic fresh waters. *Science*, 345, 925-928.
- CROSS, I. D., MCGOWAN, S., NEEDHAM, T. & POINTER, C. M. 2014. The effects of hydrological extremes on former gravel pit lake ecology: management implications. *Fundamental and Applied Limnology*, 185, 71-90.
- DAVISON, W., REYNOLDS, C. S. & FINLAY, B. J. 1985. Algal Control of Lake Geochemistry - Redox Cycles in Rostherne Mere, UK. *Water research*, 19, 265-267.
- DAVISON, W. & WOOF, C. 1984. A Study of the Cycling of Manganese and Other Elements in a Seasonally Anoxic Lake, Rostherne-Mere, UK. *Water research*, 18, 727-734.
- DE NOBEL, W. T., HUISMAN, J., SNOEP, J. L. & MUR, L. R. 1997. Competition for phosphorus between the nitrogen-fixing cyanobacteria *Anabaena* and *Aphanizomenon*. *FEMS Microbiology Ecology*, 24, 259-267.

- DEAN, W. E. 1974. Determination of Carbonate and Organic-Matter in Calcareous Sediments and Sedimentary-Rocks by Loss on Ignition - Comparison with Other Methods. *Journal of Sedimentary Petrology*, 44, 242-248.
- DEMASTER, D. J. 2003. Organic carbon, calcium carbonate and biogenic silica of sediment core TT013_41.
- DIETZ, R. D., ENGSTROM, D. R. & ANDERSON, N. J. 2015. Patterns and drivers of change in organic carbon burial across a diverse landscape: Insights from 116 Minnesota lakes. *Global Biogeochemical Cycles*, 29, 708-727.
- DOKULIL, M. T., JAGSCH, A., GEORGE, G. D., ANNEVILLE, O., JANKOWSKI, T., WAHL, B., LENHART, B., BLECKNER, T. & TEUBNER, K. 2006. Twenty years of spatially coherent deepwater warming in lakes across Europe related to the North Atlantic Oscillation. *Limnology and Oceanography*, 51, 2787-2793.
- DONG, X. H., BENNION, H., BATTARBEE, R., YANG, X. D., YANG, H. D. & LIU, E. F. 2008. Tracking eutrophication in Taihu Lake using the diatom record: potential and problems. *Journal of Paleolimnology*, 40, 413-429.
- DOUGLAS, R. W., RIPPEY, B. & GIBSON, C. E. 2002. Interpreting sediment trap data in relation to the dominant sediment redistribution process in a lake. *Archiv Fur Hydrobiologie*, 155, 529-539.
- DOWNING, J. A., WATSON, S. B. & MCCAULEY, E. 2001. Predicting Cyanobacteria dominance in lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 58, 1905-1908.
- EASTERLING, D. R., MEEHL, G. A., PARMESAN, C., CHANGNON, S. A., KARL, T. R. & MEARN, L. O. 2000. Climate Extremes: Observations, Modeling, and Impacts. *Science*, 289, 2068-2074.
- EIXLER, S., KARSTEN, U. & SELIG, U. 2006. Phosphorus storage in *Chlorella vulgaris* (Trebouxiophyceae, Chlorophyta) cells and its dependence on phosphate supply. *Phycologia*, 45, 53-60.
- EKSTROM, M., FOWLER, H. J., KILSBY, C. G. & JONES, P. D. 2005. New estimates of future changes in extreme rainfall across the UK using regional climate model integrations. 2. Future estimates and use in impact studies. *Journal of Hydrology*, 300, 234-251.
- ELLIOTT, J. A. 2010. The seasonal sensitivity of Cyanobacteria and other phytoplankton to changes in flushing rate and water temperature. *Global Change Biology*, 16, 864-876.
- ELLIOTT, J. A. 2012a. Is the future blue-green? A review of the current model predictions of how climate change could affect pelagic freshwater cyanobacteria. *Water Research*, 46, 1364-1371.
- ELLIOTT, J. A. 2012b. Predicting the impact of changing nutrient load and temperature on the phytoplankton of England's largest lake, Windermere. *Freshwater Biology*, 57, 400-413.
- ELLIOTT, J. A. & DEFEEW, L. 2012. Modelling the response of phytoplankton in a shallow lake (Loch Leven, UK) to changes in lake retention time and water temperature. *Hydrobiologia*, 681, 105-116.
- ELLIOTT, J. A., IRISH, A. E. & REYNOLDS, C. S. 2010. Modelling Phytoplankton Dynamics in Fresh Waters: Affirmation of the PROTECH Approach to Simulation. *Freshwater Reviews*, 3, 75-96.
- ELLIOTT, J. A., MCELARNEY, Y. R. & ALLEN, M. 2016. The past and future of phytoplankton in the UK's largest lake, Lough Neagh. *Ecological Indicators*, 68, 142-149.

- ENGSTROM, D. & ROSE, N. 2013. A whole-basin, mass-balance approach to paleolimnology. *Journal of Paleolimnology*, 49, 333-347.
- ENVIRONMENTAGENCY 2016. Nitrate vulnerable zone designation (NVZ) 2017 Eutrophic Waters (Lakes). EnvironmentAgency.
- EUROPEAN_COMMISSION 2000. Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 Establishing a Framework for Community Action in the Field of Water Policy. *In*: COMMISSION, E. (ed.). Official Journal 22: European Commission, Brussels.
- EVANS, C. D., MONTEITH, D. T. & COOPER, D. M. 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, 137, 55-71.
- FAHRNER, S., RADKE, M., KARGER, D. & BLODAU, C. 2008. Organic matter mineralisation in the hypolimnion of an eutrophic Maar lake. *Aquatic Sciences*, 70, 225-237.
- FERLAND, M.-E., DEL GIORGIO, P. A., TEODORU, C. R. & PRAIRIE, Y. T. 2012. Long-term C accumulation and total C stocks in boreal lakes in northern Quebec. *Global Biogeochemical Cycles*, 26, GB0E04-GB0E04.
- FLAIM, G., ECCEL, E., ZEILEIS, A., TOLLER, G., CERASINO, L. & OBERTEGGER, U. 2016. Effects of re-oligotrophication and climate change on lake thermal structure. *Freshwater Biology*, 61, 1802-1814.
- GACHTER, R. & BLOESCH, J. 1985. Seasonal and Vertical Variation in the C-P Ratio of Suspended and Settling Seston of Lakes. *Hydrobiologia*, 128, 193-200.
- GALE, P. M., REDDY, K. R. & GRAETZ, D. A. 1992. Mineralization of Sediment Organic-Matter Under Anoxic Conditions. *Journal of environmental quality*, 21, 394-400.
- GALMAN, V., RYDBERG, J., DE-LUNA, S. S., BINDLER, R. & 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, 1076-1082.
- GAUTHIER, J., PRAIRIE, Y. T. & BEISNER, B. E. 2014. Thermocline deepening and mixing alter zooplankton phenology, biomass and body size in a whole-lake experiment. *Freshwater Biology*, 59, 998-1011.
- GEORGE, D. G., MABERLY, S. C. & HEWITT, D. P. 2004. The influence of the North Atlantic Oscillation on the physics, chemistry and biology of four lakes in the English Lake District. *Freshwater Biology*, 49, 760 - 774.
- GEVREY, M., RIMET, F., PARK, Y. S., GIRAUDEL, J. L., ECTOR, L. & LEK, S. 2004. Water quality assessment using diatom assemblages and advanced modelling techniques. *Freshwater Biology*, 49, 208-220.
- GHAFFAR, S., STEVENSON, R. J. & KHAN, Z. 2017. Effect of phosphorus stress on *Microcystis aeruginosa* growth and phosphorus uptake. *PLOS ONE*, 12, e0174349.
- GIBSON, C. E., ANDERSON, N. J. & HAWORTH, E. Y. 2002. *Aulacoseira subarctica*: taxonomy, physiology, ecology and palaeoecology. *European Journal of Phycology*, 38, 83-101.
- GIBSON, C. E., WANG, G. & FOY, R. H. 2000. Silica and diatom growth in Lough Neagh: the importance of internal recycling. *Freshwater Biology*, 45, 285-293.
- GODLEWSKA, M., MAZURKIEWICZ-BORON, G., POICIECHA, A., WILK-WOZNIAK, E. & JELONEK, M. 2003. Effects of flood on the functioning of the Dobczyce reservoir ecosystem. *Hydrobiologia*, 504, 305-313.

