Using diatoms to understand climate-nutrient interactions in Esthwaite Water, England: evidence from observational and palaeolimnological records

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Declaration of authenticity

The work contained in this thesis is the result of my own investigations, except where due acknowledgement is made to other sources.

This work has not already been accepted in candidature for any degree, and is not being concurrently submitted in candidature for any other degree to any other university.

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Abstract

Numerous aquatic systems have experienced eutrophication for several decades and now face the additional pressure of climate change. In order to effectively manage lake systems, a fuller understanding of the impacts of climate and nutrients on lake ecosystems, as well as a knowledge of how current and future climate change interact with nutrient dynamics, is required.

This thesis employs contemporary and palaeolimnological records, using diatoms as the key indicator, to understand how climate and nutrients have impacted the lake ecosystem of Esthwaite Water, UK, over a range of timescales from months to several centuries. Firstly, the seasonal variability of planktonic diatom assemblages was examined based on a two-year monitoring dataset. Secondly, the influence of climate and nutrients on the diatom flora of this lake was quantitatively assessed based on statistical analyses (redundancy analysis and generalized additive modelling) of monitoring datasets (a two-year and a 60-year series of physico-chemical lake characteristics and diatoms). Thirdly, historical environmental change, in terms of climatic conditions and lake trophic status, was reconstructed for the last ~1200 years using diatoms, grain size, LOI, pollen, and geochemical analysis combined with ^{210}Pb and ^{14}C dating techniques. The analyses illustrate the complexity of climate-nutrient interactions and the roles of the two drivers on different timescales and at various stages of the lake's history. Overall, climate impacts were more pronounced when nutrient concentrations were relatively stable. In contrast, during phases of enrichment and particularly in recent decades, the nutrient signal outweighs that of climate.

This thesis also highlights the importance of integrating contemporary limnology and palaeolimnology to improve our understanding of environmental change. The combination of these approaches offers an opportunity to test sedimentary diatom representativity and core integrity, and the ecological information derived from contemporary limnology is particularly valuable for refining palaeolimnological inferences.

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Glossary of Acronyms

AIC	Akaike's Information Criterion
AirT	Air temperature
AMM	Additive mixed model
ANAO	Annual NAO index
ANOVA	Analysis of variance
BEIF	Bloomsbury Environmental Isotope Facility
CAR	Autoregressive correlation structures
CCA	Canonical Correspondence Analysis
CET	Central England Temperature
Chl-a	Chlorophyll-a
CRS	Constant rate of ^{210}Pb supply
DAR	Diatom accumulation rates
DCA	Detrended Correspondence Analysis
DI-TP	Diatom-inferred total phosphorus
DOC	Dissolved organic carbon
DW	Sediment dry weight
EDDI	European Diatom Database
EF	Sedimentary element fluxes
FBA	Freshwater Biological Association
FD	Fossil diatom assemblage
GAM	Generalized Additive Model
Geo-P	Geochemical phosphorus concentration
GLM	Generalized Linear Models
IPCC	Intergovernmental Panel of Climate Change
LD	English Lake District

LIA	Little Ice Age
LOI	Loss on ignition
MD	Medium grain size
MWP	Medieval Warm Period
NAO	North Atlantic Oscillation
NERC	Natural Environment Research Council
OECD	Organisation for Economic Co-operation and Development
P	Phosphorus
PCA	Principal Components Analysis
PD	Planktonic diatom record
R^2_{adjust}	Adjusted coefficients of determination
RDA	Redundancy analysis
SAR	Sediment accumulation rate
SCD	Squared chord distance
SCP	Spheroidal Carbonaceous Particles
SD	Secchi depth
SDCA	Scores of DCA axis
SEM	Scanning Electron Microscope
SR	Sedimentation rate
SRP	Soluble reactive phosphorus
ST	Surface water temperature
TM	Thermal bathymetric map
TP	Total phosphorus
WL	Lake water level
WNAO	Winter NAO index

Chapter 1 Introduction

With rapid economic, social development and population growth, water quality deterioration is a growing concern in most areas throughout the world. The conservation and management of aquatic systems is therefore paramount. A particularly challenge is the reduction of pollutant loading from both point and non-point sources (Gleick, 2004). Many lakes have become severely degraded over the last few hundred years as a result of pollution from urban, industrial and agricultural activities, even including some of the most pristine alpine lakes (Williamson *et al.,* 2008; Battarbee, Kernan and Rose, 2009). One characteristic of the degradation is that the speed of decline in biodiversity is higher for freshwater than for either terrestrial or marine organisms (Jenkins, 2003). The main water quality problems are acidification, salinization, contamination and eutrophication (Smol, 2002), the last being the principal focus of this study.

1.1 Lake eutrophication

Eutrophication is a worldwide phenomenon and refers to the nutrient enrichment of waters that stimulates an array of symptomatic changes that can include increased phytoplankton and rooted aquatic plant production, fisheries and water quality deterioration, and other undesirable changes concerning water use (Bartsch, 1972). Lakes can be categorized on the basis of their trophic status and consequences of this for plant growth. Oligotrophic and mesotrophic lakes are generally clear, having a low concentration of plant life. Eutrophic lakes are enriched with nutrients, resulting in elevated plant growth and often algal blooms. The trophic status classification developed by the Organisation for Economic Co-operation and Development (OECD, 1982) based on total phosphorus (TP), chlorophyll a (Chl-a) and Secchi depth is given in Table 1.1.

Table 1.1 Classification of trophic status by OECD (1982)

Trophic category	Mean total P, µg L^{-1}	Mean Chl-a µg L^{-1}	Max. chl-a µg L^{-1}	Mean Secchi depth, m	Min. Secchi depth, m
Oligotrophic	<10	<2.5	<8	>6	>3
Mesotrophic	10 - 35	2.5 - 8	8-25	6-3	3 - 1.5
Eutrophic	>35	>8	>25	<3	<1.5

There are two forms of eutrophication: natural and cultural. The elemental composition of soil and its exposure to draining water are important determinants of the chemistry of water exported from the drainage basin. Soil fertility is related to the chemistry of its parent rock material. For example, lakes on igneous geology can be naturally more nutrient-poor than lakes on sedimentary geology (Rawson, 1960). Further, there is more potential for leaching or biological decay of soils in drainage basins with longer exposure to water. Therefore, low relief drainage basins, and those that are located in areas of low precipitation, are more likely to export much higher nutrient concentrations into lakes (D'Arcy & Carignan, 1997). Lake water retention time, calculated from the ratio between the volume of the lake and the volume of its outflow, is another important factor affecting the nutrient status of lakes. Shorter retention time speeds up the nutrient replacement in lakes. Consequently, flat drainage basins with low precipitation and fertile catchment soils could potentially contain naturally productive lake systems. In contrast, cultural eutrophication is anthropogenically induced and has become widespread especially since the Second World War, when rapid population growth and industrial development followed (Blenckner, 2005). More intensive human activities including agriculture, deforestation, reclamation and nutrient-rich sewage discharge have greatly increased nutrient loading to aquatic systems. This process has occurred over short timescales and brings with it more serious consequences than the natural eutrophication process.

In an attempt to prevent further degradation and improve water quality, many eutrophic lakes have been subjected to restoration in recent decades including techniques such as reducing external nutrient loading, biomanipulation and suction-dredging (Søndergaard *et al.*, 2007). However, despite these endeavours, eutrophication remains a major problem. Furthermore, today many lakes are facing additional pressures such as climate change, industrial pollution and exotic species invasion (Smol, 2005). These can potentially obscure or exaggerate the eutrophication process, since nutrient status heavily depends on the interplay between nutrient availability, light conditions, temperature, residence time, and biological absorption (Carvalho & Kirika, 2003; Jeppesen *et al.*, 2005). Such confounding factors, particularly climate change, may make it increasingly difficult to restore enriched lakes (Søndergaard *et al.*, 2007).

1.2 Climate effects on lake ecosystems

Recently, the Third Assessment Report from the Intergovernmental Panel of Climate Change (Houghton *et al.*, 2001; IPCC, 2007) pointed out that global average surface air temperature has increased by about 0.6 °C over the 20th century. Without proper actions against anthropogenic greenhouse effects the IPCC predicts increases in global average surface temperatures of 1.4 to 5.8 °C by the year 2100 (Houghton *et al.*, 2001). Meanwhile, evidence suggests that the increase of atmospheric greenhouse gas concentrations could increase the frequency of heavy precipitation in many regions of the globe (Frei *et al.*, 2006). Undoubtedly, higher frequency of droughts or floods, higher rates of soil erosion, decreasing biodiversity and degradation of ecological functions will occur under such a scenario.

Generally, climate has effects on the physiology, distribution, phenology and adaptation of organisms, and on the structure and function of lake ecosystems via changes in temperature, rainfall, wind and solar irradiation (Hughes, 2000). Small, shallow lakes are likely to be particularly susceptible to climate-related changes, since in most, heat or light energy is easily transferred over the whole water column and biological communities (e.g. fish, macrophyte) have limited buffering range due to the relatively small lake volume.

1.2.1 Thermal effects

In shallow lakes, water temperatures, which can be highly correlated with regional scale air temperatures, exhibit a rapid and direct response to climatic forcing (Livingstone, 2003; Arhonditsis *et al.*, 2004a). For deep lakes, hypolimnetic temperatures exhibit a much more complex behaviour owing to stratification (Gerten & Adrian, 2001; Straile, Jöhnk & Rossknecht, 2003).

Temperature is probably the most important regulating variable for aquatic ecosystems since it determines not only metabolic rates and food requirements for organisms, but also controls physical-chemical-biological interactions. Most chemical reactions and bacteriological processes run faster at higher temperatures. Experiments have shown, for example, that the seasonality of internal phosphorus loading and retention capacity is strongly linked to temperature (BoersVan Raaphorst & Van der Molen, 1997; Søndergaard, Jensen & Jeppesen, 1999) and the release of inorganic phosphate from lake sediments increases with higher temperatures (Gomez *et al.*, 1998). Temperature also controls the growth rates of phytoplankton, aquatic plants and epiphytes, making lake ecosystems sensitive to changes in temperature (Whitehead & Hornberger, 1984; Wade *et al.*, 2002). Most aquatic species, being scarcely able to regulate their own body heat, are sensitive to temperature variation. Lower temperature reduces their enzyme activity, membrane fluidity, and electron chain transfer and constrains the process of photosynthesis, respiration, nutrient uptake, and subsequent growth (Falkowski & Raven, 1997).

Stratification, which is mainly driven by temperature changes, is a distinct characteristic of lake systems, particularly in deep lakes located in temperate regions. Because water density varies when the temperature changes, the water in lakes in temperate climates mixes once a year. When the temperature of the surface water reaches the temperature at which water is most dense, the entire water column becomes mixed, bringing oxygen starved water up from the depths, and taking oxygen down to decomposing sediments. This process also triggers several other physical effects, such as changes in light conditions and in the thermal gradient. For example, earlier thermal stratification shortens the period of deep mixing, thus improving the average light conditions experienced by the algae (Huisman & Sommeijer, 2002). Thus stratification patterns play an important role in shaping the seasonality of phytoplankton communities.

1.2.2 Hydrological effects

Changes in precipitation (quantity, intensity and timing), combined with higher temperatures, leading to increased evapotranspiration, have the potential to alter the water cycle within catchments. This water cycle, connecting the terrestrial surroundings and lake systems, is a critical process for transporting nutrient, energy and mass within the earth system.

Precipitation exhibits high spatial heterogeneity and seasonality. For lake ecosystems, it directly affects the volume of water entering a lake via the inflow, the residence time, and the supply of nutrients and other substances (e.g. dissolved organic carbon, DOC) to the lake (Gergel, Turner & Kratz 1999). More intense rainfall can result in increased water input to the lake, and higher loads of suspended solids (Lane *et al.*, 2007) and sediment yields (Wilby, Dalgleish & Foster, 1997). The residence time of the lake heavily depends on the amount of precipitation and the volume of the inflow. It controls the concentrations and accumulative capacity of all the substances entering a lake basin, whether naturally or artificially.

1.2.3 Wind effects

Higher wind speed reduces lake stability, and enhances the mixing of nutrients (George, Hurley & Hewitt, 2007). Surface epilimnetic water is dragged downwind, whilst a deeper return current, flowing upwind, is established lower in the epilimnion

(Smith, 1992). The result is that planktonic organisms with a tendency to accumulate in relatively quiescent areas will exhibit high vertical and horizontal spatial heterogeneity in a wind-stressed lake. In turn these patterns may affect the abundance and composition of aquatic organisms. For example, recent long-term studies of plankton dynamics in Esthwaite Water have shown that wind is a key controlling variable affecting the community structures (George *et al.*, 1990). The annual changes in the late summer crop of *Aphanizomenon* in the lake between 1956 and 1972 were strongly linked to year-to-year variations in late summer mean wind speeds.

Wave action is also a key factor affecting the interaction between the sediment and water (Qin *et al.*, 2004). In particular, wind-induced waves frequently disturb the water-sediment interface and often cause intensive sediment resuspension in shallow lakes. Consequently, the suspended solid (SS) concentration in overlying water and the nutrient release activities from sediments is enhanced (Søndergaard, Kristensen & Jeppesen, 1992; Zhu, Qin & Gao, 2004). For example in Taihu Lake (China), wave processes occur frequently due to its shallowness and large surface area. From 1997 to 1999, daily maximum wind speeds higher than 5 m s^{-1} and 8 m s^{-1} occurred 89.5% and 34.2% of the time, respectively (Fan *et al.*, 2004). A simulation study on its sediment showed that water disturbance caused soluble reactive phosphorus (SRP) release from sediment which was 8-10 times higher than release under undisturbed conditions (Fan, Zhang & Qu, 2001). Consequently, nutrients released from sediment resuspension caused by wind-induced wave action may be the main type of internal nutrient loading in Taihu Lake and shallow lakes elsewhere.

1.3 Interactions of climate change and eutrophication

Climate change affects lake ecosystems via changes in temperature, rainfall, wind and solar irradiation, and indirectly through interaction with other stressors. Numerous studies have focused on the effects of climate change on nutrient enrichment in lake systems (e.g. Weyhenmeyer, 2001; McKee *et al.*, 2003; George, Maberly & Hewitt, 2004; Liboriussen *et al.*, 2005; Malmaeus *et al.*, 2006; Blenckner *et al.*, 2007; Battarbee *et al.*, 2008; Jeppesen *et al.*, 2009; Whitehead *et al.* 2009; George *et al.*, 2010; Markensten, Moore & Persson, 2010; Pierson *et al.*, 2010). Many of these studies concluded that nutrient loading from land to lakes was expected to increase due to higher rainfall (particularly in winter), warmer temperature and a more arid climates. For example, McKee *et al.* (2003) showed that warming did not promote phytoplankton blooming but increased P concentrations and deoxygenation. George, Maberly & Hewitt (2004) showed that the main factor influencing the winter P concentration in Blelham Tarn and Esthwaite Water was the inter-annual variation in the winter rainfall. They found that higher SRP concentrations were recorded after heavy rain in these lakes. Similarly, Whitehead *et al.* (2009) concluded that increasing temperatures not only lengthen the period of thermal stratification but also bring more nitrates into lakes as higher temperatures increase soil mineralization.