- GOMEZ, N., RIERA, J. L. & SABATER, S. 1995. Ecology and morphological variability of *Aulacoseira granulata* (bacillariophyceae) in spanish reservoirs. *Journal of Plankton Research*, 17, 1-16.
- GRAHAM, M. D. & VINEBROOKE, R. D. 2009. Extreme weather events alter planktonic communities in boreal lakes. *Limnology and Oceanography*, 54, 2481-2492.
- GUDASZ, C., BASTVIKEN, D., STEGER, K., PREMKE, K., SOBEK, S. & TRANVIK, L. J. 2010. Temperature-controlled organic carbon mineralization in lake sediments. *Nature*, 466, 478-481.
- GUILDFORD, S. J. & HECKY, R. E. 2000. Total nitrogen, total phosphorus, and nutrient limitation in lakes and oceans: Is there a common relationship? *Limnology and Oceanography*, 45, 1213-1223.
- HADLEY, K. R., DOUGLAS, M. S. V., MCGHEE, R., BLAIS, J. M. & SMOL, J. P. 2010. Ecological influences of Thule Inuit whalers on high Arctic pond ecosystems: a comparative paleolimnological study from Bathurst Island (Nunavut, Canada). *Journal of Paleolimnology*, 44, 85-93.
- HALL, R. I. & SMOL, J. P. 1999. *Diatoms as indicators of lake eutrophication*.
- HANSSON, L. A., ANNADOTTER, H., BERGMAN, E., HAMRIN, S. F., JEPPESEN, E., KAIRESALO, T., LUOKKANEN, E., NILSSON, P. A., SONDERGAARD, M. & STRAND, J. 1998. Biomanipulation as an application of food-chain theory: Constraints, synthesis, and recommendations for temperate lakes. *Ecosystems*, 1, 558-574.
- HARRISON, R. & ROGERS, D. A. 1977. The birds of Rostherne Mere. Banbury: Nature Conservancy.
- HAUSMANN, S. & PIENITZ, R. 2007. Seasonal climate inferences from high-resolution modern diatom data along a climate gradient: a case study. *Journal of Paleolimnology*, 38, 73-96.
- HEAD, R. M., JONES, R. I., BAILEY-WATTS, A. E. 1999. Vertical movements by planktonic cyanobacteria and the translocation of phosphorus: implications for lake restoration. *Aquatic Conservation: Marine and Freshwater Ecosystems*, 9, 111-120.
- HEATHCOTE, A. J., ANDERSON, N. J., PRAIRIE, Y. T., ENGSTROM, D. R. & DEL GIORGIO, P. A. 2015. Large increases in carbon burial in northern lakes during the Anthropocene. *Nature Communications*, 6, 6.
- HEATHCOTE, A. J. & DOWNING, J. A. 2012. Impacts of Eutrophication on Carbon Burial in Freshwater Lakes in an Intensively Agricultural Landscape. *Ecosystems*, 15, 60-70.
- HECKY, R. E., CAMPBELL, P. & HENDZEL, L. L. 1993. The Stoichiometry of Carbon, Nitrogen, and Phosphorus in Particulate Matter of Lakes and Oceans. *Limnology and Oceanography*, 38, 709-724.
- HECKY, R. E., MUGIDDE, R., RAMLAL, P. S., TALBOT, M. R. & KLING, G. W. 2010. Multiple stressors cause rapid ecosystem change in Lake Victoria. *Freshwater Biology*, 55, 19-42.
- HEDGES, J. I., HU, F. S., DEVOL, A. H., HARTNETT, H. E., TSAMAKIS, E. & KEIL, R. G. 1999. Sedimentary organic matter preservation: A test for selective degradation under oxic conditions. *American Journal of Science*, 299, 529-555.
- HERING, D., BORJA, A., CARSTENSEN, J., CARVALHO, L., ELLIOTT, M., FELD, C. K., HEISKANEN, A. S., JOHNSON, R. K., MOE, J., PONT, D., SOLHEIM, A. L. & VAN DE BUND, W. 2010. The European Water Framework Directive

- at the age of 10: A critical review of the achievements with recommendations for the future. *Science of the Total Environment*, 408, 4007-4019.
- HERING, D., CARVALHO, L., ARGILLIER, C., BEKLIOGLU, M., BORJA, A., CARDOSO, C., DUEL, H., FERREIRA, T., GLOBEVNIK, L., HANGANU, J., HELLSTEN, S., PANAGOPOULOS, SCHMUTZ, S., VENOHR, M. & BIRK, S. 2015. Managing aquatic ecosystems and water resources under multiple stress - An introduction to the MARS project. *Science of the Total Environment*, 503-504, 10-21.
- HILLEBRAND, H., DURSELEN, C. D., KIRSCHTEL, D., POLLINGHER, U. & ZOHARY, T. 1999. Biovolume calculation for pelagic and benthic microalgae. *Journal of Phycology*, 35, 403-424.
- HILTON, J. 1985. A Conceptual-Framework for Predicting the Occurrence of Sediment Focusing and Sediment Redistribution in Small Lakes. *Limnology and Oceanography*, 30, 1131-1143.
- HILTON, J., LISHMAN, J. P. & ALLEN, P. V. 1986. The Dominant Processes of Sediment Distribution and Focusing in a Small, Eutrophic, Monomictic Lake. *Limnology and Oceanography*, 31, 125-133.
- HORPPILA, J. & NURMINEN, L. 2005. Effects of calculation procedure and sampling site on trap method estimates of sediment resuspension in a shallow lake. *Sedimentology*, 52, 903-913.
- HUBER, V., ADRIAN, R. & GERTEN, D. 2008. Phytoplankton response to climate warming modified by trophic state. *Limnology and Oceanography*, 53, 1-13.
- HUPFER, M., REITZEL, K., KLEEBOEG, A. & LEWANDOWSKI, J. 2016. Long-term efficiency of lake restoration by chemical phosphorus precipitation: Scenario analysis with a phosphorus balance model. *Water Research*, 97, 153-161.
- HUSER, B. J., EGEMOSE, S., HARPER, H., HUPFER, M., JENSEN, H., PILGRIM, K. M., REITZEL, K., RYDIN, E. & FUTTER, M. 2016a. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Research*, 97, 122-132.
- HUSER, B. J., FUTTER, M., LEE, J. T. & PERNIEL, M. 2016b. In-lake measures for phosphorus control: The most feasible and cost-effective solution for long-term management of water quality in urban lakes. *Water Research*, 97, 142-152.
- HUSZAR, V. L. D. & REYNOLDS, C. S. 1997. Phytoplankton periodicity and sequences of dominance in an Amazonian flood-plain lake (Lago Batata, Para, Brazil): responses to gradual environmental change. *Hydrobiologia*, 346, 169-181.
- HUTCHINSON, G. E. & LÖFFLER, H. 1956. The thermal classification of lakes. *Proceedings of the National Academy of Sciences*, 42, 84 - 86.
- IMMERS, A. K., BAKKER, E. S., VAN DONK, E., TER HEERDT, G. N. J., GEURTS, J. J. M. & DECLERCK, S. A. J. 2015. Fighting internal phosphorus loading: An evaluation of the large scale application of gradual Fe-addition to a shallow peat lake. *Ecological Engineering*, 83, 78-89.
- IZMEST'EVA, L. R., MOORE, M. V., HAMPTON, S. E., FERWERDA, C. J., GRAY, D. K., WOO, K. H., PISLEGINA, H. V., KRASHCHUK, L. S., SHIMARAEVA, S. V. & SILOW, E. A. 2016. Lake-wide physical and biological trends associated with warming in Lake Baikal. *Journal of Great Lakes Research*, 42, 6-17.
- JARVIE, H. P., SHARPLEY, A. N., SPEARS, B., BUDA, A. R., MAY, L. & KLEINMAN, P. J. A. 2013a. Water Quality Remediation Faces Unprecedented

- Challenges from "Legacy Phosphorus". *Environmental Science & Technology*, 47, 8997-8998.
- JARVIE, H. P., SHARPLEY, A. N., WITHERS, P. J. A., SCOTT, J. T., HAGGARD, B. E. & NEAL, C. 2013b. Phosphorus Mitigation to Control River Eutrophication: Murky Waters, Inconvenient Truths, and "Postnormal" Science. *Journal of Environmental Quality*, 42, 295-304.
- JENSEN, H. S., REITZEL, K. & EGEMOSE, S. 2015. Evaluation of aluminum treatment efficiency on water quality and internal phosphorus cycling in six Danish lakes. *Hydrobiologia*, 751, 189-199.
- JEPPESEN, E., KRONVANG, B., OLESEN, J. E., AUDET, J., SONDERGAARD, M., HOFFMANN, C. C., ANDERSEN, H. E., LAURIDSEN, T. L., LIBORIUSSEN, L., LARSEN, S. E., BEKLIOGLU, M., MEERHOFF, M., OZEN, A. & OZKAN, K. 2011. Climate change effects on nitrogen loading from cultivated catchments in Europe: implications for nitrogen retention, ecological state of lakes and adaptation. *Hydrobiologia*, 663, 1-21.
- JEPPESEN, E., SONDERGAARD, M., JENSEN, J. P., HAVENS, K. E., ANNEVILLE, O., CARVALHO, L., COVENEY, M. F., DENEKE, R., DOKULIL, M. T., FOY, B., GERDEAUX, D., HAMPTON, S. E., HILT, S., KANGUR, K., KOHLER, J., LAMMENS, E. H. H. R., LAURIDSEN, T. L., MANCA, M., MIRACLE, M. R., MOSS, B., NOGES, P., PERSSON, G., PHILLIPS, G., PORTIELJE, R., SCHELSKE, C. L., STRAILE, D., TATRAI, I., WILLEN, E. & WINDER, M. 2005. Lake responses to reduced nutrient loading - an analysis of contemporary long-term data from 35 case studies. *Freshwater Biology*, 50, 1747-1771.
- JEWSON, D. H. 1992. LIFE CYCLE OF A STEPHANODISCUS SP. (BACILLARIOPHYTA)1. *Journal of Phycology*, 28, 856-866.
- JEWSON, D. H., RIPPEY, B. H. & GILMORE, W. K. 1981. LOSS RATES FROM SEDIMENTATION, PARASITISM, AND GRAZING DURING THE GROWTH, NUTRIENT LIMITATION, AND DORMANCY OF A DIATOM CROP. *Limnology and Oceanography*, 26, 1045-1056.
- JONES, M. R., FOWLER, H. J., KILSBY, C. G. & BLENKINSOP, S. 2013. An assessment of changes in seasonal and annual extreme rainfall in the UK between 1961 and 2009. *International Journal of Climatology*, 33, 1178-1194.
- JONSSON, A., MEILI, M., BERGSTROM, A. K. & JANSSON, M. 2001. Whole-lake mineralization of allochthonous and autochthonous organic carbon in a large humic lake (Ortrasket, N. Sweden). *Limnology and Oceanography*, 46, 1691-1700.
- KALFF, J. 2002. *Limnology : inland water ecosystems*, Upper Saddle River, NJ, Prentice Hall.
- KATZ, S. L., IZMEST'EVA, L. R., HAMPTON, S. E., OZERSKY, T., SHCHAPOV, K., MOORE, M. V., SHIMARAEVA, S. V. & SILOW, E. A. 2015. The "Melosira years" of Lake Baikal: Winter environmental conditions at ice onset predict under-ice algal blooms in spring. *Limnology and Oceanography*, 60, 1950-1964.
- KEAVENEY, E. M., RADBOURNE, A. D., MCGOWAN, S., RYVES, D. B. & REIMER, P. J. in progress. Carbon source and production rate influence carbon sequestration in a deep eutrophic lake.
- KELLERMAN, A. M., KOTHAWALA, D. N., DITTMAR, T. & TRANVIK, L. J. 2015. Persistence of dissolved organic matter in lakes related to its molecular characteristics. *Nature Geoscience*, 8, 454-457.