Meanwhile, nutrients may relieve or intensify the limnological processes triggered by climate change through the alteration of ecological structure and function. For example, nutrients have been known as one important driving factor on the shift from macrophyte-dominated lakes to algal-dominated ones (Scheffer *et al.*, 1993; Janse, 1997; Beisner, Haydon & Cuddington, 2003; Jeppesen *et al.*, 2005). Increasing phytoplankton production may decrease light penetration, reduce plant colonization depth and coverage, which in turn will have implications for the biological structure and stability of lake ecosystems (Jeppesen *et al.*, 1990, 2007). This process thus may potentially decrease the water column stability which is mainly controlled by climate factors. In addition, nutrient deficiency or over-supply could delay or interrupt the normal development cycle of biological communities (Winder & Schindler, 2004). Seasonal changes in temperature and radiation lead to a predictable succession of physical processes and phytoplankton and zooplankton growth (e.g. the spring phytoplankton bloom) in pelagic ecosystems (Sommer *et al.*, 1986). On a longer timescale, however, palaeoecological records and seasonal macrophyte data established for lakes in the same region suggest that the seasonality of aquatic plants may change under increasing nutrient concentrations (Sayer *et al.*, 2010a , 2010b).

Whilst there is considerable knowledge about the concurrent effects of climate and nutrients on lake ecosystems (Carvalho and Kirika, 2003; Winder and Schindler, 2004), much less is known about how the two stressors interact (Elliott, Jones & Thackeray, 2006; Battarbee *et al.*, 2008). Many long-term monitoring data show that effects of climate on nutrient accumulation in lakes can be contradictory such that the net effect therefore is difficult to predict (e.g. Adrian *et al.*, 1995; Carvalho & Kirika, 2003; Jeppesen *et al.*, 2007). Perhaps only in remote lakes can climate effects on lake ecosystems be isolated from human impact. For example, studies in circumpolar Arctic lakes have revealed that widespread diatom community changes are primarily driven by climate warming (Smol *et al.*, 2005). In most lowland regions, however, lake systems are impacted by a range of pressures, not least eutrophication and therefore it becomes difficult to disentangle the effects of climate from that of nutrients.

1.4 Approaches to understanding lake ecosystem change

Lakes are complex systems involving several mass-energy transfer processes. In order to ensure sound management and sustainable use of the resource, it is important to understand how systems respond to the changing environment. Many lakes across the world are impacted to some degree, which makes the need to better understand and protect these ecosystems increasingly urgent. Three approaches, namely monitoring (contemporary limnology), palaeolimnology and mesocosm experiments, are now widely used to provide such information.

1.4.1 Long-term monitoring

Continuous long-term monitoring data provide a direct, high resolution description of lake history. Data on water quality, climate and biological structure can be collected in the field or measured in the laboratory to access how an aquatic ecosystem has responded to changes in climate and catchment variables (Blindow *et al*., 1993; Talling, 1993; Maberly *et al*., 1994b; Carvalho & Kirika, 2003; Jeppesen *et al*., 2005; Phillips *et al*., 2005; Thackeray *et al*., 2008; Ferguson *et al*., 2008). For example, Carvalho & Kirika (2003) revealed the response patterns of phytoplankton and zooplankton to nutrient dynamics based on a 34-year monitoring record at Loch Leven (Scotland). Whilst multi-decadeal records are relatively rare, they do exist for a small number of well studied sites including Windermere, Blelham Tarn and Esthwaite Water in the English Lake District, where records now span over 60 years (Maberly *et al*., 1994a). Long-term datasets, such as these, can be used to define the range of natural variability of ecological systems and provide a baseline from which to assess whether a system has changed significantly (Kratz *et al*., 2003). Caution must be exercised, however, where analytical or sampling method and locations have changed during the life of the monitoring programme.

1.4.2 Palaeolimnology

Palaeolimnology is a multidisciplinary science that uses physical, biological and chemical information preserved in sediments to reconstruct past environmental conditions in lake systems (Smol, 2002).

Palaeolimnological proxy data may come in many forms based on the different sources of the sediment material. Allochthonous material, originating from outside the lake, such as soil particles, pollen grains from trees or atmospheric fly-ash particles, reflects the regional or catchment environmental background. By contrast, autochthonous material, such as plant remains or chemical precipitates from processes occurring within the lake basin, mirrors the inner lake condition. Consequently, palaeolimnological analyses based on these sedimentary remains have been widely employed to provide important sources of palaeoenvironmental proxy data, particularly for those regions where long-term instrumental data are absent (see review in Fritz, 1996; Battarbee, 2000; Smol, 2002; Birks & Birks, 2006).

Palaeolimnological studies have also been used to provide theoretical support for lake restoration. For effective lake restoration, it is important to establish the timing and rate of water quality deterioration and to distinguish anthropogenic impacts from natural processes. One of the most popular applications of palaeolimnology in the last decade or so has been to define reference conditions to act as restoration targets for lake management. Combined with reliable dating techniques, lake sediment can provide information on long-term ecosystem processes, and the pre-disturbance condition of a lake (Battarbee, 1999; Smol, 2002). This information can be used to assess the baseline conditions with regard to nutrients, pH, salinity and ecosystem functioning (e.g. Sayer & Roberts, 2001; Ryves, McGowan & Anderson, 2002; Bennion & Battarbee, 2007). At a regional scale, a low resolution palaeolimnological application, the "Top-Bottom method", has been adopted to help define reference conditions and assess degree of change by comparing the core top (present day) and bottom (reference state, *c.* 1850 AD) samples in some European countries (e.g. Bennion, Fluin & Simpson, 2004, Leira *et al.*, 2006) and in North America (e.g. Cumming *et al.*, 1992; Dixit *et al.*, 1999).

One of the most widely used groups in palaeo studies of eutrophication and climate change are diatoms (Bacillariophyceae: single-celled, siliceous algae) (e.g. Sabater, 2000; Stoermer & Smol, 2001). First, they are taxonomically diverse and relatively easy to identify to species-level using light microscope. Second, they are important primary producers in many aquatic environments and they exploit a wide range of aquatic microhabitats from littoral to open-water pelagic areas making them excellent environmental indicators (Round, Crawford & Mann, 1990). Third, their siliceous cell walls are well preserved and abundant in lake sediments in most aquatic environments. Finally, and most importantly, diatoms can respond rapidly and sensitively to changes in their environment owing to their fast reproduction rates and the narrow tolerances of many taxa to a range of physical and chemical limnological conditions (Stoermer & Smol, 2001).

In the context of both contemporary limnology and palaeolimnology, diatoms have been widely used in recent decades. In contemporary monitoring research, many diatom-based indices which evaluate biological integrity have been established (e.g. TDI-Trophic Diatom Index，Kelly & Whitton, 1995; IBD-biological diatom index，Prygiel & Coste, 1999) and diatoms have become one of the five biological indicators (i.e. fish, zooplankton, macrobenthos, diatoms, and riparian birds) that were selected as indicators of lake condition in the U.S. Environmental Protection Agency's Environmental Monitoring and Assessment Program (EPA, 2002). In the palaeolimnological field, diatoms have been an essential proxy for environmental change research, particularly in recent decades, facilitated by the development of statistical techniques such as ordination (ter Braak & Smilauer, 2002), weighted averaging (WA) regression and calibration (Braak & Dam, 1989; Birks, 1998), and transfer functions (Birks *et al.*, 1990). Diatoms have been shown to be good indicators of temperature and nutrient conditions in lakes and therefore diatom-based transfer functions have been developed for numerous regions to reconstruct nutrient (e.g. Bennion, 1994; Bennion, Juggins & Anderson, 1996; Anderson, 1997; Lotter *et al.*, 1998; Tibby, 2004; Reid, 2005; Yang *et al.*, 2008; Chen *et al.*, 2008) and climate change (e.g. Lotter *et al.*, 1997; Roberts & McMinn, 1998; Joynt, 1999; Bigler & Hall, 2002; Mackay *et al.*, 2003; Bigler & Hall, 2003; Mackay *et al.*, 2005).

1.4.3 Mesocosm experiments

Experimental study is a powerful way of investigating change in aquatic ecosystems. Tanks containing water, sediments, plants, algae, invertebrates and fish from the natural environment (mesocosms) are used to simulate different environmental conditions and biological communities (Moss *et al.*, 2003; Feuchtmayr *et al.*, 2009). They can be used to study the ecosystem response to different environmental scenarios. Such experiments can involve the creation of some extreme or pristine conditions, which rarely exist in natural ecosystems. For example, Liboriussen *et al.* (2005) and Michels *et al.* (2007) used mesocosm experiments to examine the effects of temperature increases on both shallow lake and littoral wetlands, with the former supplemented by molecular techniques to quantify micro-evolutionary responses to anthropogenic stress. Recently Vanderstukken *et al.* (2010) conducted an outdoor mesocosm experiment to study the effect of submerged macrophytes (*Elodea nuttallii*) on phytoplankton and zooplankton biomass.

However, mesocosms suffer from the inherent problem that an experimental set up with controlled treatments such as water chemistry, sediment, temperature and nutrient loading, may give divergent results in its replicates, or when it is carried out on different occasions (Battarbee *et al.*, 2008). Additionally, experiments can be costly in terms of time and resources.

1.5 Integrating limnology and palaeolimnology to understand environmental changes

Long-term lake monitoring records are valuable but rarely extend back for more than 50 years anywhere in the world. Where they do exist they provide a high-resolution picture of different stages in the recent history of a lake ecosystem. However, care must be taken in interpretation if analytical methods have been inconsistent over the monitoring period (Blenckner, 2005). In contrast, in most cases, lake sediments are deposited in a continuous fashion through time. Consequently, the sediments accumulated in a lake can then be employed to infer historical changes and can be used to augment relatively short-term, observational records (e.g. Smol & Cumming, 2000; Battarbee *et al.*, 2005a).

The combination of contemporary limnology (including monitoring and mesocosm experiments) and palaeolimnology provides several benefits. Firstly, palaeolimnological research benefits from contemporary aquatic ecology, as the latter provides information on species' habitat preferences, seasonality and interactions (Sayer *et al.*, 2010b). Secondly, monitoring records derived from contemporary limnological studies can be used to validate palaeolimnological interpretations. For example, diatom-inferred water quality variables (TP, pH, salinity, and others) can be compared with measured data (e.g. Lotter, 1998; Bennion *et al.*, 2005; Dong *et al.*, 2008). Thirdly, modern monitoring records can be employed to test how faithfully the fossil remains in the sediment reflect the organisms' abundance in the water column (Haworth, 1980; Battarbee, 1981; Manca *et al.*, 2007; Nykänen *et al.*, 2009). Fourthly, palaeo-data can greatly enhance our understanding of lake ecosystems by enabling ecological theories to be posed and tested within a long-term framework (Sayer *et al.*, 2010b). The two approaches are, therefore, highly complementary. In recent years there has been increased interest in integrating contemporary and palaeolimnological studies to understand environmental processes in lake systems (see examples in Saros, 2009; Sayer *et al.*, 2010b). This has been particularly successful in studies of lake acidification, for example, where long-term datasets for epilithic diatoms, diatoms in annually exposed sediment traps and diatoms from sediment cores have been used together to indicate changes in lake water pH over the last 200 years (Battarbee *et al.*, 2005c).

Both contemporary limnology and palaeolimnology have been widely used to elucidate the issue concerning climate and nutrient effects on lake ecosystems (see examples in Battarbee, 2000; Smol & Cumming, 2000; Jeppesen *et al.*, 2010; Smol, 2010). Particularly with development of statistical techniques, more studies have attempted to disentangle the interaction of climate and nutrient effects. For example, Lotter & Birks (1997) revealed that climate outperformed trophic state and explained more of the diatom variance using a variance partitioning approach. Ferguson *et al.* (2008) conducted no-parameter models to identify ecological trends and changes in response to nutrient and climatic factors using a 35-year monitoring dataset from Loch Leven, Scotland. However, few of these studies are based on the integration of contemporary and palaeolimnological records. Given the existence of long-term monitoring records (>60 years) and eutrophication in recent decades in Esthwaite Water, the combination of two kinds of limnological records can potentially provide a rare opportunity to understand nutrient-climate interactions.

1.6 Study site

Esthwaite Water is situated in the southern part of the Lake District, NW England (N 54°21.56', W 002°59.15', see Fig. 1.1 & Fig. 1.2), and is 65 m above sea level. Due to the high diversity of its macrophyte communities, Esthwaite Water has been classified as a Grade 1 Site of Special Scientific Interest (SSSI). It was designated as a RAMSAR site in 1997 in recognition of its international importance as a wetland.

Fig. 1.1 Photos of Esthwaite Water. (a) View from the west side, with farm land on the west bank and forest on the east bank shown. Photo was taken in October, 2009; (b) View from the east side, with several houses near the bank shown. Photo was taken in July, 2007.

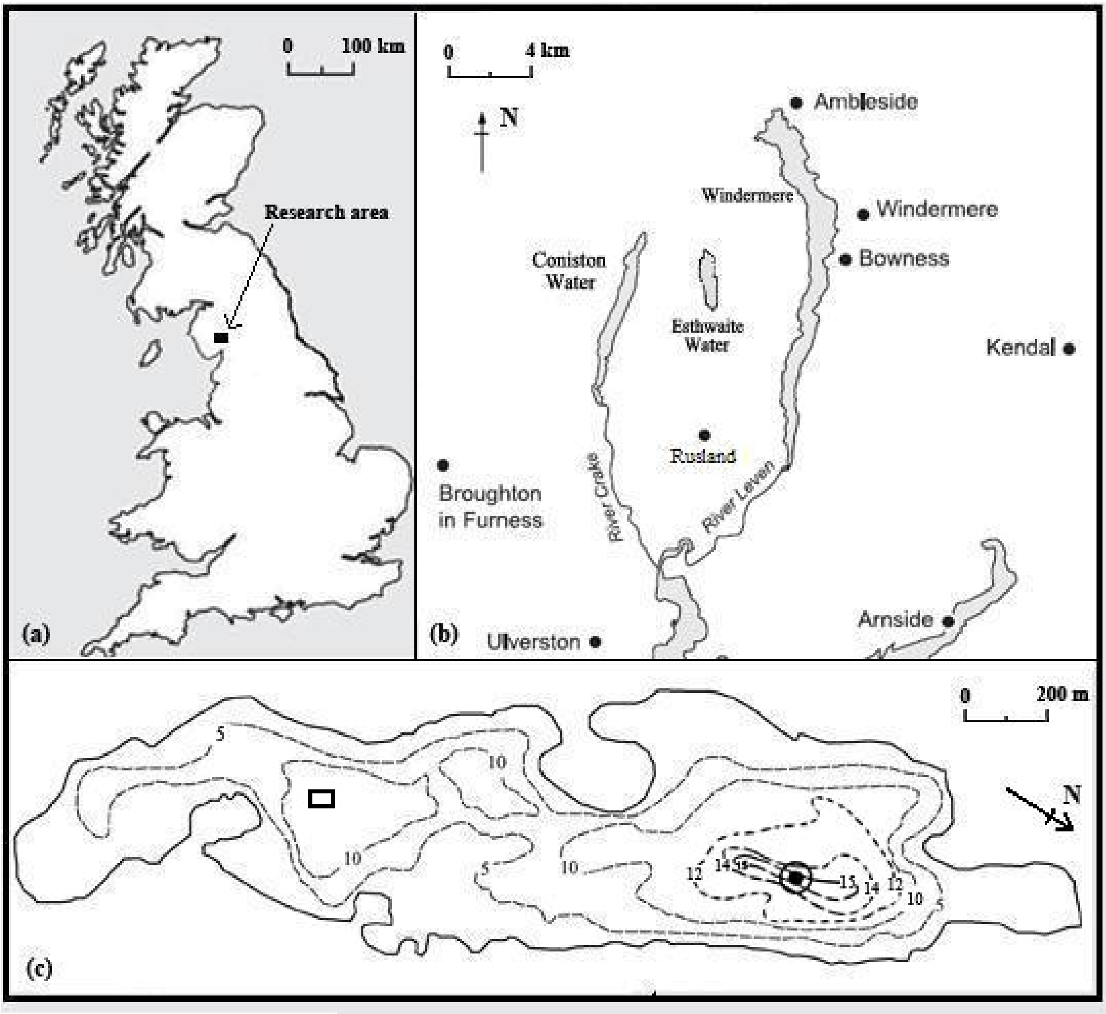


Fig. 1.2 Maps of the study area. (a) The location of Esthwaite Water catchment, UK, shaded area is expanded in (b). (b) Location of Esthwaite Water in the Windermere catchment. (c) Bathymetric map of the lake (unit: m), with the circled dot and hollow square representing the coring area of the palaeolimnological studies (including all the sediments in following chapters) and fish farm, respectively.