- KILHAM, P. & KILHAM, S. S. 1990. ENDLESS SUMMER - INTERNAL LOADING PROCESSES DOMINATE NUTRIENT CYCLING IN TROPICAL LAKES. *Freshwater Biology*, 23, 379-389.
- KIRILOVA, E. P., BLUSZCZ, P., HEIRI, O., CREMER, H., OHLENDORF, C., LOTTER, A. F. & ZOLITSCHKA, B. 2008. Seasonal and interannual dynamics of diatom assemblages in Sacrower See (NE Germany): a sediment trap study. *Hydrobiologia*, 614, 159-170.
- KIRILOVA, E. P., CREMER, H., HEIRI, O. & LOTTER, A. F. 2010. Eutrophication of moderately deep Dutch lakes during the past century: flaws in the expectations of water management? *Hydrobiologia*, 637, 157-171.
- KIRILOVA, E. P., HEIRI, O., BLUSZCZ, P., ZOLITSCHKA, B. & LOTTER, A. F. 2011. Climate-driven shifts in diatom assemblages recorded in annually laminated sediments of Sacrower See (NE Germany). *Aquatic Sciences*, 73, 201-210.
- KOEHLER, B., LANDELIUS, T., WEYHENMEYER, G. A., MACHIDA, N. & TRANVIK, L. J. 2014. Sunlight-induced carbon dioxide emissions from inland waters. *Global Biogeochemical Cycles*, 28, 696-711.
- 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., NÖGES, T., ROMO, S. & SCHEFFER, M. 2012. Warmer climates boost cyanobacterial dominance in shallow lakes. *Global Change Biology*, 18, 118-126.
- KOTHAWALA, D. N., STEDMON, C. A., MULLER, R. A., WEYHENMEYER, G. A., KOHLER, S. J. & TRANVIK, L. J. 2014. Controls of dissolved organic matter quality: evidence from a large-scale boreal lake survey. *Global Change Biology*, 20, 1101-1114.
- KRIVTSOV, V., SIGEE, D. & BELLINGER, E. 2001. A one-year study of the Rostherne Mere ecosystem: seasonal dynamics of water chemistry, plankton, internal nutrient release, and implications for long-term trophic status and overall functioning of the lake. *Hydrological Processes*, 15, 1489-1506.
- KULBE, T., OHLENDORF, C. & STURM, M. 2006. Lacustrine particle dynamics in high-altitude Estany Redo (Spain) - a high resolution sediment trap study. *Journal of Limnology*, 65, 89-99.
- LANGDON, P. G., RUIZ, Z., BRODERSEN, K. P. & FOSTER, I. D. L. 2006. Assessing lake eutrophication using chironomids: understanding the nature of community response in different lake types. *Freshwater Biology*, 51, 562-577.
- LASKOV, C., AMELUNG, W. & PEIFFER, S. 2002. Organic matter preservation in the sediment of an acidic mining lake. *Environmental Science & Technology*, 36, 4218-4223.
- LEAVITT, P. R., FRITZ, S. C., ANDERSON, N. J., BAKER, P. A., BLENCKNER, T., BUNTING, L., CATALAN, J., CONLEY, D. J., HOBBS, W. O., JEPPESEN, E., KORHOLA, A., MCGOWAN, S., RUHLAND, K., RUSAK, J. A., SIMPSON, G. L., SOLOVIEVA, N. & 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.
- LEWIN, R. A. 1990. THE DIATOMS - BIOLOGY AND MORPHOLOGY OF THE GENERA - ROUND, FE. *Nature*, 346, 619-620.
- LIND, E. 1944. The phytoplankton of some Cheshire meres. *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, 86, 83-105.

- LIU, W. T., BOCANIOV, S. A., LAMB, K. G. & SMITH, R. E. H. 2014. Three dimensional modeling of the effects of changes in meteorological forcing on the thermal structure of Lake Erie. *Journal of Great Lakes Research*, 40, 827-840.
- LIVINGSTONE, D. 1979. *Algal remains in recent lake sediments*. Doctor of Philosophy, University of Leicester.
- LIVINGSTONE, D. & CAMBRAY, R. S. 1978. Confirmation of Cs-137 Dating by Algal Stratigraphy in Rostherne Mere. *Nature*, 276, 259-261.
- LIVINGSTONE, D. & REYNOLDS, C. S. 1981. Algal Sedimentation in Relation to Phytoplankton Periodicity in Rostherne Mere. *British Phycological Journal*, 16, 195-206.
- LOTTER, A. F. 1998. The recent eutrophication of Baldeggersee (Switzerland) as assessed by fossil diatom assemblages. *Holocene*, 8, 395-405.
- LOUCAIDES, S., CAHOON, L. B. & HENRY, E. J. 2007. Effects of watershed impervious cover on dissolved silica loading in storm flow. *Journal of the American Water Resources Association*, 4, 841-849.
- LUND, J. W. G., KIPLING, C. & LE CREN, E. D. 1958. The inverted microscope method of estimating algal numbers and the statistical basis of estimations by counting. *Hydrobiologia*, 11, 143-170.
- MABERLY, S. C., HURLEY, M. A., BUTTERWICK, C., CORRY, J. E., HEANEY, S. I., IRISH, A. E., JAWORSKI, G. H. M., LUND, J. W. G., REYNOLDS, C. S. & ROSCOE, J. V. 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, 19-34.
- MACKAY, E. B., FOLKARD, A. M. & JONES, I. D. 2014. Interannual variations in atmospheric forcing determine trajectories of hypolimnetic soluble reactive phosphorus supply in a eutrophic lake. *Freshwater Biology*, 59, 1646-1658.
- MACKERET, F. J. 1969. A short core sampler for subaqueous deposits. *Limnology and Oceanography*, 14, 145-151.
- MAERKI, M., MULLER, B. & WEHRLI, B. 2006. Microscale mineralization pathways in surface sediments: A chemical sensor study in Lake Baikal. *Limnology and Oceanography*, 51, 1342-1354.
- MARCHI, L., BORGA, M., PRECISO, E. & GAUME, E. 2010. Characterisation of selected extreme flash floods in Europe and implications for flood risk management. *Journal of Hydrology*, 394, 118-133.
- MCGOWAN, S., BARKER, P., HAWORTH, E. Y., LEAVITT, P. R., MABERLY, S. C. & PATES, J. 2012. Humans and climate as drivers of algal community change in Windermere since 1850. *Freshwater Biology*, 57, 260-277.
- MEIS, S., SPEARS, B. M., MABERLY, S. C. & PERKINS, R. G. 2013. Assessing the mode of action of Phoslock (R) in the control of phosphorus release from the bed sediments in a shallow lake (Loch Flemington, UK). *Water Research*, 47, 4460-4473.
- MEIS, S., THACKERAY, S. J. & JONES, I. D. 2009. Effects of recent climate change on phytoplankton phenology in a temperate lake. *Freshwater Biology*, 54, 1888-1898.
- MENZEL, A., SPARKS, T. H., ESTRELLA, N., KOCH, E., AASA, A., AHAS, R., ALM-KUBLER, K., BISSOLLI, P., BRASLAVSKA, O., BRIEDE, A., CHMIELEWSKI, F. M., CREPINSEK, Z., CURNEL, Y., DAHL, A., DEFILA, C., DONNELLY, A., FILELLA, Y., JATCZA, K., MAGE, F., MESTRE, A., NORDLI, O., PENUELAS, J., PIRINEN, P., REMISOVA, V., SCHEIFINGER, H., STRIZ, M., SUSNIK, A.,

- VAN VLIET, A. J. H., WIELGOLASKI, F. E., ZACH, S. & ZUST, A. 2006. European phenological response to climate change matches the warming pattern. *Global Change Biology*, 12, 1969-1976.
- MIDDELBURG, J. J. 1989. A Simple Rate Model for Organic-Matter Decomposition in Marine-Sediments. *Geochimica et Cosmochimica Acta*, 53, 1577-1581.
- MIHALJEVIC, M. & STEVIC, F. 2011. Cyanobacterial blooms in a temperate river-floodplain ecosystem: the importance of hydrological extremes. *Aquatic Ecology*, 45, 335-349.
- MILLS, K., RYVES, D. B., ANDERSON, N. J., BRYANT, C. L. & TYLER, J. J. 2014. Expressions of climate perturbations in western Ugandan crater lake sediment records during the last 1000 years. *Climate of the Past*, 10, 1581-1601.
- MILLS, K., SCHILLEREFF, D., SAULNIER-TALBOT, E., GELL, P. A., ANDERSON, N. J., ARNAUD, F., DONG, X., JONES, M., MCGOWAN, S., MASSAFERRO, J., MOORHOUSE, H., PEREZ, L. & RYVES, D. B. 2017. Deciphering long-term records of natural variability and human impact as recorded in lake sediments: a palaeolimnological puzzle. *WIREs Water*, 4.
- MONISMITH, S. G. 1985. Wind-forced motions in stratified lakes and their effect on mixed-layer shear. *Limnology and Oceanography*, 30, 771-783.
- MONTEITH, D. T., STODDARD, J. L., EVANS, C. D., DE WIT, H. A., FORSIUS, M., HOGASEN, T., WILANDER, A., SKJELKVALE, B. L., JEFFRIES, D. S., VUORENMAA, J., KELLER, B., KOPACEK, J. & VESELY, J. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, 450, 537-U9.
- MOORE, R. J. 2007. The PDM rainfall-runoff model. *Hydrology and Earth System Sciences*, 11, 483-499.
- MOSCHEN, R., LUCKE, A., PARPLIES, J., RADTKE, U. & SCHLESER, G. H. 2006. Transfer and early diagenesis of biogenic silica oxygen isotope signals during settling and sedimentation of diatoms in a temperate freshwater lake (Lake Holzmaar, Germany). *Geochimica Et Cosmochimica Acta*, 70, 4367-4379.
- MOSCHEN, R., LUCKE, A., PARPLIES, J. & SCHLESER, G. H. 2009. Controls on the seasonal and interannual dynamics of organic matter stable carbon isotopes in mesotrophic Lake Holzmaar, Germany. *Limnology and Oceanography*, 54, 194-209.
- MOSS, B., BARKER, T., 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., BEKLIOGLU, M., CARVALHO, L., KILINC, S., MCGOWAN, S. & STEPHEN, D. 1997. Vertically-challenged limnology; Contrasts between deep and shallow lakes. *Hydrobiologia*, 342, 257-267.
- MULLER, B., BRYANT, L. D., MATZINGER, A. & WUEST, A. 2012. Hypolimnetic Oxygen Depletion in Eutrophic Lakes. *Environmental Science & Technology*, 46, 9964-9971.
- MURPHY, J. M., SEXTON, D. M. H., JENKINS, G. J., BOOTH, B. B. B., BROWN, C. C., CLARK, R. T., COLLINS, M., HARRIS, G. R., KENDON, E. J., BETTS, R. A., BROWN, S. J., HUMPHREY, K. A., MCCARTHY, M. P., MCDONALD, R. E., STEPHENS, A., WALLACE, C., WARREN, R., WILBY, R. & WOOD, R. A. 2009. *UK Climate Projections Science Report: Climate Change Projections*, Exeter, UK, Meteorological Office Hadley Centre.

- NURNBERG, G. K. 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. *Limnology and Oceanography*, 29, 111-124.
- ODUM, H. T. 1956. Primary Production in Flowing Waters¹. *Limnology and Oceanography*, 1, 102-117.
- PAERL, H. W., HALL, N. S. & CALANDRINO, E. S. 2011. Controlling harmful cyanobacterial blooms in a world experiencing anthropogenic and climatic-induced change. *Science of The Total Environment*, 409, 1739-1745.
- PAERL, H. W. & HUISMAN, J. 2008. Climate - Blooms like it hot. *Science*, 320, 57-58.
- PARRY, S., MARSH, T. & KENDON, M. 2013. 2012: from drought to floods in England and Wales. *Weather*, 68, 268-274.
- PEARSALL, W. 1923. The phytoplankton of Rostherne Mere. *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, 67, 45-55.
- POIKANE, S., PORTIELJE, R., VAN DEN BERG, M., PHILLIPS, G., BRUCET, S., CARVALHO, L., MISCHKE, U., OTT, I., SOSZKA, H. & VAN WICHELEN, J. 2014. Defining ecologically relevant water quality targets for lakes in Europe. *Journal of Applied Ecology*, 51, 592-602.
- POWELL, N., SHILTON, A., CHISTI, Y. & PRATT, S. 2009. Towards a luxury uptake process via microalgae - Defining the polyphosphate dynamics. *Water Research*, 43, 4207-4213.
- PRETTY, J. N., MASON, C. F., NEDWELL, D. B., HINE, R. E., LEAF, S. & DILS, R. 2003. Environmental costs of freshwater eutrophication in England and Wales. *Environmental science & technology*, 37, 201-208.
- RADBOURNE, A. D., RYVES, D. B., ANDERSON, N. J. & SCOTT, D. R. 2017. The historical dependency of organic carbon burial efficiency. *Limnology and Oceanography*, 62, 1480 - 1497.
- REAVIE, E. D., HALL, R. I. & SMOL, J. P. 1995. An Expanded Weighted-Averaging Model for Inferring Past Total Phosphorus Concentrations from Diatom Assemblages in Eutrophic British-Columbia (Canada) Lakes. *Journal of Paleolimnology*, 14, 49-67.
- REDDY, K. R., NEWMAN, S., OSBORNE, T. Z., WHITE, J. R. & FITZ, H. C. 2011. Phosphorous Cycling in the Greater Everglades Ecosystem: Legacy Phosphorous Implications for Management and Restoration. *Critical Reviews in Environmental Science and Technology*, 41, 149-186.
- REDFIELD, A., KETCHUM, B. & RICHARDS, F. 1963. The influence of organisms on the composition of seawater. 2, 26.
- RENNBERG, I. 1990. A procedure for preparing large sets of diatom slides from sediment cores. *Journal of Paleolimnology*, 4, 87-90.
- RENNBERG, I. 1991. The Hon-Kajak Sediment Corer. *Journal of Paleolimnology*, 6, 167-170.
- REYNOLDS, C. S. 1978. Notes on Phytoplankton Periodicity of Rostherne Mere, Cheshire, 1967-1977. *British Phycological Journal*, 13, 329-335.
- REYNOLDS, C. S. 1979. The Limnology of the Eutrophic Meres of the Shropshire-Cheshire Plain: A Review. *Field Studies*, 5, 93-173.
- REYNOLDS, C. S. 2006. *Ecology of phytoplankton*, Cambridge, Cambridge University Press.
- REYNOLDS, C. S. & BELLINGER, E. G. 1992. Patterns of abundance and dominance of the phytoplankton of Rostherne Mere, England - Evidence from an 18-year data set. *Aquatic Sciences*, 54, 10-36.

- REYNOLDS, C. S., IRISH, A. E. & ELLIOTT, J. A. 2001. The ecological basis for simulating phytoplankton responses to environmental change (PROTECH). *Ecological Modelling*, 140, 271-291.
- REYNOLDS, C. S., MORISON, H. R. & BUTTERWICK, C. 1982. The Sedimentary Flux of Phytoplankton in the South Basin of Windermere. *Limnology and Oceanography*, 27, 1162-1175.
- REYNOLDS, C. S. & REYNOLDS, J. B. 1985. The atypical seasonality of Phytoplankton in Crose Mere, 1972 - An independent test of the hypothesis that variability in the physical-environment regulates community dynamics and structure. *British Phycolological Journal*, 20, 227-242.
- RIPPEY, B., ANDERSON, N. J., RENBERG, I. & KORSMAN, T. 2008. The accuracy of methods used to estimate the whole-lake accumulation rate of organic carbon, major cations, phosphorus and heavy metals in sediment. *Journal of Paleolimnology*, 39, 83-99.
- RIPPEY, B. & MCSORLEY, C. 2009. Oxygen depletion in lake hypolimnia. *Limnology and Oceanography*, 54, 905-916.
- RITCHIE, R. J. 2010. Modelling photosynthetic photon flux density and maximum potential gross photosynthesis. *Photosynthetica*, 48, 596-609.
- RITCHIE, R. J. & LARKUM, A. W. D. 2012. Modelling photosynthesis in shallow algal production ponds. *Photosynthetica*, 50, 481-500.
- RIVERA, S. F., VASSELON, V., JACQUET, S., BOUCHEZ, A., ARIZTEGUI, D. & RIMET, F. 2017. Metabarcoding of lake benthic diatoms: from structure assemblages to ecological assessment. *Hydrobiologia*, 807, 37-51.
- ROELKE, D. L., GABLE, G. M., VALENTI, T. W., GROVER, J. P., BROOKS, B. W. & PINCKNEY, J. L. 2010. Hydraulic flushing as a *Prymnesium parvum* bloom-terminating mechanism in a subtropical lake. *Harmful Algae*, 9, 323-332.
- ROSE, V., ROLLWAGEN-BOLLENS, G. & BOLLENS, S. M. 2017. Interactive effects of phosphorus and zooplankton grazing on cyanobacterial blooms in a shallow temperate lake. *Hydrobiologia*, 788, 345-359.
- RUHLAND, K. M., PATERSON, A. M. & SMOL, J. P. 2015. Lake diatom responses to warming: reviewing the evidence. *Journal of Paleolimnology*, 54, 1-35.
- RYVES, D. B., ANDERSON, N. J., FLOWER, R. J. & RIPPEY, B. 2013. Diatom taphonomy and silica cycling in two freshwater lakes and their implications for inferring past lake productivity. *Journal of Paleolimnology*, 49, 411-430.
- RYVES, D. B., BATTARBEE, R. W., JUGGINS, S., FRITZ, S. C. & ANDERSON, N. J. 2006. Physical and chemical predictors of diatom dissolution in freshwater and saline lake sediments in North America and West Greenland. *Limnology and Oceanography*, 51, 1355-1368.
- RYVES, D. B., JEWSON, D. H., STURM, M., BATTARBEE, R. W., FLOWER, R. J., MACKAY, A. W. & GRANIN, N. G. 2003. Quantitative and qualitative relationships between planktonic diatom communities and diatom assemblages in sedimenting material and surface sediments in Lake Baikal, Siberia. *Limnology and Oceanography*, 48, 1643-1661.
- SABATER, S. & HAWORTH, E. Y. 1995. An assessment of recent trophic changes in Windermere South Basin (England) based on diatom remains and fossil pigments. *Journal of Paleolimnology*, 14, 151-163.
- SAÑÉ, E., ISLA, E., BÁRCENA, M. A. & J., D. D. 2013. A shift in the biogenic silica of sediment in the Larsen B continental shelf, off the Eastern Antarctic Peninsula, resulting from climate change *PLoS ONE*, 8, e52632.