1.6.1 Climate background

The Lake District has two distinctive climatic features: high annual rainfall and extreme heterogeneity in its spatial distribution (Barker, Wilby & Borrows, 2004). The mountains of the Lake District are relatively high and, as they lie near the western seaboard, they produce one of the wettest parts of England. Due to the mountain geomorphology, annual total rainfall varies from over 3,000 mm at Seathwaite (Manley, 1946) to 920 mm at Kendal (Tufnell, 1997). The Esthwaite Water catchment receives annual average precipitation of around 1,000 mm (Reynolds and Irish, 2000), since it is situated in the lower latitude part of the Lake District. In terms of intra-annual variability, precipitation is highest in winter, decreases in the middle of the year and then rises in the autumn (Macan, 1970). The climate in the English Lake District is significantly affected by the North Atlantic Oscillation (NAO, e.g. George, Maberly & Hewitt, 2004). During positive phases of the NAO Index, westerly air flows from the Atlantic, and oceanic conditions bring moisture which leads to a wet climate (Rodwell and Folland, 2002). Inversely, drier weather occurs during negative phases of the NAO index.

Latitude is an important factor in controlling the local temperature. At Esthwaite Water, higher annual temperatures have been observed than in the northern area of the district around Keswick. The average monthly air temperature records from a nearby station, Newton Rigg (<50 km far from Esthwaite Water), during 1971-2000, show that there are relatively moderate temperature variations through the year (Fig. 1.3). The seasonal variation in temperature results in thermal stratification of Esthwaite Water, typically from late April to early October.

1.6.2 Lake characteristics

The lake has a surface area of 1.0 km^2 with maximum and mean depths of 15.5 m and 4.3 m, respectively. It lies in a relatively fertile lateral valley of the Windermere catchment, with a drainage area of 17.1 km^2. Hills around the lake are composed geologically of Bannisdale slates and grits. Lowland mixed forest of alder (*Alnus glutinosa*), oak (*Quercus petraea*, *Quercus robur*) and Wych elm (*Ulmus glabra*) surround the southern and eastern parts of the lake. The remaining land is used chiefly for agriculture and forestry, comprising 42.2% and 38.4% of the total catchment area, respectively (Fig. 1.4). The lake catchment contains a small rural population in the village of Hawkshead, which increased slightly from 494 in 1,909 to 523 in 1988. The population of sheep in 1988 had, however, increased by 200-300% compared to the 1950s (Bennion *et al.*, 2005).

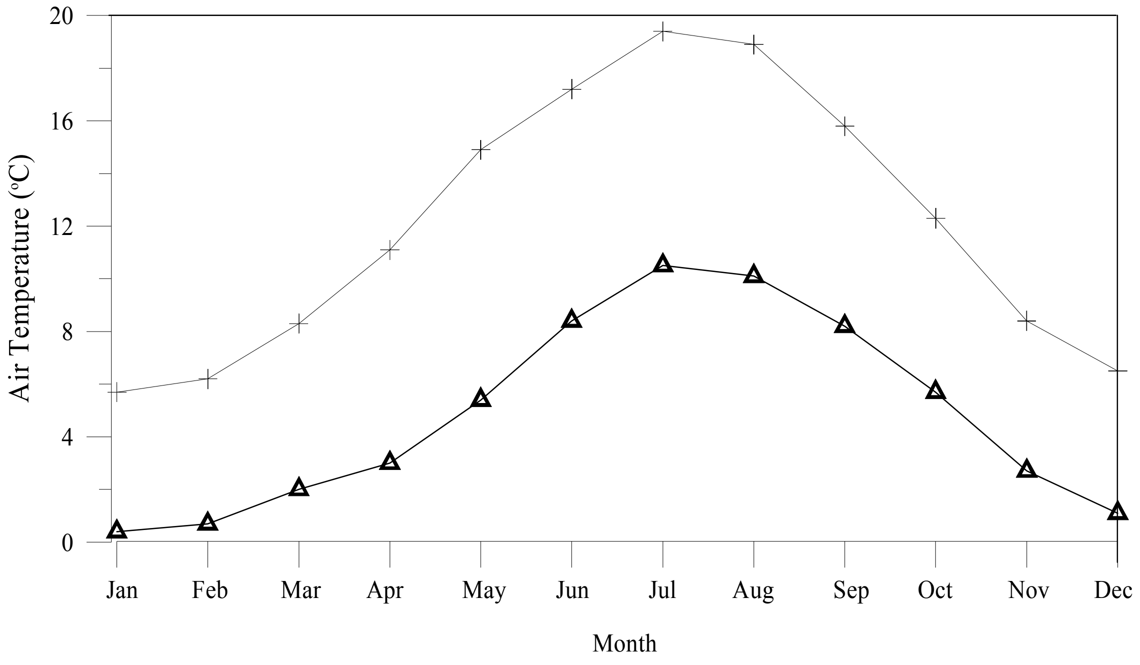


Fig. 1.3 The average monthly maximum (line with crosses) and minimum (line with triangles) air temperature records from the nearest gauge station, Newton Rigg, during 1971-2000. Data from Met Office website http://www.metoffice.gov.uk/climate/uk/averages/19712000/sites/newton_rigg.html

The main basin inflow named Black Beck enters at the shallow northern bay. Black Beck receives not only the runoff from the northern highlands, but also the domestic waste water from the residence of Hawkshead, which in total accounts for ~50% of the total water supply to the lake, as all other inflows are small streams (Davison, 1981; see Fig 1.4). The average retention time of Esthwaite Water is ~90 days (Talling & Heaney, 1988).

Due to the high precipitation in the catchment, the concentrations of dissolved substances in the lake are greatly influenced by the nature and porosity of the soils and underlying rocks. The lake receives high nutrient inputs, relative to many other lakes from the Lake District, and is therefore relatively productive (Pearsall & Pennington, 1973). The current total phosphorus (TP) concentration is around 28 μg L^{-1} (mean of fortnightly data in 2008), classifying the lake as eutrophic. The chemical characteristics of the lake (annual average for 2007) are given in Table 1.2.

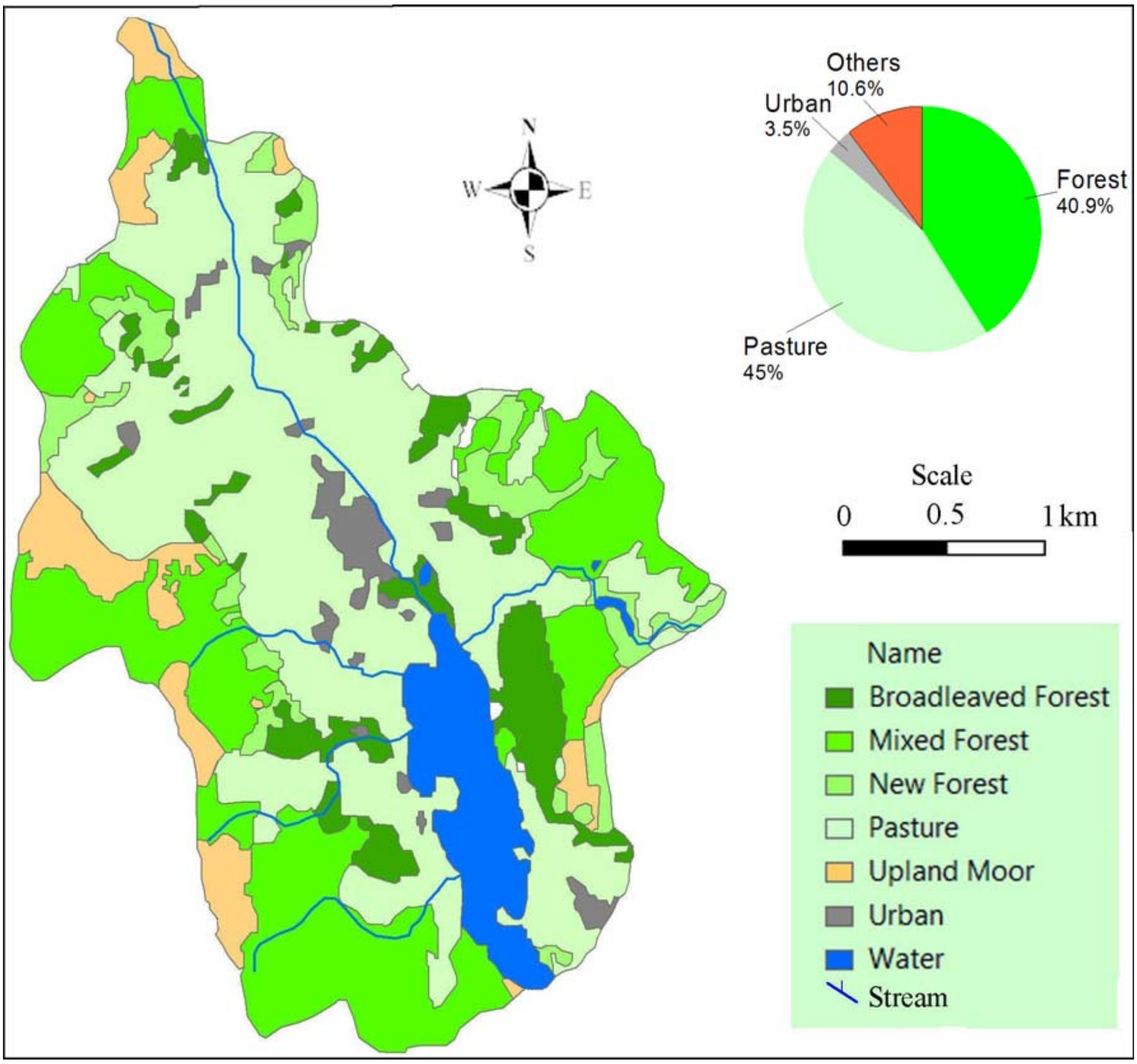


Fig. 1.4 Land use characteristics of the Esthwaite Water catchment in 1988 (modified from May, Place & George, 1997). The original land cover data were obtained from the Lake District National Parks Authority.

The phytoplankton in Esthwaite Water is diverse and periodically abundant. As in several other lakes in the English Lake District, the seasonal variation in biomass regularly includes a smaller spring and a larger late summer maximum (Talling, 1993). The former is dominated by diatoms such as *Asterionella formosa*, while the summer maximum is often dominated by blue-green algae and sometimes by slow-growing populations of one or two species of the dinoflagellate *Ceratium*. In autumn and winter, diatoms such as *Fragilaria crotonensis*, and *Aulacoseira subarctica*, along with Cladocera species, are usually dominant (Heaney, Smyly & Talling, 1986). These community shifts are governed by year-to-year differences in physical as well as chemical factors and the stability of summer stratification (George & Heaney, 1978, Heaney & Butterwick, 1985; Heaney *et al*., 1988; Talling, 1993; George *et al*., 2004).

Table 1.2 Annual water chemistry of Esthwaite Water in 2007 and 2008

(data were provided by the Centre of Ecology and Hydrology (CEH))

Parameters	2007	2008
Chl-a (μg L^{-1})	19.98	17.18
pH	7.36	7.37
Alkalinity (meq L^{-1})	0.43	0.41
Total P (μg L^{-1})	32.4	28.3
PO_4-P (μg L^{-1})	4.5	3.8
SiO_2 (μg L^{-1})	1295.2	1378.5
NH_4-N (μg L^{-1})	52.8	27.4
NO_3-N (μg L^{-1})	497.4	501.6

Aquatic plants are abundant in Esthwaite Water. The lake supports an aquatic flora of pondweeds (*Potamogeton* spp, *Elodea canadensis*), stoneworts (*Chara* spp), water lobelia (*Lobelia dortmanna*), shoreweed (*Littorella uniflora*), water lilies (*Nuphar lutea* and *Nymphaea alba*) and further the lake is enclosed by reedbeds dominated by *Phragmites australis*. The nationally rare slender naiad (*Najas flexilis*) has been found at the southern end of the lake. Tall herbs in the wetlands include meadowsweet (*Filipendula ulmaria*), common valerian (*Valeriana officinalis*) and angelica (*Angelica sylvestris*). The lower depth limit of macrophyte growth is about 3.8 metres, and plant beds are especially well developed in the shallow area near to the main inflow. The plant biomass contributes organic matter to the littoral sediments in which there is a high diversity of lower fungi (Willoughby, 1961).

1.6.3 Historical human activities in the catchment

The English Lake District has experienced a long history of human activity. From detailed excavations undertaken by Clark (1954) at Star Carr near Scarborough, it appears that early man occupied Northern England approximately 9550 years ago, and furthermore these hunter/fisher/food-gathering peoples travelled there from the Baltic region on foot before the North Sea was fully formed. Pearsall and Pennington (1973) also proposed that the first human settlement in the Lake District probably began at least 5000 years ago, when mountains became the source of stone for axes and the sites of stone circles at Castlerigg, Long Meg, and elsewhere. Later, a variety of human activities, such as agriculture, farming, deforestation, mining, and tourism became more significant along with the expansion of the population. Palaeolimnological studies have revealed that soil erosion has increased over the past 5000 years and so too the rate of sediment accumulation in lakes (Pennington & Tutin, 1964; Pennington, 1978; Pennington, 1981; Pennington, 1991).