- SARTORY, D. P. & GROBBELAAR, J. U. 1984. Extraction of chlorophyll a from freshwater phytoplankton for spectrophotometric analysis. *Hydrobiologia*, 114, 177-187.
- SAS, H. 1989. *Lake restoration by reduction of nutrient loading: Expectation, experiences, extrapolation.*, Berlin, Academia.
- SCHEFFER, M., CARPENTER, S., FOLEY, J. A., FOLKE, C. & WALKER, B. 2001. Catastrophic shifts in ecosystems. *Nature*, 413, 591 - 596.
- SCHINDLER, D. W. 2006. Recent advances in the understanding and management of eutrophication. *Limnology and Oceanography*, 51, 356-363.
- SCOTT, D. R. 2014. *Carbon fixation, flux and burial efficiency in two contrasting eutrophic lakes in the UK (Rostherne Mere & Tatton Mere)*. PhD Thesis, Loughborough University.
- SEDDON, A. W. R., FROYD, C. A., WITKOWSKI, A. & WILLIS, K. J. 2014. A quantitative framework for analysis of regime shifts in a Galapagos coastal lagoon. *Ecology*, 95, 3046-3055.
- SHARPLEY, A., JARVIE, H. P., BUDA, A., MAY, L., SPEARS, B. & KLEINMAN, P. 2013. Phosphorus Legacy: Overcoming the Effects of Past Management Practices to Mitigate Future Water Quality Impairment. *Journal of Environmental Quality*, 42, 1308-1326.
- SMITH, V. H. 2003. Eutrophication of freshwater and coastal marine ecosystems - A global problem. *Environmental Science and Pollution Research*, 10, 126-139.
- SMITH, V. H., JOYE, S. B. & HOWARTH, R. W. 2006. Eutrophication of freshwater and marine ecosystems. *Limnology and Oceanography*, 51, 351-355.
- SMITH, V. H., TILMAN, G. D. & NEKOLA, J. C. 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution*, 100, 179-196.
- SMOL, J. P. & STOERMER, E. F. 2010. *The diatoms: applications for the environmental and earth sciences*, Cambridge University Press.
- SOBEK, S., ANDERSON, N. J., BERNASCONI, S. M. & DEL SONTRO, T. 2014. Low organic carbon burial efficiency in arctic lake sediments. *Journal of Geophysical Research-Biogeosciences*, 119, 1231-1243.
- SOBEK, S., DURISCH-KAISER, E., ZURBRUEGG, R., WONGFUN, N., WESSELS, M., PASCHE, N. & WEHRLI, B. 2009. Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnology and Oceanography*, 54, 2243-2254.
- SOBEK, S., TRANVIK, L. J. & COLE, J. J. 2005. Temperature independence of carbon dioxide supersaturation in global lakes. *Global Biogeochemical Cycles*, 19, GB2003-GB2003.
- SOBEK, S., TRANVIK, L. J., PRAIRIE, Y. T., KORTELAINE, P. & COLE, J. J. 2007. Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnology and Oceanography*, 52, 1208-1219.
- SONDERGAARD, M., JENSEN, J. P. & JEPPESEN, E. 2005. Seasonal response of nutrients to reduced phosphorus loading in 12 Danish lakes. *Freshwater Biology*, 50, 1605-1615.
- SORANNO, P. A., CHERUVELIL, K. S., WAGNER, T., WEBSTER, K. E. & BREMIGAN, M. T. 2015. Effects of Land Use on Lake Nutrients: The Importance of Scale, Hydrologic Connectivity, and Region. *PLoS ONE*, 10, e0135454.

- SPEARS, B. M., CARVALHO, L., PERKINS, R., KIRIKA, A. & PATERSON, D. M. 2012. Long-term variation and regulation of internal phosphorus loading in Loch Leven. *Hydrobiologia*, 681, 23-33.
- SQUIRES, M. M. & LESACK, L. F. W. 2003. Spatial and temporal patterns of light attenuation among lakes of the Mackenzie Delta. *Freshwater Biology*, 48, 1-20.
- SRIYASAK, P., CHITMANAT, C., WHANGCHAI, N., PROMYA, J. & LEBEL, L. 2015. Effect of water de-stratification on dissolved oxygen and ammonia in tilapia ponds in Northern Thailand. *International Aquatic Research*, 7, 287-299.
- STERNER, R. W., ANDERSEN, T., ELSE, J. J., HESSEN, D. O., HOOD, J. M., MCCAULEY, E. & URABE, J. 2008. Scale-dependent carbon : nitrogen : phosphorus seston stoichiometry in marine and freshwaters. *Limnology and Oceanography*, 53, 1169-1180.
- STHAPIT, E., OCHS, C. A. & ZIMBA, P. V. 2008. Spatial and temporal variation in phytoplankton community structure in a southeastern US reservoir determined by HPLC and light microscopy. *Hydrobiologia*, 600, 215-228.
- STOERMER, E. F. & SMOL, J. P. 1999. *The diatoms: Applications for the environmental and earth sciences*.
- STOOF-LEICHSENRING, K. R., HERZSCHUH, U., PESTRYAKOVA, L. A., KLEMM, J., EPP, L. S. & TIEDEMANN, R. 2015. Genetic data from algae sedimentary DNA reflect the influence of environment over geography. *Scientific Reports*, 5.
- TADONLEKE, R. D. 2010. Evidence of warming effects on phytoplankton productivity rates and their dependence on eutrophication status. *Limnology and Oceanography*, 55, 973-982.
- TATTERSALL, W. M. & COWARD, T. A. 1914. Faunal Survey of Rostherne Mere: Introduction and Methods. *Memoirs and Proceedings of the Manchester Literary & Philosophical Society*, 58, 1-21.
- TERANES, J. L. & BERNASCONI, S. M. 2000. The record of nitrate utilization and productivity limitation provided by delta N-15 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., JONES, I. D. & MABERLY, S. C. 2008. Long-term change in the phenology of spring phytoplankton: species-specific responses to nutrient enrichment and climatic change. *Journal of Ecology*, 96, 523-535.
- THOMSEN, U., THAMDRUP, B., STAHL, D. A. & CANFIELD, D. E. 2004. Pathways of organic carbon oxidation in a deep lacustrine sediment, Lake Michigan. *Limnology and Oceanography*, 49, 2046-2057.
- THUNELL, R. C., VARELA, R., LLANO, M., COLLISTER, J., MULLER-KARGER, F. & BOHRER, R. 2000. Organic carbon fluxes, degradation, and accumulation in an anoxic basin: Sediment trap results from the Cariaco Basin. *Limnology and Oceanography*, 45, 300-308.
- TILMAN, D., KILHAM, S. S. & KILHAM, P. 1982. PHYTOPLANKTON COMMUNITY ECOLOGY - THE ROLE OF LIMITING NUTRIENTS. *Annual Review of Ecology and Systematics*, 13, 349-372.
- TISON, D. L. & POPE, D. H. 1980. Effect of temperature on mineralization by heterotrophic bacteria. *Applied and Environmental Microbiology*, 39, 584-587.
- TITZE, D. J. & AUSTIN, J. A. 2014. Winter thermal structure of Lake Superior. *Limnology and Oceanography*, 59, 1336-1348.

- TOLOTTI, M., BOSCAINI, A. & SALMASO, N. 2010. Comparative analysis of phytoplankton patterns in two modified lakes with contrasting hydrological features. *Aquatic Sciences*, 72, 213-226.
- TRANVIK, L. 2014. Biogeochemistry Carbon cycling in the Arctic. *Science*, 345, 870-870.
- TRANVIK, L. J., DOWNING, J. A., COTNER, J. B., LOISELLE, S. A., STRIEGL, R. G., BALLATORE, T. J., DILLON, P., FINLAY, K., FORTINO, K., KNOLL, L. B., KORTELAINE, P. L., KUTSER, T., LARSEN, S., LAURION, I., LEECH, D. M., MCCALLISTER, S. L., MCKNIGHT, D. M., MELACK, J. M., OVERHOLT, E., PORTER, J. A., PRAIRIE, Y., RENWICK, W. H., ROLAND, F., SHERMAN, B. S., SCHINDLER, D. W., SOBEK, S., TREMBLAY, A., VANNI, M. J., VERSCHOOR, A. M., VON WACHENFELDT, E. & WEYHENMEYER, G. A. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54, 2298-2314.
- VAN DEN WYNGAERT, S., MOST, M., FREIMANN, R., IBELINGS, B. W. & SPAAK, P. 2015. Hidden diversity in the freshwater planktonic diatom *Asterionella formosa*. *Molecular Ecology*, 24, 2955-2972.
- VERBURG, P. & HECKY, R. E. 2009. The physics of the warming of Lake Tanganyika by climate change. *Limnology and Oceanography*, 54, 2418-2430.
- VERPOORTER, C., KUTSER, T., SEEKELL, D. A. & TRANVIK, L. J. 2014. A global inventory of lakes based on high-resolution satellite imagery. *Geophysical Research Letters*, 41, 6396–6402.
- VON WACHENFELDT, E., SOBEK, S., BASTVIKEN, D. & TRANVIK, L. J. 2008. Linking allochthonous dissolved organic matter and boreal lake sediment carbon sequestration: The role of light-mediated flocculation. *Limnology and Oceanography*, 53, 2416-2426.
- WALTHER, G. R., POST, E., CONVEY, P., MENZEL, A., PARMESAN, C., BEEBEE, T. J. C., FROMENTIN, J. M., HOEGH-GULDBERG, O. & BAIRLEIN, F. 2002. Ecological responses to recent climate change. *Nature*, 416, 389-395.
- WANG, Q., YANG, X. D., ANDERSON, N. J. & JI, J. F. 2015. Diatom seasonality and sedimentation in a subtropical alpine lake (Lugu Hu, Yunnan-Sichuan, Southwest China). *Arctic Antarctic and Alpine Research*, 47, 461-472.
- WETZEL, R. G. 2001. *Limnology : lake and river ecosystems*, San Diego, Calif. ;, Academic.
- WFD. 2014. *RE: European Water Framework Directive*.
- WICKHAM, H. 2009. *ggplot2: Elegant Graphics for Data Analysis*. , New York, Springer-Verlag.
- WIGDAHL-PERRY, C. R., SAROS, J. E., SCHMITZ, J., CALCOTE, R., RUSAK, J., ANDERSON, D. & HOTCHKISS, S. 2016. Response of temperate lakes to drought: a paleolimnological perspective on the landscape position concept using diatom-based reconstructions. *Journal of Paleolimnology*, 55, 339-356.
- WILLIAMSON, C. E., SAROS, J. E. & SCHINDLER, D. W. 2009a. Climate change Sentinels of Change. *Science*, 323, 887-888.
- WILLIAMSON, C. E., SAROS, J. E., VINCENT, W. F. & SMOL, J. P. 2009b. Lakes and reservoirs as sentinels, integrators, and regulators of climate change. *Limnology and Oceanography*, 54, 2273-2282.
- WINEGARDNER, A. K., BEISNER, B. E., LEGENDRE, P. & GREGORY-EAVES, I. 2014. Are the landscape-level drivers of water column and surface sediment diatoms different? *Freshwater Biology*, n/a-n/a.