The predominant land use in the Lake District is agriculture, in particular sheep farming. A steady decline in tree cover is indicated by published pollen diagrams (Pennington, 1975; Oldfield, 1960). For example, Oldfield (1960) suggested that the first human-induced forest clearance occurred in lowland Lonsdale approximately 4500 years ago. Although these early people were partly hunter-fisherman, they were also farmers and would, therefore, establish themselves in areas where grain could be cultivated and stock reared (Rollinson, 1967). With the population growth thereafter, more and more land was reclaimed, mainly for the pasturing of sheep, and this gradually extended from the lowlands to the uplands. As a consequence of the increase in sheep farming, Hawkshead became an important centre of the woollen industry from the early 16th century. By the early nineteenth century Cumberland, despite its landscape of mountains and moorland, had become markedly urbanized. In 1811 it contained 12 towns with 1,000 or more inhabitants and about 45% of them depended directly or indirectly on agriculture for a living (Bouch & Jones, 1961). In addition to sheep, the thin acid soils of the Lake District were used for the cultivation of oats and barley, both grains being used for making bread and barley also for brewing. Farm equipment was still primitive but by the 17th century carts were replacing packhorses for agricultural transport and several roads were constructed.

Mining was also historically a major industry in this area. As early as the 12th Century there is evidence of mining and quarrying in Cumbria, and it probably dates back to Roman times (Postlethwaite, 1913). Minerals such as lead, copper, zinc, baryte, haematite, tungsten, graphite, fluorite, and coal were being mined and quarried. The period of greatest prosperity and mineral output was in the latter half of the 19th century (Pickering & Sutcliffe, 2001). Mining works accelerated the soil erosion directly. Meanwhile, woodland clearance was used extensively to provide charcoal for smelting, which also led to more soil loss. Interestingly, "-thwaite" in the place-name Esthwaite means "clearing" (Collingwood, 1925), which suggests that clearance events have a long history in the area. For example, large-scale forest clearance in Cumbria was recorded during the Bronze Age (4000-2800 ago) and, particularly in the lowlands, successive clearances of land for cereal cultivation and pastoral agriculture had permanently reduced the woodland cover (Hodgkinson *et al.*, 2000).

1.6.4 Recent eutrophication history

Today Esthwaite Water is probably one of the most productive of the Cumbrian lakes, and in recent decades it has shown evidence of nutrient-enrichment with increased abundance of phytoplankton. Nutrient loading to Esthwaite Water has always been relatively high due to the relatively rich soils in the catchment, but loads increased rapidly in the 1970s when a new sewage works opened discharging treated effluent into the main inflow. Talling and Heaney (1988) reported that up to 67% of the P loading to the lake was attributable to sewage discharge from Hawkshead sewage treatment works. Prior to that, more than 60% of the TP load from land cover sources was found to come from improved pasture, with forestry accounting for a further 24%

(May, Place & George, 1997).

In 1981, a fish farm was established in the southern basin of Esthwaite to support commercial rainbow trout with the consequent introduction of waste from cages to the system (Talling, 1999). Hall, Corry & Lishman (1993) estimated the farm produced approximately 100 tonnes biomass (wet weight) fish per annum and it has been estimated from other studies that for every tonne of rainbow trout produced, approximately 150-300 kg of waste food and 250-300 kg dry weight of faeces are introduced into the aquatic environment (Phillips *et al.*, 1985). The influence of the fish farm as a source of P and the resultant nutrient dynamics with respect to algal blooms has been documented (Hall, Corry & Lishman, 1993).

After 1986 the phosphorus input from sewage was reduced by tertiary chemical treatment, although input from the fish farm increased. The total annual loading to Esthwaite Water in 1986 was estimated to be *ca.* 1.65 g P per m^2, which was significantly less than the levels prior to sewage treatment (Heaney *et al.*, 1992). In recent decades, intensive human activities, particularly tourism in the catchment, continue to exert pressure on the lake system. For example, the average number of visitors to the Lake District reaches about 15.5 million people per year (http://www.lakedistrictwiki.co.uk/Tourist_Statistics).

An effective descriptor of the increased loading is the average winter concentration of soluble reactive phosphorus (SRP). Fig. 1.5 shows the long-term trend in January SRP in the lake between 1960 and 1990. These results show that SRP concentrations increased rapidly in the early 1970s with the introduction of sewage effluent and remained relatively high throughout the 1980s and 1990s.

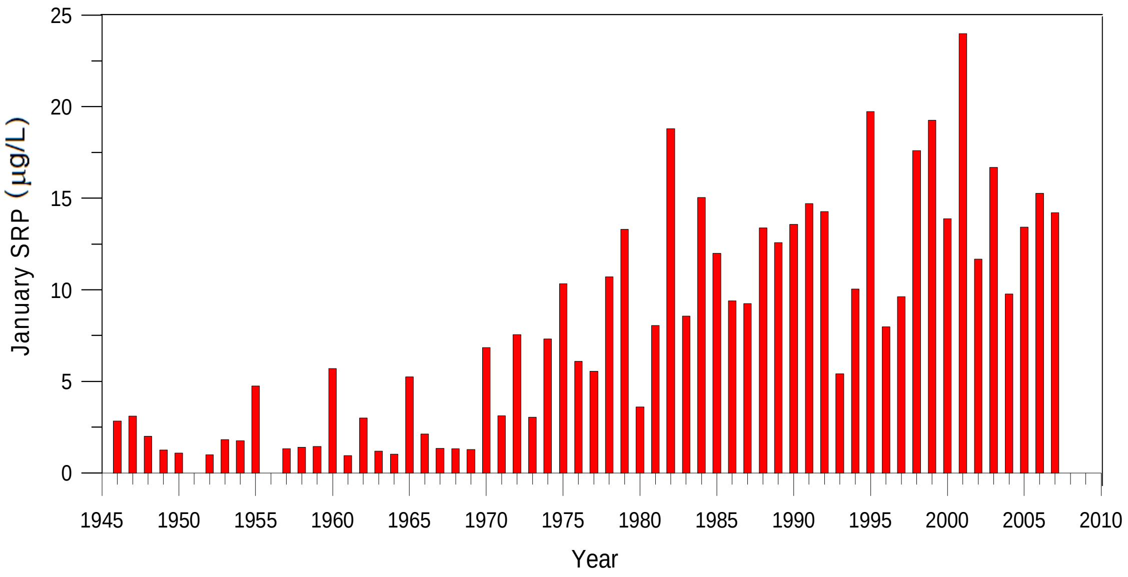


Fig. 1.5 Average January SRP concentrations in Esthwaite Water from 1946 to 2007.

(Dater were provided by CEH)

1.7 Previous studies and long-term datasets

Esthwaite Water is one of the best studied lakes in the world. Over the past century a great deal of contemporary limnological research, as well as several palaeoecological studies, has been conducted.

Contemporary limnological studies have mainly focused on the lake physico-chemical and biological characteristics especially phytoplankton and zooplankton dynamics. A long-term monitoring programme in Esthwaite Water, started in the earlier 1940s by the Freshwater Biological Association and subsequently implemented by the CEH, provides an excellent resource for understanding the physico-chemical and biological community variability on a range of timescales. In particular, the seasonal and decadal periodicity of phytoplankton composition and its relationship with physical and chemical features of the lake has been most extensively examined (e.g. George & Heaney, 1978; Harris, Heaney & Talling, 1979; Heaney & Butterwick, 1985; Heaney, Smyly & Talling, 1986; Tallling & Heaney, 1988; George *et al.* 1990; Talling 1993, 2003; Maberly *et al.*, 1994b; George, Maberly & Hewitt, 2004).

Several other biological components in the lake have also been extensively studied. The spatial and temporal distribution of zooplankton (protozoans, rotifers, and microcrustaceans) has been investigated since 1977 (Bark, 1981). Macrophytes were first surveyed systematically by Pearsall in 1917 (Pearsall, 1917). Several following surveys focused on North Fen where the rivers meet the lake. The general structure of the fen and the conditions controlling the distribution of the main types of vegetation were described by Tansley (1939) and Pigott & Wilson (1978). More recently, in June 1995 a survey of the aquatic plants of the whole lake was carried out and found that several oligotrophic taxa, such as *Isoetes lacustris* and *Myriophyllum alterniflorum*, that have frequently been recorded in the past had disappeared; likely as a consequence of nutrient enrichment (Bennion, Monteith & Appleby, 2000). The lake contains brown trout (*Salmo trutta*), perch (*Perca fluviatilis*), pike (*Esox lucius*), eel (*Anguilla Anguilla*), rudd (*Scardinius erythrophthalmus*) and roach (*Rutilus rutilus*) in large quantities. However, the eel makes annual migrations in the outflowing Cunsey Beck which were studied in the 1940s for numbers trapped length-weight-age relationships (Frost, 1946). Further fish studies have been limited due to private ownership.

Esthwaite Water has also been the subject of several previous palaeolimnological studies. The sedimentation process in the lake, set as a paradigm for shallow lakes, was described by Hilton, Lishman & Allen (1986). Sediment cores from Esthwaite Water have been analysed for pollen (Franks, Pennington & Tutin, 1961), diatoms (Round, 1961; Bennion, Monteith & Appleby, 2000), cladoceran (Goulden, 1964), fish vertebrae and scales (Pennington, Tutin & Frost, 1961) and algal pigments (Fogg & Belcher, 1961). Physical and geochemical proxies have also been examined including calcium and magnesium in long sediment cores taken in the 1960s which indicated high erosion and leaching in the catchment since the post-glacial period (Mackereth, 1965; Mackereth, 1966). The organic pollution history has been explored including analysis of individual polychlorinated biphenyl (PCB) congeners and 1,1,l-trichloro-2,2-bis(p-chlorophenyl)-ethane (DDT) in a short sediment core were analyzed, which showed that persistent organochlorine pollution reached its maximum in the 1950s and decreased in the following decades, concurrent with restrictions on its production and use (Sanders *et al.* 1992).

A series of environmental changes in the Lake District have been reconstructed using the above mentioned proxies or recorded by historical documents. For example, sediment cores from the shores of Morecambe Bay and Lake Windermere were analyzed and revealed an amelioration in climate between 10000 BC and 8800 BC. However, the onset of climatic deterioration was recorded during the "Younger Dryas" period between 8800-8300 BC (Pennington, 1943; Oldfield, 1960). Additionally, there exist several long-term climate records at different spatial-temporal scales (Table 1.3), some of which extend back to the mid-eighteenth century, thus affording a rare opportunity for a direct comparison with palaeolimnological data. For example, The Central England Temperature series is the longest instrumental temperature record in the world (Parker & Horton, 2005). It records the temperature of a triangular portion of England bounded by London, Herefordshire and Lancashire, and provides mean daily temperature estimates back to 1772.

Over the past two decades, the lake model, named PROTECH (Phytoplankton RespOnses To Environmental Change, see Elliott *et al.*, 1999; Reynolds, Irish & Elliott, 2001), has been developed to experiment with the effects of elevated temperatures and increased nutrient load on phytoplankton succession and productivity. It has been successfully applied to some lakes in the Lake District such as Bassenthwaite Lake (Elliott *et al.*, 2005; Elliott, Jones & Thackeray, 2006), Blelham Tarn (Jones & Elliott, 2007) and also Esthwaite Water (Patrick *et al.*, 2004). In Esthwaite Water, the model firstly identified P loading and temperature as potentially important factors in determining the amplitude and timing of the spring bloom of a dominant diatom species, *Asterionella formosa*, by a series of substitution of input variables for specific years. Then their proportional effects were quantified using a common standard Esthwaite simulation (Patrick *et al.*, 2004). The modelling technique is promising, although higher resolution and close interval monitoring data are much preferred and most of the models can only simulate the response of a single species each time.

Table 1.3 Climatic records for Esthwaite Water and its catchment

Proxy	**Dates of records**	**Location**	**Resolution**	**Sources or literature**
Temperature	1932-present	Esthwaite (Ambleside)	Annual (fortnightly partly)	CEH & FBA
	1772-2006	Central England	Monthly	Met Office
	1850-2006	Northern Hemisphere	Monthly	Met Office
Precipitation	1945-present	Esthwaite	Fortnightly	CEH & FBA
	1788-2000	Central Lake District	Monthly	Barker *et al.* (2004)
	1766-2006	England and Wales	Monthly	Met Office
Wind	1965-2006	Ambleside	Monthly	CEH & FBA
Cloud cover	1965-2006	Ambleside	Monthly	CEH & FBA
Wind/Cloud	1945-2006	Esthwaite	Fortnight	CEH & FBA
NAO	1865-2000	Regional	Monthly	Hurrell *et al.* (2003)

In summary, numerous studies have been conducted at Esthwaite Water to understand how climate and nutrients affect the lake ecosystem. These studies have variously employed monitoring, modeling and palaeolimnological techniques separately over different timescales. Each method has its own limits, and there may, therefore, be great potential to improve our understanding by using several of these approaches in conjunction. Furthermore, the interaction between nutrient and climate change is yet to be fully explored.

1.8 Objectives and outline of thesis

This PhD project employs both contemporary (observational) and palaeolimnological (sedimentary) records, using diatoms as the key indicator, to understand how climate and nutrients have impacted the lake ecosystem of Esthwaite Water, UK, over a range of timescales from months to several centuries. Three main datasets, representing three timescales, are used (Table 1.4).

The critical research questions are:

- How faithfully do the sedimentary diatom remains record changes in the planktonic diatom populations in the water column?
- How do diatom assemblages respond to climate and nutrient changes over a range of timescales (seasonal, decadal to century scale)? Can we quantitatively disentangle their sole contributions?
- How does the combination of contemporary limnology and palaeolimnology improve our understanding of environmental change in Esthwaite Water?

The main aim of the thesis is to explore the patterns of lake diatom response to environmental changes over three timescales (seasonal, decadal and centennial). Firstly the seasonal and inter-annual variability of planktonic diatom assemblages are examined along with an array of water environmental variables based on a two-year monitoring (monthly) dataset (chapter 2). Crucially, this information will be used to facilitate interpretation of the diatom changes observed in the sediment record (chapter 5 and 6).

Table 1.4 Contemporary and palaeolimnological datasets over three timescales for Esthwaite Water Sample source and analysers were labelled (a: collected by CEH; b: analyzed by Xuhui Dong; c: collected by Xuhui Dong; d: analyzed by CEH; e: collected by Helen Bennion and Gavin Simpson; f: analyzed by Peter Appleby and Handong Yang; g: analyzed by Charlotte Bryant).

Time scale	**Data series**	**Parameters**
Fortnightly ~ Monthly	27-Jun-2007 ~ 23-Jun-2009	* Planktonic diatom composition in the water column [a, b] * Diatom composition in every 3- or 6- month sediment traps [c, b] * Physicochemical parameters describing lake environment including surface temp, SD, Chl-a, pH, Alkalinity, Total P, SRP, SiO_2, NH_4N, NO_3N [a, d]
Annual ~ decadal	1946 ~ 2003	* Annual average planktonic diatom composition [a, b] * Fossil diatom data from the last 50 years [e, b] * Physicochemical parameters describing lake environment including surface temp, SD, Chl-a, pH, Alkalinity, Total P, winter SRP, SiO_2, NH_4N, NO_3N [a, d]
Century ~ millennia	*c.a.* 800 ~ 2006 AD	Two sediment cores [e]: * ^{210}Pb [f], ^{14}C dating [g], LOI [b], Grain size [b] * Diatom composition and concentration [b] * Geo-chemical data for the sediment core [b] Past environmental information including climatic records and documentary evidence of human activity and land use change [b]

Prior to applying the short timescale information to the long-term sediment records, diatom representativity in the lake sediments is assessed by comparison of diatoms in the water column, seasonal traps and surface sediments (chapter 3). Firstly, the fossil diatom assemblages in the upper section of the sediment cores, representing the diatom crops in the period 1945-2003, are compared with the planktonic diatom records over the same period. Secondly, diatom assemblages in the water column sampled from July 2007 to June 2009 are compared with those in seasonal sediment traps collected from the same time period. Thirdly, the annual average abundances of diatoms from the water column are compared with those from the surface sediment for the same year.

Secondly, the thesis quantitatively assesses the influence of climate and eutrophication on the diatom flora of Esthwaite Water. Combined with the two year monitoring record, a 60-year monitoring series of physico-chemical lake characteristics and diatom assemblages is used to assess the influence of changes in nutrients and climate (chapter 2 & 5). The two chapters use a range of statistical methods, such as redundancy analysis (RDA) and generalized additive modelling (GAM) to understand the pattern of diatom response to nutrients and climate. The information should improve our understanding of how lake systems may respond to climate change in the future.

The last strand of the thesis involves historical lake environmental reconstruction using diatom records, grain size, LOI, and geochemical analysis combined with ^{210}Pb dating and ^{14}C dating techniques (chapters 4 & 6). In chapter 6, combined with diatom ecological information gained from both the monitoring data (from Esthwaite Water and Derwent Water) and published literature, diatom changes in the sediment core are interpreted in term of changing climatic conditions and lake trophic status, focusing on two distinct climate episodes, the Medieval Warm Period and the Little Ice Age. Furthermore, the changes observed in the palaeo data over the past 1200 years will be compared with long-term nutrient, temperature, precipitation and human activity records to evaluate the key drivers of environmental change.

The structure of the PhD is outlined in Fig 1.6.

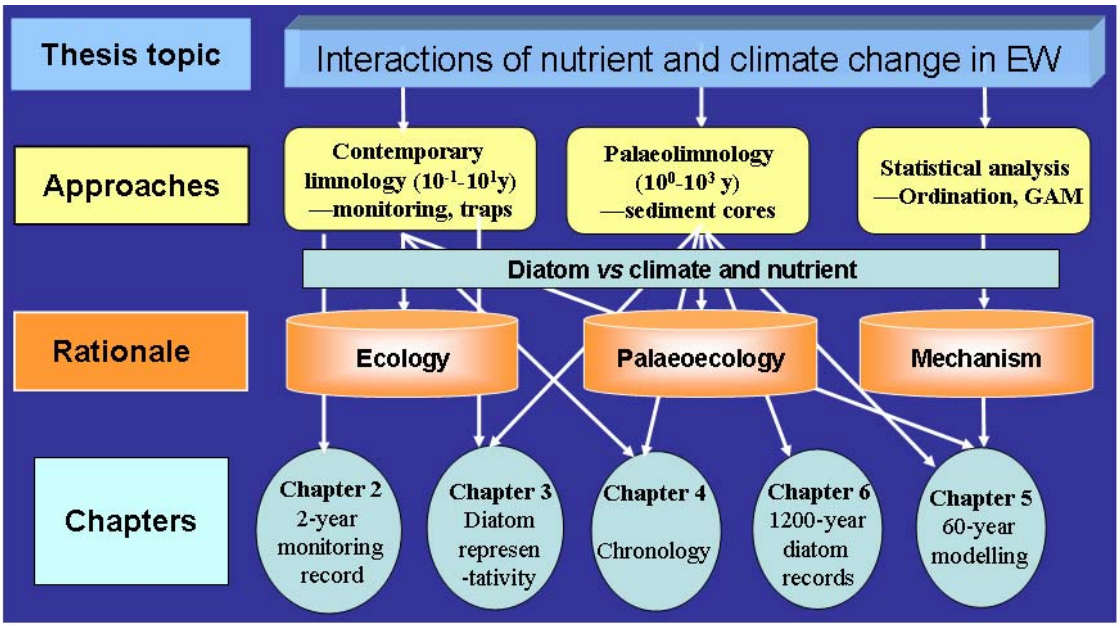


Fig. 1.6 Major chapters of this PhD Thesis

Chapter 2 Seasonal and inter-annual dynamics of planktonic diatoms and their relationship with physico-chemical factors in Esthwaite Water

2.1 Introduction

Diatoms are excellent indicators of water quality and are widely used in palaeolimnological reconstructions of lake ecosystems, since they are sensitive to lake water environmental conditions such as pH, nutrients and salinity and their valves preserve well in lake sediments (Battarbee *et al.*, 2001; Stoermer & Smol, 2001). Many diatom-based transfer functions have been successfully developed to reconstruct lake environmental change in different regions of the world (e.g. Bennion, Juggins & Anderson, 1996; Lotter *et al.*, 1998; Stoermer & Smol, 2001; Davies *et al.*, 2002; Tibby, 2004; Yang *et al.*, 2008). These models are usually based on the relationship between diatom assemblages in surface sediments and the environmental variable of interest in a training set of lakes spanning a wide environmental gradient. However, the relatively coarse resolution of the surface samples, which usually encompass several years of diatom deposition, mean that seasonal relationships with environmental factors can not be established (e.g. Sayer, 2001; Bradshaw & Anderson, 2003). Nonetheless, an understanding of ecological process at the seasonal scale is particularly important for refining palaeolimnological inferences and hence contemporary ecological information is crucially required (Battarbee *et al.*, 2005a; Anderson *et al.*, 2006; Sayer *et al.*, 2010b).

To aid the palaeolimnological interpretation of the diatom record from Esthwaite Water, contemporary planktonic diatom dynamics were investigated on a fortnightly basis over a two-year monitoring period along with a suite of physico-chemical parameters of the water column. High-resolution monitoring such as this can potentially provide information on how the aquatic system responds to changing environmental conditions (Straile & Adrian, 2001).

Numerous studies have explored the relationship between phytoplankton distribution and lake physico-chemical characteristics (e.g. Reynolds, 1980; Temponeras, Kristiansen & Moustaka-Gouni, 2000; Hubble & Harper, 2002; Chen *et al.*, 2003;

Salmaso, 2009). In Esthwaite Water, the seasonal and decadal periodicity of phytoplankton composition has also been extensively examined. For example, Harris *et al.* (1979) assessed the physiological and environmental constraints on the ecology of the planktonic dinoflagellate *Ceratium hirundinella* and Heaney *et al.* (1986) described comprehensively the spatial-temporal variability of phytoplankton and relationships with environmental parameters. George & Heaney (1978) and Heaney & Butterwick (1985) demonstrated how summer mixing influences major components of the diatom, dinoflagellate, and blue-green algae communities, and George *et al.* (1990) found that the average wind speeds in July and August significantly affected long-term variation in the average filament concentration of *Aphanizomenon.* Talling (1993) presented a 26-year sequence of total phytoplankton biomass and found that solar radiation, nutrient availability and thermal stratification were important factors in controlling phytoplankton communities. In a later study, Talling (2003) demonstrated the grazing effect of *Daphnia* by examining the inter-relationship between phytoplankton and crustacean plankton abundance.

On a regional scale, several studies have revealed that the lake surface and bottom temperatures, winter concentrations of nitrate and soluble reactive phosphorus (SRP), and rainfall are all significantly affected by the North Atlantic Oscillation and, therefore, influence the phytoplankton in the lake (e.g. Harris, Heaney & Talling, 1979; Tallling and Heaney, 1988; Maberly *et al.*, 1994b; George, Maberly & Hewitt, 2004). However, little detailed work has been carried out on diatom communities and the mechanisms controlling their seasonal distribution in Esthwaite Water. Furthermore, although long-term monitoring records of algae exist for the lake, these samples have been enumerated using microscopes with only low magnification (Lund, Kipling & Cren, 1958; Maberly *et al.*, 1994a). Whilst this method is suited to assessing phytoplankton composition, the resolution is insufficient to identify all diatom taxa to species level and is particularly problematic for distinguishing small centric species with diameters less than 10 μm. Palaeolimnological techniques, such as mounting diatom samples to slides, adding microspheres to quantify diatom concentrations, and counting under light microscope at ×1000 magnification, can potentially provide more accurate species specific information on diatom community dynamics.

In this chapter, high-resolution (fortnightly) planktonic diatom samples collected over a

2-year period and analysed on mounted slides at high magnification (×1000), are presented for Esthwaite Water. The aims of the study were: (a) to describe the seasonal and inter-annual variability of planktonic diatom species in relation to an array of environmental variables; and (b) to explore how nutrients and climatic variables in particular, influence diatom assemblages. The implications of the findings for the palaeolimnological interpretation of sedimentary diatom records in the lake are also discussed.

2.2 Site description

See chapter 1.

2.3 Methods

2.3.1 Field and laboratory methods

Approximately five litre integrated water column samples (0-5 metres) were collected from the deepest point of the northern basin at two-weekly intervals from 24-July-2007 to 23-June-2009, using a weighted plastic tube (Lund, 1949). For each sample, two litres of water were preserved with Lugol's Iodine and kept in the dark at 4 °C for planktonic diatom analysis. The remaining water was analysed for chemical variables including SRP, nitrate (NO_3-N), ammonia (NH_4-N), chlorophyll-a (Chl-a) and SiO_2 plus pH and alkalinity in the laboratory at Freshwater Biology Association using standard techniques. Briefly, SRP was measured using filtered water samples, followed the methods of Murphy & Riley (1962). NO_3-N and NH_4-N were measured on filtered samples using a nitrate-selective electrode, following the method of the Department of the Environment, National Water Council (1982). Chl-a was determined fluorimetrically after acetone extraction (Marker, 1972). SiO_2 analysis followed the methods of Strickland & Parsons (1972).

In situ surface water temperature (ST) and temperatures of other depths (at 1-2 m interval, but 2, 4, 6, 8, 10, 12, 14 m on most occasions), secchi depth (SD) and water level (WL) were also measured. WL was used as a surrogate for precipitation, as a good relationship between these variables has been observed in Esthwaite Water (Heron, 1961). The Schmidt stability (Stability, Schmidt, 1928), defined as the amount of work needed to mix the entire body of water to uniform temperature without addition or subtraction of heat (Hutchinson, 1957), was calculated from the thermistor data (from the depth of 0, 2, 4, 6, 8, 10, 12, and 14 m) and bathymetric measurements of Esthwaite Water (Ramsbottom, 1976) using the following equations:

$$S = -\frac{g}{A_0}\int_0^{z_m}(z - z_g)A_z(\rho_{\max} - \rho_z)\mathrm{d}z \tag{1}$$

$$z_g = \frac{1}{V}\int_0^{z_m} zA_z\mathrm{d}z \tag{2}$$

$$\rho_z = \left[1 - \frac{T_z + 288.9414}{508929.2 \cdot (T_z + 68.12963)}(T_z - 3.9863)^2\right] \cdot 1000 \tag{3}$$

where g is the acceleration due to gravity, A_0 is the surface area, A_z is the area at depth z, z_m is the maximum depth, z_g is the depth of the centre of gravity of the lake (calculated using equation 2), ρ_z is the density of pure water at depth z (calculated using equation 3, (Martin, McCutcheon & Schottman, 1999), $\rho_{\max}$ is the maximum density of pure water, V is the volume of the lake, and T_z is the temperature at depth z (in °C). These data were collected and analysed by the Centre for Ecology & Hydrology as part of their long-term monitoring programme.

2.3.2 Diatom analysis

Water samples treated with Lugol's Iodine were settled for 24 hours in the laboratory and thereafter the surface water was removed with a siphon. The deposited material was then prepared for diatom analysis using standard methods (Battarbee *et al.*, 2001). In order to calculate diatom concentration, a known number of microspheres was added to the diatom suspension (Battarbee & Kneen, 1982). A minimum of 500 diatom valves were identified for each sample. Taxonomy mainly followed Krammer & Lange-Bertalot (1986, 1988, 1991a, b). Given the occasional occurrence of non-planktonic species, diatom data were calculated as percentage abundance on the sum of all planktonic species.

2.3.4 Data analyses

Releationship among environmental variables (Stability, SRP, NO_3-N, SiO_2, Si:SRP ratio, SD, ST, and alkalinity) were detected by scatter-plot of paired variables. Pearson correlation coefficients were calculated within and among the environmental variables and diatom species using the software package SPSS. The statistical significance was also calculated using this programme.

Relationships between seasonal diatom communities and lake physico-chemical variables were explored using multivariate statistical techniques implemented in the computer program CANOCO 4.5 (ter Braak & Smilauer, 2002). Any species with less than two occurrences or with its highest relative abundance less than 2% were considered as 'rare' taxa and were excluded from the analyses. Firstly, a detrended correspondence analysis (DCA) was used to decide whether unimodal (canonical correspondence analysis, CCA) or linear (redundancy analysis, RDA) ordination methods were appropriate. The results showed that the floristic gradient was above 2.2 standard deviation units, thus CCA was selected (Birks, 1998). Secondly, after removing highly inter-correlated environmental variables (indicated by variance inflation factors above 20) by a primary CCA ordination, a forward manual selection CCA and Monte Carlo permutation tests identified a minimal subset of environmental variables that explained significant proportions ($p<0.05$) of variation in the species data. Thirdly, a series of partial CCAs was carried out on the dataset to explore the influence of different environmental variables on diatom species (Borcard, Legendre & Drapeau, 1992). Marginal effects were used to indicate the explanatory power of each variable determined without any assessment of possible covariance with other parameters. Conditional effects were used to assess the influence of each variable, which is independent of variables previously selected in an iterative "forward selection" process, where variables with greatest explanatory power are added first to the model. Bonferroni correction was used to adjust the significance threshold levels on each partial test where we select only the variables in the forward selection (Cabin & Mitchell, 2000). To avoid the covariance caused by time, sampling dates were used as a covariable in all the CCAs.

2.4 Results

2.4.1 Water environmental characteristics

The two year monitoring record (from June 2007 to June 2009) revealed strong seasonal patterns in the physical and chemical characteristics of the surface water of Esthwaite Water (Fig. 2.1). Surface water temperature exhibited the same seasonal pattern in both years with a gradual increase from February to maximum values of *c.a.* 20 ^{o}C in August, followed by a steady decrease towards the following January. These temperature changes resulted in stratification of the water column from late April to early October. In mid summer the lake was strongly stratified with high stability. Secchi depth was normally greater than 1.5 m throughout the year, with the highest values (>3.5 m) in February and May 2008, and lowest values in September 2007 and April 2008. Alkalinity increased steadily from minimum values in January to maximum values in October/November for both years.