- WORRALL, F. & MOODY, C. S. 2014. Modeling the rate of turnover of DOC and particulate organic carbon in a UK, peat-hosted stream: Including diurnal cycling in short-residence time systems. *Journal of Geophysical Research-Biogeosciences*, 119, 1934-1946.
- WRIGHT, H. E. 1967. A square-rod piston sampler for lake sediments. *Journal of Sedimentary Petrology*, 37, 975-976.
- YAMOAH, K. A., CALLAC, N., FRU, E. C., WOHLFARTH, B., WIECH, A., CHABANGBORN, A. & SMITTENBERG, R. H. 2016. A 150-year record of phytoplankton community succession controlled by hydroclimatic variability in a tropical lake. *Biogeosciences*, 13, 3971-3980.
- ZÄHRER, J., DREIBRODT, S. & BRAUER, A. 2013. Evidence of the North Atlantic Oscillation in varve composition and diatom assemblages from recent, annually laminated sediments of Lake Belau, northern Germany. *Journal of Paleolimnology*, 50, 231-244.
- ZAMPARAS, M. & ZACHARIAS, I. 2014. Restoration of eutrophic freshwater by managing internal nutrient loads. A review. *Science of the Total Environment*, 496, 551-562.
- ZHANG, T., SORANNO, P. A., CHERUVELIL, K. S., KRAMER, D. B., BREMIGAN, M. T. & LIGMANN-ZIELINSKA, A. 2012. Evaluating the effects of upstream lakes and wetlands on lake phosphorus concentrations using a spatially-explicit model. *Landscape Ecology*, 27, 1015-1030.
- ZHANG, Y. L., WU, Z. X., LIU, M. L., HE, J. B., SHI, K., WANG, M. Z. & YU, Z. M. 2014. Thermal structure and response to long-term climatic changes in Lake Qiandaohu, a deep subtropical reservoir in China. *Limnology and Oceanography*, 59, 1193-1202.
- ZNACHOR, P., ZAPOMELOVA, E., REHAKOVA, K., NEDOMA, J. & SIMEK, K. 2008. The effect of extreme rainfall on summer succession and vertical distribution of phytoplankton in a lacustrine part of a eutrophic reservoir. *Aquatic Sciences*, 70, 77-86.

9. Appendices

9.1. Appendix 1: Lake specific total-OC fraction

Mass-spectrometry elemental analysis was conducted for 23 sediment samples from a combination of sediment core and sediment trap sources. A range of organic matter percentage (OM%) samples were selected to generate an estimated OM to total organic carbon (TOC) conversion, specifically for application to Rostherne Mere sediment samples.

The analysis suggested the mean TOC percentage of OM at Rostherne Mere was 56% in the sediment core and 57% in the sediment traps.

The data collected is presented below:

Sample no.	d13C	%C	%N	C/N	Trap or Core	Depth	LOI%	%C / %LOI
1	-30.3	11.7	1.0	11.7	Trap	Shallow	25.02	0.47
2	-30.5	28.9	3.9	7.5	Trap	Shallow	54.52	0.53
3	-28.7	33.2	5.0	6.6	Trap	Shallow	63.64	0.52
4	-29.2	13.8	1.2	11.7	Trap	Shallow	45.94	0.30
5	-33.4	13.5	1.5	9.3	Trap	Shallow	29.14	0.46
6	-29.9	24.1	2.8	8.7	Trap	Shallow	36.92	0.65
7	-27.4	23.5	2.8	8.3	Trap	Shallow	40.00	0.59
8	-27.2	29.3	3.7	7.9	Trap	Shallow	46.54	0.63
9	-27.6	27.1	2.3	11.7	Trap	Shallow	50.92	0.53
10	-30.0	9.1	0.6	14.5	Trap	Deep	23.73	0.38
11	-33.1	24.3	3.2	7.5	Trap	Deep	38.63	0.63
12	-27.0	38.0	2.5	15.5	Trap	Deep	54.66	0.69
13	-29.8	15.3	1.3	11.5	Trap	Deep	29.61	0.52

14	-34.1	17.7	1.7	10.3	Trap	Deep	35.34	0.50
15	-32.6	28.5	3.6	7.8	Trap	Deep	42.83	0.67
16	-30.8	31.4	4.3	7.3	Trap	Deep	30.27	1.04
17	-26.4	32.1	4.0	8.0	Trap	Deep	47.81	0.67
18	-28.4	27.3	3.6	7.6	Trap	Deep	49.77	0.55
19	-28.7	14.3	1.2	11.7	Core	7.5 (~AD 1997)	21.31	0.67
20	-27.6	17.8	1.4	12.4	Core	17.5 (~AD 1985)	27.28	0.65
21	-28.7	7.6	0.6	12.7	Core	54.75 (~AD 1905)	14.06	0.54
22	-28.4	5.8	0.5	12.4	Core	82.75 (~AD 1645)	13.97	0.41
23	-28.6	7.5	0.6	12.8	Core	110.25 (~AD 1375)	14.80	0.51
<hr/>								
Total mean								0.57
Trap mean								0.57
Trap without outliers mean								0.57
Core mean								0.56
Total median								0.54
<hr/>								

9.2. Appendix 2: In-trap mineralisation experiment

Sediment traps have been widely used in lakes since the 1950s (Bloesch and Burns, 1980). These simple devices for measuring downward settling flux can be utilised for high-resolution detection of short-term flux events (Kulbe et al., 2006) and for estimating resuspension within the water column with an array of traps at multiple depths down the water column (Charlton and Lean, 1987, Bloesch, 1994). However, issues of calculating the within trap mineralisation still remain unresolved (Horppila and Nurminen, 2005). It is believed due to the variety and complexity of seasonal and lake to lake differences, a generalised solution for all lake systems unfeasible (Bloesch and Burns, 1980).

Previously it has been proposed that traps must be reset at regular intervals (>2 to 4 weeks) to limit the perceived implications of in trap mineralisation. However, with the development of automated sequencing traps allowing for a consistent monitoring of settling detritus over a long term, this regularity of trap recovery can be logistically and financially difficult. Therefore, this study provides details of an experiment to replicate the mineralisation loss within a trap over a 6-month period. The experiment design replicates the conditions of trap collections in deep, nutrient rich, anoxic stratifying lake, using an automated sequencing trap.

Materials and Procedures

The experiment design replicates the lake conditions at Rostherne Mere, UK, a deep (~30m), cool (~5°C), highly productive lake that annually stratifies with a completely anoxic hypolimnion for ~8 months of the year. The simulated trap design is an automated sequencing trap that turns to seal each collection bottle on a predetermined programme, such as the technicap PPS 4/3 (1310 mm length / 252 mm internal diameter, 1:5.1 trapping ratio, 0.05 m⁻² trapping area; <http://www.technicap.com/images/product/pps-4-3.pdf>).

To simulate trap collection, approximately 1kg of live algae was collected from the surface water of the Rostherne Mere basin in early July 2015. Additionally, 20L of hypolimnion water from a water depth of 25 m was collected in sealable HDPE bottles to provide a representative sample of anoxic bacterial microbes. All samples were

transported cool, dark and sealed to the laboratory where it was stored in a dark cold room at 5°C for 1 night to allow the algae to settle.

The following day the fresh algae containers were carefully siphoned into another container and the macro-algae was removed and placed on paper towels to remove as much of the additional water content as possible. The macro-algae were then mixed to homogenise the sample and divided into ~10 g sub-samples, weighed and placed in 54 individually labelled 250 ml HDPE bottles. The remaining water and sediment from the fresh algae containers was then filtered using a vacuum pump and GF/F paper to concentrate the micro-algae component into a well-mixed epilimnion water sample. 150 ml of the epilimnion water sample was then added to each individual sample bottle and three additional empty control bottles to assess the average micro-algae contribution. Finally, 70 ml of the well mixed hypolimnion water sample was added to the individual sample bottles to ensure fair representations of anoxic bacteria are present as they would be in the field. The bottles were then stored in a dark and cool (~ 6°C) location, except for the triplicate control 0 day set samples and the 150 ml epilimnion water control samples that were frozen.

Triplicate sets of the individual sample bottles were removed and frozen on a predetermined pattern at the same time of day (3pm on day; 1, 3, 7, 14, 28, 42, 56, 70, 84, 98, 112, 126, 140, 154, 168, 182, 196).

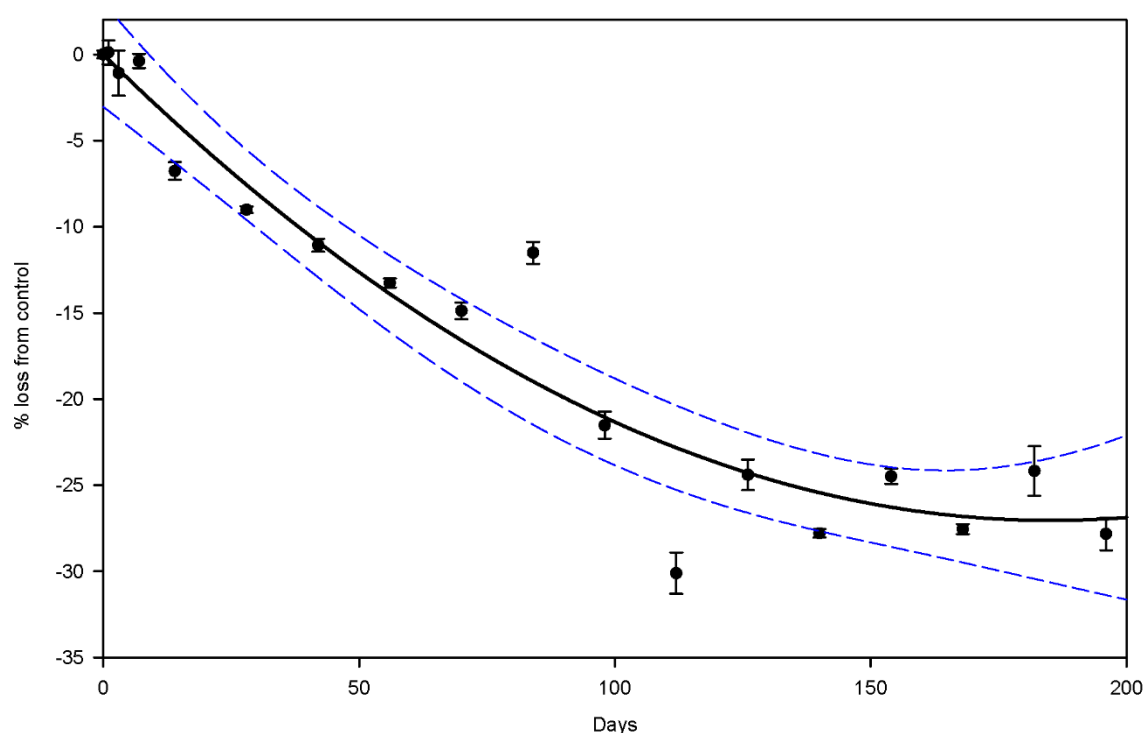
All samples were freeze-dried, weighed and analysed for organic matter (OM) using sequential loss-on-ignition, OM calculated by weight loss after 3 hrs at 550°C (Dean, 1974).