The nutrient parameters SRP, NO_3-N and SiO_2, exhibited similar seasonal patterns over the two years. The highest values occurred in winter and early spring and subsequently decreased to low concentrations in summer and autumn (Fig. 2.1). SRP reached its highest value of ~10 µg L^{-1} in February of both years and then decreased to less than 1 µg L^{-1} in May. Low concentrations of SRP, ranging from 0.3 to ~2.0 µg L^{-1}, continued until late August. In 2008, SRP started to increase in early September, somewhat earlier than the increase in 2007 which began in November. SRP remained high (~7-8 µg L^{-1}) throughout the winter in both years. NO_3-N concentrations exhibited a similar pattern, although winter average concentrations were considerably higher in 2007 than in 2008 (974 µg L^{-1} and 624 µg L^{-1} for 2007 and 2008, respectively). SiO_2 also displayed the typical pattern of winter maxima with a dramatic decline to minimum values in spring/summer before increasing again in the autumn. From May to July, the water was almost depleted of SiO_2, with values ranging from 40-310 µg L^{-1} (average 164 µg L^{-1}). By contrast, SiO_2 concentration were high in the range 1670-2590 µg L^{-1} (average 2120 µg L^{-1}) and 1530-2570 µg L^{-1} (average 2285 µg L^{-1}) from October 2007 to March 2008 and September 2008 to March 2009, respectively.

Maximum Chl-a concentrations occurred during August to October, with the highest values reaching 36 µg L^{-1} and 47 µg L^{-1} in 2007 and 2008, respectively. An additional short peak appeared in early March 2009. These peaks were followed by sharp declines in early winter, to minimum concentrations of 5 µg L^{-1} before increasing again in the spring.

Most of the environmental variables exhibited a close relationship to each other (Table 2.1 and Appendix I). Surface temperature was highly related to water column stability ($r=0.93$, $p<0.005$) and negatively related to all the measured nutrient variables such as

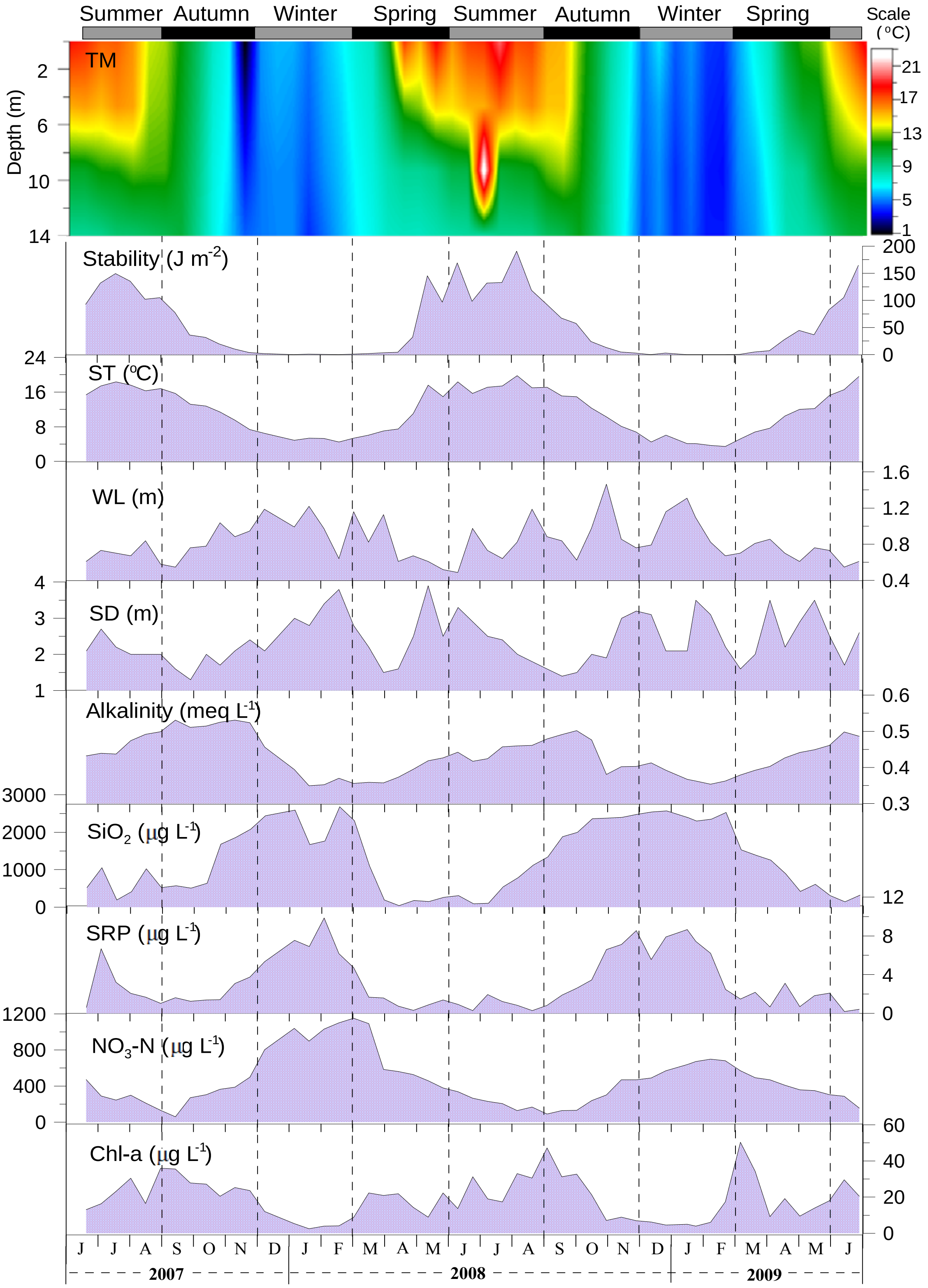


Fig. 2.1 Seasonal variation of limnological parameters: thermal bathymetric map (TM), water column stability (Stability), surface water temperature (ST), lake water level (WL), Secchi depth (SD), alkalinity, SiO_2, SRP, NO_3-N and Chlorophyll-a (Chl-a) in Esthwaite Water from June 2007 to June 2009. (Data were provided by CEH)

SRP, SiO_2, and NO_3-N at the significance level $p<0.01$. In contrast, water level was positively linked with all the nutrient variables. Chl-a and alkalinity were significantly related to all the measured variables. SD was relatively independent, only showing a close relationship with SRP and NO_3-N but no significant relationship with surface temperature, SiO_2 and water level (Appendix I).

Table 2.1 Correlation matrix of environmental variables (see methods for full names) measured at Esthwaite Water from June 2007 to June 2009. Significant values are shown in bold type ($p<0.05$ and * $p<0.001$).

	Stability	ST	SRP	SiO_2	NO_3-N	WL	SD	Chl-a
ST	**0.932***							
SRP	**-0.519***	**-0.622***						
SiO_2	**-0.661***	**-0.701***	**0.747***					
NO_3-N	**-0.646***	**-0.797***	**0.549***	**0.480***				
WL	**0.461***	**-0.453***	**0.522***	**0.547***	**0.330***			
SD	-0.086	-0.243	**0.374***	0.159	**0.428***	-0.065		
Chl-a	**0.357***	**0.477***	**-0.643***	**-0.394***	**-0.569***	**-0.318**	**-0.681***	
Alkalinity	**0.446***	**0.649***	**-0.481***	**-0.289**	**-0.721***	**-0.308**	**-0.435***	**0.535***

2.4.2 Diatom communities

The composition of planktonic diatoms showed a strong seasonal pattern that was generally consistent over the two monitoring years (Fig. 2.2). In spring, *Asterionella formosa*, sometimes along with *Aulacoseira subarctica*, formed the diatom bloom comprising over 90% of the total diatom community. *Fragilaria crotonensis* dominated in both summers (mostly over 60%) and remained at relatively high concentrations ranging from 300 to 3800 cell ml^{-1}. Winter assemblages were dominated by *A. subarctica,* accompanied by a small amount of *Aulacoseira granulata* var *angustissima*. Several other species, namely *Cyclotella comensis*, *Cyclotella pesudostelligera*, *Cyclotella radiosa* appeared in summer and *Stephanodiscus binatus* occurred in winter and early spring.

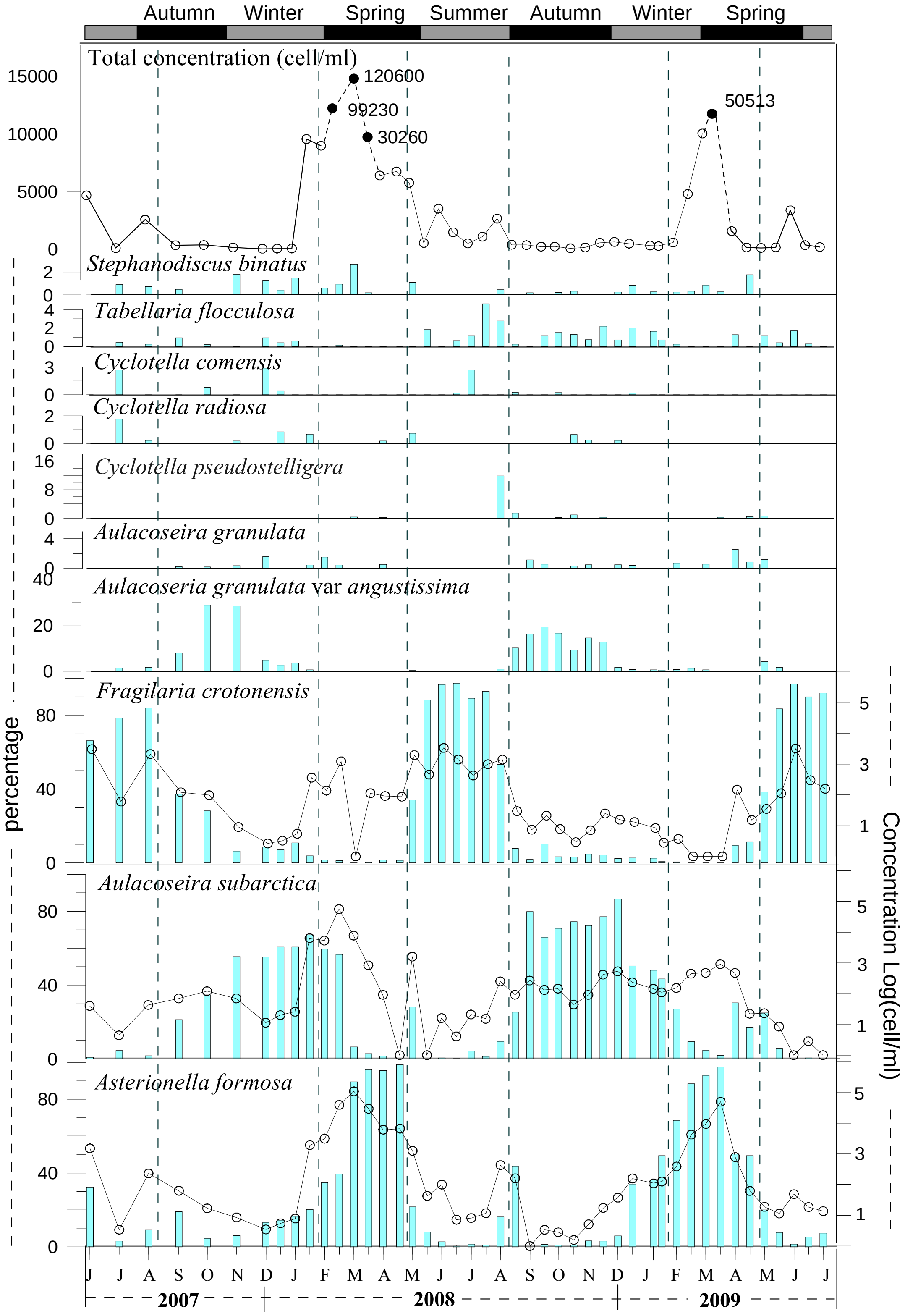


Fig. 2.2 Seasonal changes in the common planktonic diatom species (at least five occurrences over 1%). Filled bars represent percentages and lines with open circles represent diatom concentrations (note the different scales). Numbers in the total concentration graph represent several peak values (labelled with filled circles) that exceed the range of the y-axis shown.

Diatom concentrations exhibited high intra-annual variability. The highest concentration reached 1.21×10^5 cell ml^{-1} on 1st April 2008 and concentrations of >5000 cell ml^{-1} were recorded on numerous occasions in mid-late spring. In other seasons, concentrations were generally less than 4000 cell ml^{-1} (Fig. 2.2).

2.4.3 Diatom-environment relationships

Correlation coefficients between the six most abundant diatom species in the water column and the environmental variables are given in Table 2.2. *A. formosa*, *A. subarctica* and *S. binatus*, which tend to grow at lower temperatures in spring or winter, were negatively related to ST and Stability. In contrast, *F. crotonensis* was positively correlated with temperature, reflecting its tendency to dominant in summer. For *Tabellaria flocculosa*, the only significant correlation was a negative one with NO_3-N. Positive correlations were found between *A. subarctica* and nutrient variables including SRP, SiO_2, and NO_3-N. In contrast, *F. crotonensis* showed a negative response to the above three variables. There was also a weak positive correlation between NO_3-N and the total diatom concentrations. Alkalinity was another important variable being positively correlated with *A. granulata* var *angustissima* and *F. crotonensis*, and negatively with *A. formosa*.

The species-environment correlations are further illustrated in the ordination bi-plot (Fig. 2.3). Manual selection CCA revealed SiO_2, ST, SRP, and alkalinity to be the most important and significant factors controlling diatom community over the two-year monitoring period. CCA constrained to the four significant variables, resulted in eigenvalues of 0.21 and 0.16 for the first two canonical axes respectively, and captured 26.7% of the cumulative variance in the species data. Of these variables, partial CCA revealed that SRP accounted independently for the highest proportion of variance in the species data (8.3%), followed by SiO_2 (6.5%), ST (5.5%) and alkalinity (4.7%) (Fig. 2.3), and all were significant at $p<0.01$ after Bonferroni adjustment. Taxa typically found in summer such as *F. crotonensis* and *C. pseudostelligera* were located in the upper-right of the plot associated with higher temperatures. *A. subarctica* was located in the lower left of the plot associated with high SiO_2 and SRP concentrations.