The total weight remaining in each bottle after freeze-drying was then compared as a ratio loss to the start weight (macro-algae weight added + mean epilimnion water sample micro-algae weight). Each triplicate set was calculated to form a mean ratio for comparison to the control set 0.

Data Assessment

The experiment result shows that during the first 7 days the loss in the samples showed no noticeable pattern of mineralisation (Appendix 2 - Figure 1). However, trap exposure lengths from this stage onwards shows significant mineralisation loss (Appendix 2 - Figure 1). The quickest loss rate is seen during the first ~70 days of

exposure, which then begins to slow gradually, plateauing to near no loss by ~180days (Appendix 2 - Figure 1).



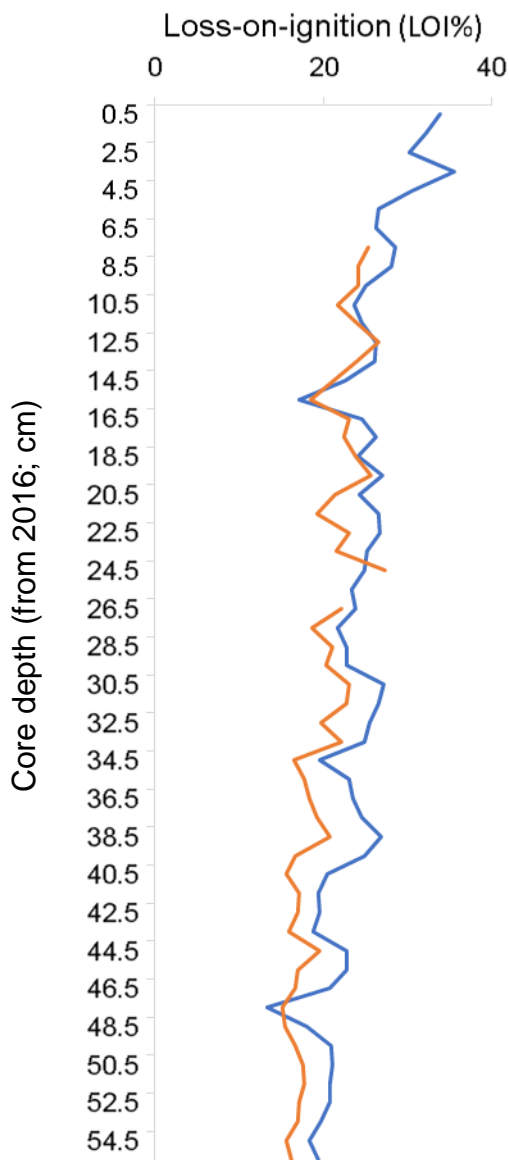
Appendix 2 - Figure 1. Sediment trap experiment loss from control set 0. Each date contains triplicate set with mean error. Quadratic regression curve fitted with 95% confidence bands.

This experiment can be used as an example of sediment trap mineralisation corrections against time (still to be assessed further), providing a reliable assessment of longer term automated sediment trap studies in deep, nutrient rich lakes. The wider application of this experiment is potentially limited by the representation of lake type and the focus on autochthonous production as the dominant sediment source. Future analysis is planned to determine the wider application of this experimental data set.

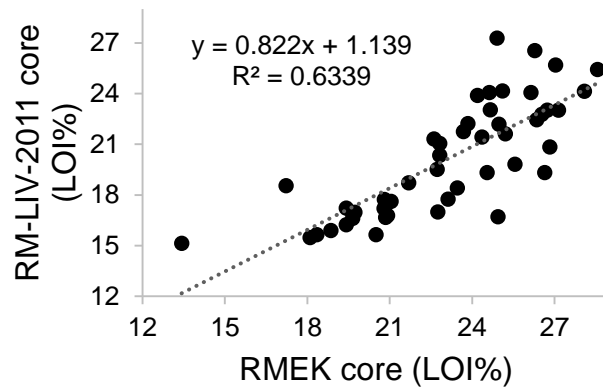
9.3. Appendix 3: Sediment core diatom analysis

In addition to the studies conducted in this thesis, a sediment core was collected and analysed for diatom assemblages in 2016. A 55 cm long sediment core (RM-EK-2016, hereafter the RMEK core) was collected at 26 m water depth in March 2016 using a 0.75 m HON-Kajak gravity corer (Renberg, 1991), extruded at 0.5 cm intervals on-site, sealed and stored cold for transport to the laboratory. For all samples organic matter (OM) was determined using sequential loss-on-ignition, where OM was calculated by weight-loss after 3 hrs at 550°C (Dean, 1974). The %OM profile for RMEK was correlated to the %OM of a previous long sediment core (RM-LIV-2011; see chapter 3; Radbourne et al., 2017). Samples from RM-LIV-2011 had been analysed via alpha spectrometry for ^{210}Pb activity (by Dr. D. R. Engstrom of the Science Museum of Minnesota) to determine chronology and sediment accumulation rates according to the CRS (constant rate of supply) model with confidence intervals calculated by first-order error analysis of counting uncertainty (Appleby, 2001).

The comparison of the %OM profiles in the RMEK and RM-LIV-2011 sediment cores showed a strong correlation (Fig. 7.1. and Fig. 7.2.), enabling the confident estimation of sediment age to be applied to the RMEK sediment core. Core sediment was prepared for diatom identification and analysis conducted using the same methods outlined in chapter 5 (Renberg, 1990). Total diatom abundance was calculated from the diatom to microsphere ratio, given known additions of microspheres, using methods outlined in Battarbee and Kneen (1982), with diatom valve accumulation rate calculated from sediment dry density and core bulk sedimentation rate. Historical observations of diatom crops at Rostherne Mere have been made since 1941 (Lind, 1944) and have been monitored almost continuously from 1962 to 1999 (Belcher and Storey, 1968, Reynolds and Bellinger, 1992, Moss et al., 2005). This data series was transformed into a record of relative abundance at an annual scale using three categories; absence (not present), present (1-40% seasonal bloom size) or dominant (41+% seasonal bloom size). Diatom identifications were conducted using an inverted microscope (x400 magnification) for live sample analysis, although this method provides a suitably quick assessment of the diatom assemblage, it may not provide a clear image for specific identification of similar taxa or may miss small taxa altogether.



Appendix 3 figure 1. Down core LOI% comparison of RMEK sediment core and RM-LIV-2011 sediment core.



Appendix 3 figure 2. Scatter LOI% comparison of RMEK sediment core and RM-LIV-2011 sediment core.

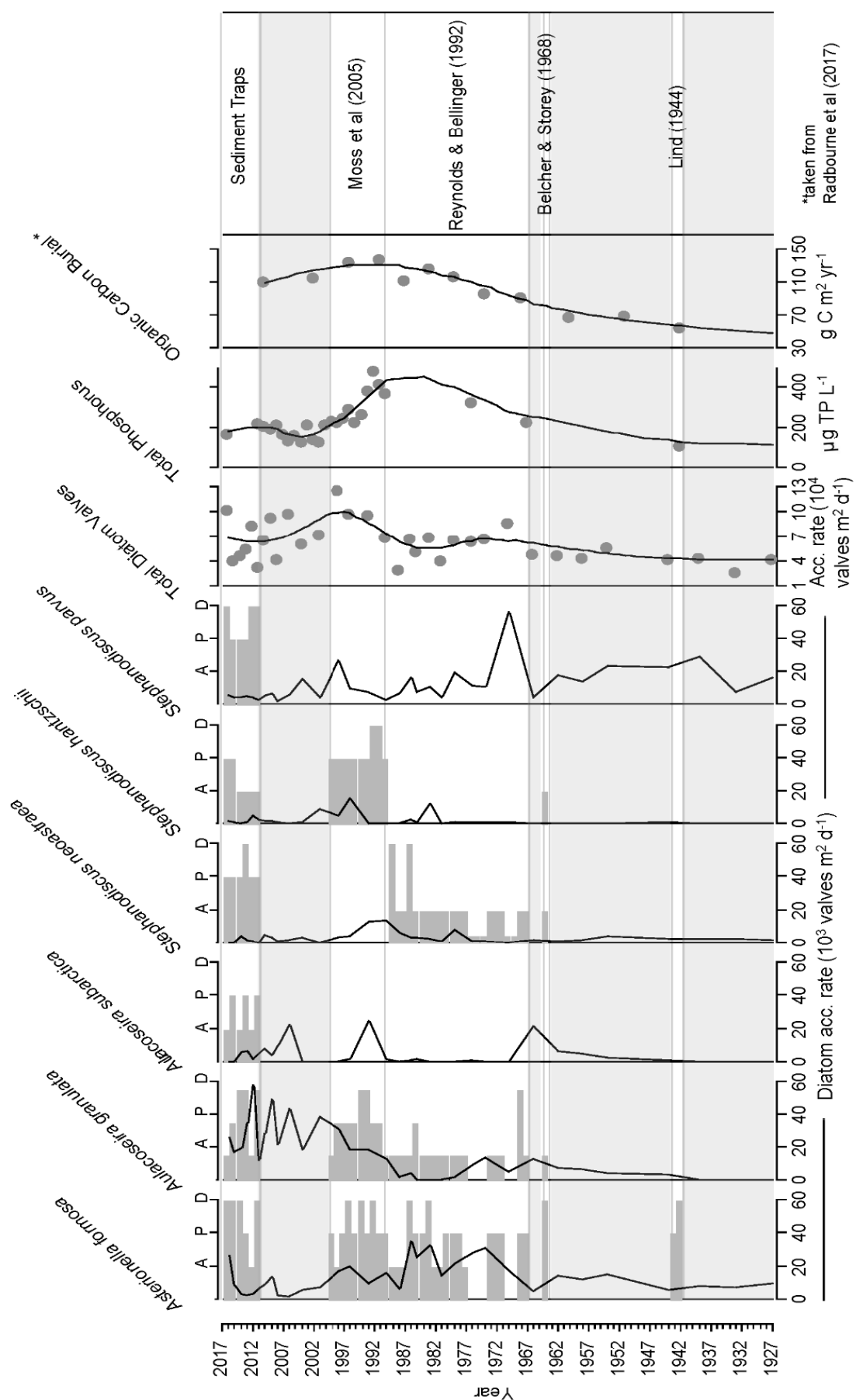
Additionally, name changes and phenotypic reorganisation of some taxa during this timeframe, may have resulted in some taxa being combined in the historical data (specific implications for this study discussed below).