Table 2.2 Correlation coefficients between the percentages of most abundant species and key environmental variables. Significance levels are marked by bold type ($p<0.05$ and * $p<0.001$)

Diatom species	Stability	ST	Alkalinity	SRP	SiO_2	NO_3-N	WL	N/P	Si:P
Asterionella formosa	**-0.30***	**-0.47***	**-0.59***	-0.09	-0.06	**0.36**	-0.03	**0.43***	-0.01
Aulacoseira subarctica	**-0.58***	**-0.44***	-0.13	**0.69***	**0.81***	**0.33**	**0.56***	**-0.44***	0.05
Aulacoseira granulata var *angustissima*	-0.234	0.03	**0.51***	0.089	**0.39***	-.196	0.23	**-0.31**	0.28
Fragilaria crotonensis	**0.78***	**0.75***	**0.51***	**-0. 50***	**-0.68***	**-0.54***	**-0.52***	0.07	-0.12
Stephanodiscus binatus	**-0.33***	**-0.32**	-0.18	0.10	0.12	**0.41***	0.25	-0.10	-0.07
Tabellaria flocculosa	0.27	0.23	0.18	0.06	0.07	**-0.30**	0.09	-0.26	0.11
Total diatom Concentration	-0.21	-0.24	**-0.34**	-0.12	-0.10	**0.37**	0.11	0.13	-0.04

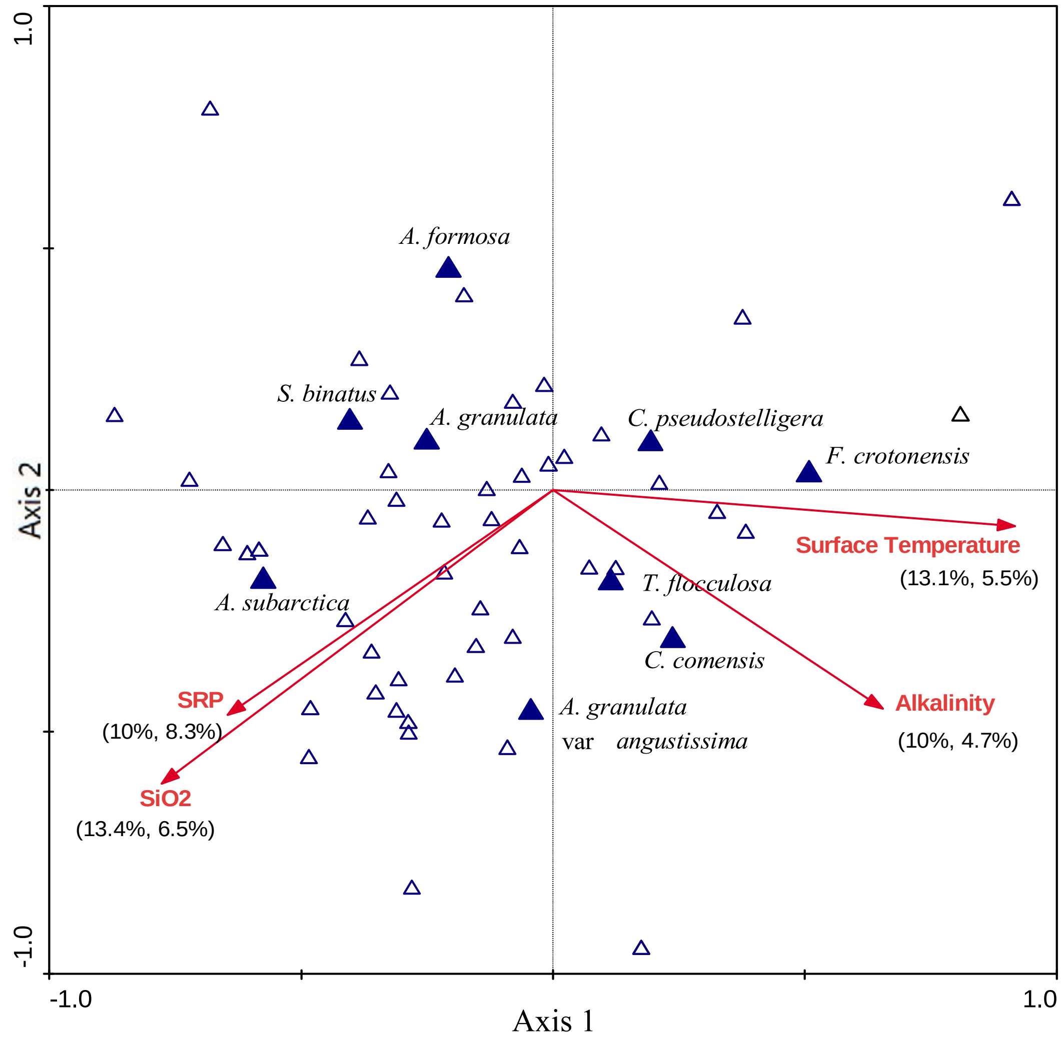


Fig. 2.3 Species-environment bi-plot derived from CCA of fortnightly relative diatom abundance data and key environmental variables. Only dominant species, represented by filled triangles, are labelled with names. The marginal and conditional effects (expressed as the amount of diatom variance explained) are given in parentheses for each environmental variable.

2.5 Discussion

2.5.1 Limnological characteristics

The physico-chemical characteristics of Esthwaite Water exhibit strong seasonal patterns, similar to those observed in other temperate lakes, which are primarily evoked by changes in solar radiation and wind-induced transfers of kinetic energy (Heaney, Smyly & Talling, 1986). For example, the seasonal changes of water temperatures lead to thermal stratification every year. Also, temperature changes impact significantly on the rate of nutrient release and accumulation, which exhibit distinct seasonal cycles and further affect the biological characteristics of the lake (Fig. 2.1).

The climatic variables, temperature and rainfall (reflected by water level data) are closely related to all the measured chemical variables (Table 2.2). Concentrations of SRP, SiO_2, and NO_3-N are negatively correlated with temperature and positively correlated with water level. Increasing temperatures accelerate growth rates of phytoplankton, macrophytes and epiphytes, which consume nutrients. This process is also supported by the significant negative relationship between Chl-a and nutrient variables, which suggests that phytoplankton communities take up a large amount of nutrients during their growth period. Rainfall has been shown to be an important regulator of chemical conditions in relative shallow lakes (e.g. Tucker, 1958; Loaiciga *et al.*, 1996). In Esthwaite Water, high rainfall brings nutrients into the lake via the inflow from surrounding farms and via the drainage channel and thus enhanced nutrient concentrations are often observed following periods of heavy rains (Fig. 2.1).

Alkalinity is closely correlated with all the measured variables and has highest correlation coefficient with NO_3-N (Table 2.1). Changes in alkalinity can be induced by a variety of redox reactions (e.g. photosynthesis, respiration) (Heaney, Smyly & Talling, 1986). In Esthwaite Water, higher alkalinity values are coincident with low nutrient concentrations. This may be due to biological uptake and reduction of nutrients, particularly nitrate, either by plants or the phytoplankton (Brewer & Goldman, 1976).

The nutrients variables SRP, NO_3-N and SiO_2 are strongly correlated with each other (Table 2.1). All nutrient parameters start to increase from autumn, reach maxima in winter and decrease gradually from early spring. This synchronicity suggests that their rise and fall are largely controlled by the same drivers, although there are slight differences in the timing of the changes between the nutrient variables. For example, the length of time to decline from the highest to the lowest value for each nutrient concentration is in the order of NO_3-N > SiO_2 > SRP (Fig. 2.1).

2.5.2 Seasonal patterns of diatom communities

The planktonic diatoms in Esthwaite Water exhibit distinctive seasonal fluctuations in composition and biomass with peaks in the spring, a decrease in early summer, followed by a slight increase in the autumn before decreasing again to a winter minimum. This pattern is typical of temperate lakes (Arhonditsis *et al.*, 2004) and has been observed in many lakes in the English Lake District (Heron, 1961; Reynolds & Irish, 2000). Factors influencing this "seasonal succession" may include temperature, nutrient availability, light intensity, grazing by zooplankton, sinking and viruses (Reynolds, 1980). Here, we focus on the four variables (mainly related to climate and nutrient factors) which were shown to significantly influence the diatom distributions in CCA (SRP, ST, SiO_2 and Alkalinity). There were three notable shifts (labeled as 1, 2, and 3 in Fig. 2.4) in the assemblages during the year.

The first shift was a replacement of *A. formosa* by *F. crotonensis* in late spring (Fig. 2.2, 2.4). In contrast to *A. formosa*, *F. crotonensis* is a thermophilic species (Interlandi, Kilham & Theriot, 1999) and therefore the changes in temperature may be important in driving this species shift. Meanwhile it has also been reported to be a good P-competitor, a fair Si-competitor and a poor N-competitor and thus it tends to reach high abundances when N:P is high (Tilman, 1981; Interlandi & Kilham, 1998; Interlandi, Kilham & Theriot, 1999). The median values of ST increased from 7.4 °C in the spring to 17.0 °C in the summer. In terms of nutrients, SRP, NO_3-N and SiO_2 were at low concentrations in the summer. Conversely alkalinity was higher in the summer than in late-winter/early spring, with median values of 0.39 and 0.46 meq L^{-1}, respectively. The elevated alkalinity values may be a consequence of the consumption of NO_3-N (Brewer & Goldman, 1976) and CO_2 by phytoplankton (Talling, 1976). In

2008 *F. crotonensis* flourished in late June but it appeared somewhat earlier in 2009, reaching 3200 cell ml^{-1} in 26 May 2009. The earlier appearance in 2009 occurred after a relatively smaller bloom of *A. formosa*, compared with that in 2008. The differences between years may therefore reflect the competition for resources between the two species, the smaller *A. formosa* crop in 2008 sparing enough nutrients for the growth of *F. crotonensis*, once suitable temperatures were reached.

The second shift was from *F. crotonensis* to *Aulacoseira* species including *A. subarctica*, *A. granulata* and its subspecies, *A. granulata* var *angustissima,* in early autumn (Fig. 2.2). These three *Aulacoseira* species in Esthwaite Water are commonly found in relatively shallow, alkaline and turbid lakes and have high optima for silica and nitrate (Kilham, Theriot & Fritz, 1996; Interlandi, Kilham & Theriot, 1999). These three *Aulacoseira* species therefore thrived when the temperature decreased and SiO_2 increased dramatically in the water column in the autumn and early winter. This was accompanied by a steady increase in the concentrations of SRP and NO_3-N. However, the three *Aulacoseira* species have different temperature optima. *A. granulata* and its subspecies, *A. granulata* var *angustissima,* are thermophilic species, associated with water temperatures in excess of 15 °C (Stoermer & Ladewski, 1976; Poulickova, 1992). In contrast, *A. subarctica* has an apparent temperature preference near to 4 °C (Stoermer & Ladewski, 1976). Given the relatively low temperature in Esthwaite Water in autumn and winter (with a median value of 5.5 °C), the occurrence of *A. granulata* and its subspecies *A. granulata* var *angustissima* was surprising. This perhaps suggests that the temperature requirement for diatom growth can be altered by other factors, such as plentiful nutrients.

The third shift in the assemblages was from *A. subarctica* to *A. formosa* in late winter. *A. formosa*, although normally considered a meso- or eutrophic taxon, is a high Si:P specialist (Tilman, Kilham & Kilham, 1982), exhibiting low P requirements if N and Si are in moderate supply (Michel *et al.*, 2006). In spring, SiO_2 values were more variable than those in winter. In late winter-early spring, as silica was being consumed by *A. subarctica*, a large decrease in SRP occurred contributing to an increase in the Si:P ratio. Temperature seemed not to be important in facilitating the growth of *A. formosa*, as whilst temperature increased from 6.1 to 17.6 °C in 2008 it remained low at <11 °C in 2009 during its blooms. The maximum concentration of *A. formosa* differed between years with a maximum of 107,800 cell ml^{-1} in 2008, compared to only 49,200 cell ml^{-1} (all other measured concentrations were less than 9323 cell ml^{-1}) in 2009. The substantial *A. formosa* bloom in 2008 resulted in sharp decreases in nutrient concentrations.

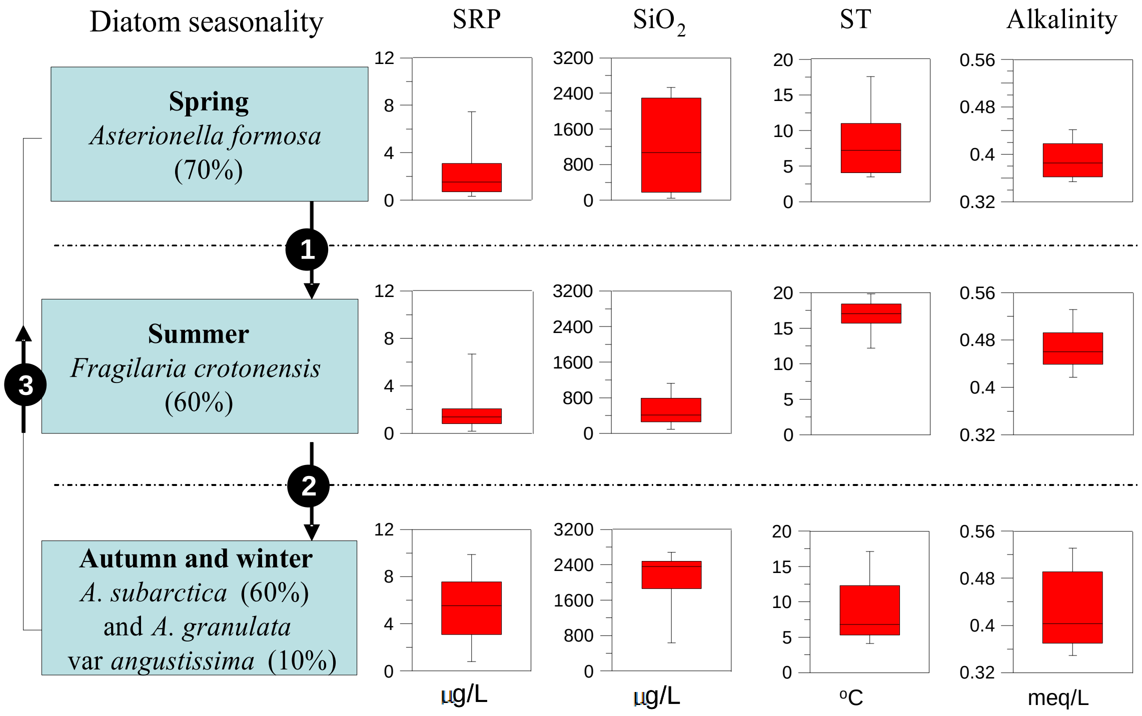


Fig. 2.4 Diatom seasonality and corresponding environmental ranges. In the boxplots, the horizontal lines represent median values, edges of boxes are the 25th percentile surrounding the mean value, and error bars indicate range.

2.5.3 Inter-annual patterns of diatom communities

In general, the diatom communities shift in the same sequence during the two monitoring years, although the timing and abundances differ slightly between years. As mentioned above, the three dominant species *A. subarctica*, *A. formosa* and *F.*

crotonensis all appeared earlier and in relatively lower abundance in the second year. Given the small differences in climatic factors (such as temperature and rainfall) between the two years, the observed inter-annual variations in the diatom populations is more likely to be due to differential nutrient availability between years, although nutrient availability is largely dependent on climatic factors such as ice cover duration and circulation of the water column (Bailey-Watts *et al.*, 1990; Battarbee, 2000; Korhola *et al.*, 2002; George, Maberly & Hewitt, 2004). Anderson (2000) suggested that the seasonal succession of diatoms might be driven directly by nutrient availability and only indirectly by temperature changes. Long-term monitoring records of Esthwaite Water show that the timing of the spring bloom of *A. formosa* has varied from week 7 to week 22 (from late February to early May) and it has appeared progressively earlier over the period 1945-2005 (Patrick *et al.*, 2004; Thackeray, Jones & Maberly, 2008). The drivers of the earlier bloom potentially include climate and nutrients as both have changed significantly over the monitoring period.