The diatom absence, presence and dominance (A, P, D) from upper sediment trap collections between 2011 to 2016 and previously published live observation data (Lind, 1944, Belcher and Storey, 1968, Reynolds, 1978, Reynolds and Bellinger, 1992, Carvalho, 1993, Moss et al., 2005), support the use of the sediment record at Rostherne Mere as a reliable inventory, with diatom preservation being

good, at inter-annual scales of planktonic algal crops (as shown by Livingstone and Cambray, 1978), through the correlation in species peaks and troughs, enabling the analysis of the whole sediment core timeframe (~90 years; Appendix 3 Fig. 3.). Sedimentary diatom analysis from RMEK shows *Aulacoseira* spp. have dominated annual diatom crops over the last 25 years (predominantly *Aulacoseira granulata* Simonsen), and again in the 1960s (predominantly *Aulacoseira subarctica* Müller with some *A. granulata*), with only minor appearances at other times, while *Asterionella formosa* Hasall has been present throughout, but especially in the 1970s-80s

(Appendix 3 Fig. 3.). *Stephanodiscus parvus* Stoermer & Håkansson showed a gradual declining trend in dominance over the last 90 years, with a peak bloom in the early-1970s (Appendix 3 Fig. 3.). *Stephanodiscus neoastraea* Håkansson & Hickel increased in abundance during the height of eutrophication during the 1980s and 1990s, with *Stephanodiscus hantzschii* Grunow increasing in abundance for a time in the late-1990s and early-2000s, following STW diversion as TP concentrations were falling (Appendix 3 Fig. 3.). Total diatom valve accumulation rate (DAR) shows an increasing trend from the 1930s to the 1970s similar to the trajectories of TP concentrations and OC burial (DAR ~ 4.1 to $6.7 \cdot 10^4$ valves $\text{m}^{-2} \text{d}^{-1}$, OC burial ~ 50 to $110 \text{ g C m}^{-2} \text{yr}^{-1}$; Appendix 3 Fig. 3.). However, as TP and OC burial continue to increase until post-STW diversion, total DAR declines slightly for a time during the 1980s, before increasing to the highest levels in the late-1990s (DAR 1980s low $\sim 5.5 \cdot 10^4$ valves $\text{m}^{-2} \text{d}^{-1}$, 1990s high $9.9 \cdot 10^4$ valves $\text{m}^{-2} \text{d}^{-1}$; Appendix 3 Fig. 3.). Following STW diversion in 1991, TP (from ~ 1993), OC burial (from \sim late-1990s) and total diatom valves (from \sim early-2000s) decline to present day (DAR $\sim 6.4 \cdot 10^4$ valves $\text{m}^{-2} \text{d}^{-1}$, OC burial $\sim 110 \text{ g C m}^{-2} \text{yr}^{-1}$; Appendix 3 Fig. 3.).

The comparison of the core assemblage to historical observations of diatom populations present in the lake confirms the dating method used, with good agreement between scaled abundance from observations and core assemblages, especially when an increasing potential error for sediment age estimation in the sediment core samples is considered. These comparative data sets support the use of the sediment core to track whole-lake chronological changes in diatom species presence and abundance, and highlighted as a key methodological approach (Livingstone and Cambray, 1978, Battarbee et al., 2012). The only major difference between the sediment core and historical observations is evident for the *S. parvus* accumulations. However, its absence in the historical monitoring records may be explained by the seasonal sample timing of Reynolds and Bellinger (1992) who sampled from April each year potentially missing the early-spring bloom (\sim March; see chapter 5), or as a possible influence of the use of inverted microscopes making the smaller taxa difficult to identify. Therefore, at Rostherne Mere, the sediment archive can be used as a reliable record of past algal communities, in essence providing a continuous, high-resolution monitoring history.



Appendix 3 figure 3. (Previous page) Diatom assemblages over the last 90 years. Diatom species accumulation rates (10^3 valves $m^{-2} d^{-1}$) in a ^{210}Pb -dated sediment core (solid black line) taken in 2016 (RMEK), including total diatom valve accumulation rate (10^4 valves $m^{-2} d^{-1}$), annual average TP from historical observation records ($\mu g TP L^{-1}$), and OC burial rate in the RM_LIV_2011 sediment core ($g C m^{-2} yr^{-1}$; taken from chapter 3). Total diatom valves, total phosphorus and organic carbon burial data includes a loess smoother line for easy comparison. Confirmation of core reliability through comparison to absent (A), present (P) and dominant (D) records in the sediment traps (2011-2016) and published observation data (Lind, 1944, Belcher and Storey, 1968, Reynolds and Bellinger, 1992, Moss et al., 2005), with times of no observational record shaded in grey.

The total DAR increased with the early rise of eutrophication to the 1980s, declining as TP concentrations reached peak values, and increasing again following STW diversion with declining in-lake TP (Appendix 3 Fig. 3.). It is likely eutrophication also affected silica dynamics in the lake, with increased P loading allowing greater utilisation of available Si by diatom crops from the 1930s, which then declined (in the 1970s-80s) as (given similar catchment input) more Si was permanently buried in sediments than was recycled from lake sediments. Other algae without the physiological need for Si could then outcompete diatoms, such as cyanobacteria, as has been found in other UK lakes (Battarbee, 1977, Anderson, 1990). The dip in DAR at Rostherne Mere in the 1970s-1980s, the time of peak TP concentrations, during a continued rise in OC burial rate, suggests a greater Si utilisation and thus limitation impacted the diatom crop during this time with increasing net primary production sustained by other algae (Appendix 3 Fig. 3.). Light limitation may also have played a part, with the peak in cyanobacterial blooms during this period (Reynolds and Bellinger, 1992).

The most abundant diatom species present in the RMEK sediment core exhibited the increasing eutrophication and recovery (oligotrophication) trajectories at Rostherne Mere over the last 90 years (Appendix 3 Fig. 3.), while the high-resolution sediment trap provided a detailed insight into the seasonal progression of the taxa present. Combination of these limnological and paleolimnological techniques provides an important insight into the ecological change that has taken place (Battarbee et al.,

2012). Early signs of the increasingly eutrophic conditions are evident from the 1960s (Appendix 3 Fig. 3.), with greater accumulations of *A. formosa* being able to make use of the abundant spring Si and P availability (Maberly et al., 1994) and the *A. subarctica* peak in the 1960s a feature of early eutrophication seen in other lake systems (Sabater and Haworth, 1995, Gibson et al., 2002, Kirilova et al., 2010). *A. subarctica* showed two other peaks in the sedimentary record, all during times of similar TP concentrations either side of peak P concentrations (1966 TP = 227 $\mu\text{g L}^{-1}$; 1994 TP = 230 $\mu\text{g L}^{-1}$; 2006 TP = 170 $\mu\text{g L}^{-1}$), yet was largely absent at other times, with preferential growth of *A. granulata*. Furthermore, the reduced DAR at the height of TP concentrations in the 1980s suggested above to be as an influence of limited Si availability, is here supported by the increasing accumulations of *S. neoastreae* at that time, because the larger cell size of the taxon requires a greater Si utilisation (Jewson, 1992), removing Si available for other taxa, reducing the total DAR.

Towards maximum TP concentrations in the 1980s *Stephanodiscus* spp. began to increase in accumulation rate (Appendix 3 Fig. 3.), with *S. neoastreae* increasing in prominence and *S. hantzschii* prevalent shortly after STW diversion, while in-lake nutrient concentrations were still very high, as has been seen in other impacted lake systems (Kilham and Kilham, 1990, Dong et al., 2008). The autumnal bloom of *A. granulata* became more abundant following nutrient recovery, as Si availability increased in relation to the seasonal reduction of P, becoming more dominant to present, yet with a large seasonal variation linked to their sensitivity to light and turbulence (Gomez et al., 1995).

The presence of *S. parvus* in the sedimentary record at Rostherne Mere is particularly interesting. In other similar lakes that have undergone eutrophication, such as Windermere and Baldeggersee (Sabater and Haworth, 1995, Lotter, 1998), there is usually a peak *S. parvus* accumulation at the highest P values. However, in this study, *S. parvus* shows a declining accumulation trend throughout the sediment record, despite the continued dominant seasonal peak in early spring evident in recent sediment trap collections. The reasons for the decline could be as an influence of changing climatic conditions limiting the growth period for *S. parvus* as it is out competed by other taxa (e.g. *S. neoastreae*, *A. formosa*) or a changing nutrient availability (i.e. Si and P) at this time of the year due to changes in other algal uptake during other times of the year (e.g. increasing *A. granulata* in autumn).