Esthwaite Water has experienced significant enrichment since 1970 (Bennion, Monteith & Appleby, 2000), hence existing diatom records from 1958-1959 provide an opportunity to compare directly with the 2007-2009 data to explore the annual patterns under different nutrient regimes. A comparison of monitoring records from January 1958 to December 1959 with those in this study shows similar seasonal patterns in the physico-chemical parameters and planktonic diatom communities (Fig. 2.5). However, diatom data from the two monitoring periods vary in composition and concentrations. Firstly, a higher percentage of *F. crotonensis* was observed in the current study compared to the 1950s with values of 37% and 4%, respectively. There was also a higher species evenness in the recent samples. In the 1950s, the diatom assemblage was co-dominated by *A. formosa* and *A. subarctica*, whose total combined percentage reached 92%. Secondly, much higher diatom concentrations were measured in 2007-2009, with monthly average concentrations >141.9 cell ml^{-1} for all months and a peak value of 96,776 cell ml^{-1}. In 1958-1959, all average monthly concentrations were lower than 10,000 cell ml^{-1}. The higher percentage of *F. crotonensis* and total diatom productivity in the recent dataset is most likely due to nutrient enrichment over the last 50 years. For example, the average winter SRP and SiO_2 increased from 2 and 690 µg L^{-1} during 1958-1959 to 6 and 2348 µg L^{-1} over 2007-2009, respectively (Heron, 1961). Additionally, changes in summer climatic conditions, as the most direct factors affecting the growth of this species, have been relatively small over this time period (e.g. average summer temperatures are ~17.4 °C for both).

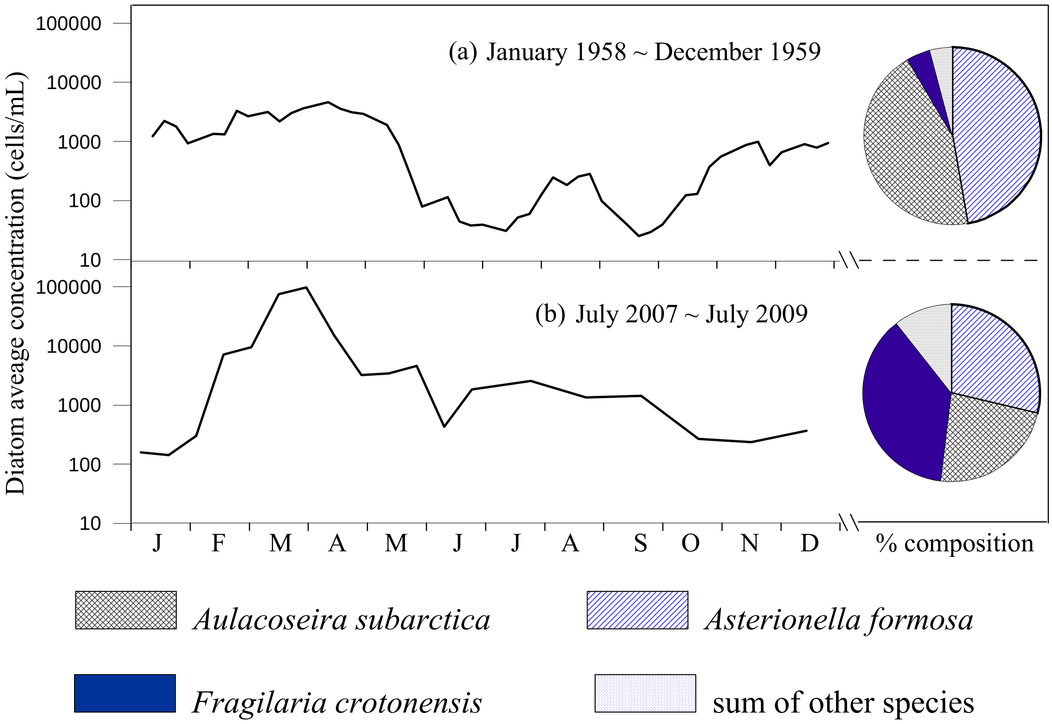


Fig. 2.5 Diatom concentrations (monthly average) and composition in two monitoring periods. (a) January 1958 to December 1959, diatom data from (Heron, 1961); (b) July 2007 to July 2009 (this study).

2.5.4 Overview of controlling factors

Partial CCAs revealed that SRP and SiO_2 were the most important factors in controlling diatom dynamics in the two year dataset. Phosphorus is cited as the dominant limiting nutrient in temperate fresh waters (Wetzel, 2001; Lewis Jr & Wurtsbaugh, 2008), although nitrogen has frequently been reported as a limiting element in recent years (Elser *et al.*, 2009a; Elser *et al.*, 2009b). Esthwaite Water has been nutrient-rich for several decades, having received sewage effluent since early 1970s, and consequently SRP concentrations are high (Talling & Heaney, 1988). However, seasonal P depletion still occurs in late-spring and summer and triggers a shift to diatom species that compete well in low P water such as *A. formosa* and *F. crotonensis*. Sediment records show that the annual diatom standing crop (measured as sedimentary diatom flux) increased from 1.6x10^8 cells cm^{-2} $year^{-1}$ in 1950 to 5.3x10^8 cells cm^{-2} $year^{-1}$ in 2000 (see chapter 6 for more details on diatom concentration). This suggests that whilst productive lakes may have high annual nutrient concentrations, on a seasonal basis they still experience nutrient depletion because of the large algal crops that are sometimes produced. SiO_2 concentrations are obviously important for diatom growth, and exhibit a similar seasonal pattern to SRP. Nitrogen appears to have less influence on diatom communities of Esthwaite Water, since our results showed that NO_3-N concentrations were relatively high and decrease more gently than SRP and SiO_2 during the diatom growing seasons (Fig. 2.1).

Climate has a profound effect on diatom dynamics through hydrology, light availability, wind, stratification, and other processes (Reynolds, 1984). More importantly, climate may affect diatom communities via its links with nutrient availability (Kilham, Theriot & Fritz, 1996). In Esthwaite Water, high precipitation may accelerate nutrient cycling due to its relatively short retention time. Partial CCA revealed that surface temperature is an important factor affecting diatom dynamics, explaining a relatively large amount of diatom variance (13.1%). However, half of that variance (5.6%) is explained by the interaction of temperature and other variables, such as SRP and SiO_2 (see Table 2.2). The “pure effect” of temperature on diatoms in the two year dataset explained only 5.5% of the diatom variance (i.e. when other variables were set as covariables to remove the collinear effect). This indicates that some of the temperature effect on the diatom communities was contributed by SRP and SiO_2. This also explains the observation that the growth of *F. crotonensis* in the summer of the two years varies under different nutrient concentrations as long as the temperature requirements are met.

Alkalinity was another important controlling factor revealed by partial CCAs (Fig. 2.3). Alkalinity reflects carbonate, bicarbonate and hydroxide ions in the water column. In a survey of Esthwaite Water in 1971 and 1972, Talling (1976) observed high alkalinity and nitrogen minimum during summer stratification and attributed this to higher densities of phytoplankton at that time. In Esthwaite Water, the summer phytoplankton maxima is often dominated by cyanobacteria (Lund, 1972; George *et al.*, 1990), which consume a large amount of nitrogen and CO_2 thus inducing a pH and alkalinity increase. Indeed, this process would explain the significant negative relationship observed between alkalinity, NO_3-N and SD (Table 2.2). Alkalinity is also negatively correlated to the total diatom concentration (r=-0.34, p<0.05), suggesting that other algae override diatoms in abundance and consume nitrogen, leading to high values of alkalinity. Hence, fluctuations in alkalinity are more likely a consequence of phytoplankton dynamics (including diatoms) rather than a cause. However, it has been shown that an increase in epilimnetic pH can independently favor P release from lake sediments (Heaney, Smyly & Talling, 1986; Drake & Heaney, 1987), resulting in enhanced P concentrations in the water column. This in turn would influence diatom growth.

Many other factors, such as stratification (Reynolds, 1980), light and grazing, may affect seasonal diatom dynamics in lakes such as Esthwaite Water. Several climatic variables are excluded in this analysis such as stratification, light, and wind strength, although they may be partially reflected by variables such as temperature, precipitation or SD (Heaney, Smyly & Talling, 1986). Consequently, our results can provide only limited information on the climate effects on diatom communities. Clearly more variables would need to be measured to explain climate effects on the diatom communities on a seasonal timescale more fully. Furthermore, given that the analyses (correlation analysis, ordination) were based on only a two-year dataset (a short time-scale to discern causes and consequences), care is needed to take the next step to causation. However, based on the two year monitoring dataset from Esthwaite Water, we can conclude that nutrient factors play a more important role than climate factors in explaining the diatom periodicity, although climate may be the ultimate driver of many of these changes on a seasonal timescale.

2.5.5 Implications for palaeolimnological interpretation

This study provides detailed information on the seasonal and inter-annual succession of planktonic diatoms and on the effects of nutrients and temperature on diatom assemblages in Esthwaite Water. Importantly, these observations can aid the qualitative and quantitative interpretation of the fossil diatom assemblages in the lake sediments. Our study has demonstrated that nutrients, such as SRP and SiO_2, play crucial roles in regulating not only diatom composition but also whole diatom productivity at seasonal and inter-annual scales. This suggests that changes in diatom communities can reflect well the seasonal nutrient changes in the lake, and hence diatom-based nutrient reconstructions should provide a means of describing the historical nutrient evolution of the lake.

The monitoring results show that the inter-annual diatom composition and particularly individual species concentrations exhibit high variability. The average daily crops also vary considerably, for example, *A. formosa* was present at values of 32,010 and 9,128 cell ml^{-1} day^{-1} in the spring of 2008 and 2009, respectively. This variability is smoothed in the lake sediment record due to sediment resuspension effects, bioturbation, and resolution of the samples. Consequently, information on seasonal and annual variability gained from monitoring data is a good complement to palaeolimnological records in understanding how aquatic ecosystems respond to environmental changes.

2.6 Conclusions

The physcio-chemical variables and diatom communities in Esthwaite Water exhibited distinct seasonal variability over the two-year monitoring period. There were three principle shifts in the diatom assemblages each year, from dominance of i) *A. formosa* in spring to *F. crotonensis* in summer; ii) *F. crotonensis* to *Aulacoseira* species in autumn and winter; iii) *Aulacoseira* species to *A. formosa* in the spring. The exact timing and abundance of the crop varied between the two years and the environmental parameters differed accordingly.

Close correlations were found among physico-chemical parameters, as well as between environmental variables and the growth of individual diatom species. Each diatom taxon responded to climate variables (temperature) and nutrient variables (SRP, SiO_2 and NO_3-N) at different significance levels. Nutrient variables SRP, NO_3-N and SiO_2, which negatively responded to changes in surface temperatures, imposed significant impacts on the growth of all species.

Multivariate statistical analysis revealed that SRP was the most important factor in explaining the diatom data, accounting independently for 8.3% of variance in the species data, followed by SiO_2 (6.5%), ST (5.5%), and alkalinity (4.7%) on a monthly timescale. This indicates that nutrients play a more important role in regulating diatom growth than climatic factors in this dataset. This was also suggested by the comparison of our data with those from January 1958 to December 1959, which showed that diatom composition and concentrations had changed substantially as a result of eutrophication. Nutrient enrichment had occurred over the past 50 years but there had been only relatively small changes in climate.

In terms of palaeolimnology, the study suggests that diatoms can be used as a reliable indicator of past nutrient status in Esthwaite Water since the communities are mainly controlled by nutrients. However, sediment resuspension effects and sample resolution may disguise the detailed seasonal variability of diatom communities and, therefore, palaeo-reconstructions may provide only a coarse resolution compared to that achieved by contemporary monitoring studies. Monitoring records can thus complement palaeo-records in understanding environmental change in aquatic systems.

Chapter 3 Diatom representativity: comparison of phytoplankton, sediment trap and sediment core data

3.1 Introduction

A major goal of palaeolimnological studies is to reconstruct past environmental conditions. Typically, subfossil assemblages of selected organisms are used to derive environmental reconstructions either qualitatively based on species shifts or quantitatively via transfer functions. These reconstructions are based on two important assumptions: i) that the fossil organisms have the same ecological preferences as those of the present-day organisms (Birks *et al.*, 1990), and ii) that fossil assemblages accurately reflect living communities of the organism in question. The latter assumption, often termed "sediment representativity", has been examined by comparisons of old algal records with stratigraphic records (e.g. Haworth, 1980), by comparison between standing crops and surface sediment (see Cameron, 1995), and by evaluating the influence of within-lake variability on different organisms, such as pollen, diatoms, chironomids, macrofossils, and cladocerans (e.g. Anderson, 1990; Heiri, 2004; Zhao *et al.*, 2006; Kattel *et al.*, 2007; Nykänen *et al.*, 2009).

Sediment deposition processes depend on climatic conditions, morphometric characteristics, food-web structure and trophic status of the lake (Ryves *et al.*, 2003; Ryves *et al.*, 2006). For diatom applications in palaeolimnology, an important issue that has to be considered is the representativity of individual diatom species and the means by which they deposit into the sediment (Ryves, Battarbee & Fritz, 2009). Specific lake conditions can result in large differences in diatom accumulation and loss rates, and may result in within-lake variation (Anderson, 1990). Additionally, the different habitats occupied by diatoms (e.g. benthic, epiphyton and epilithon) add complexity to the diatom representation issue. One approach to achieving a fuller understanding of diatom representativity in the sediment record is to compare the diatom assemblages found in surface sediments, the water column, and sediment traps. For example, Ryves *et al.* (2003) utilized such an approach to quantitatively define the relationships between planktonic diatom communities in Lake Baikal, Siberia. On the basis of this study, Battarbee *et al.* (2005b) further investigated the differential dissolution of diatoms in Lake Baikal and developed a series of species-specific correction factors that allow more reliable palaeo-environmental reconstructions.

Esthwaite Water is a productive lake located in the English Lake District. It covers an area of *c.a.* 1 km^2 and has a mean depth of 6.4 m and a maximum depth of 15.5 m. Further details can be found in Heaney, Smyly & Talling (1986). It is a small lake with an uneven surface on the lake bottom, which may add complexity to the sedimentation process. It has one major outlet and five inflow streams, which results in a short retention time of *c.a.* 90 days. Such a short water renewal period may result in significant losses of phytoplankton biomass and may have implications for the sedimentary representation of diatom communities (Maberly *et al.*, 1994a). Additionally, chapter 4 of this thesis demonstrated high spatio-temporal variability of diatom assemblages in the lake (see chapter 4). Consequently, it is vital to assess the representativity of sedimentary diatoms for further palaeolimnological interpretation. Esthwaite Water is an ideal site for examining sedimentary diatom representativity because of the relatively high resolution of the sediment record (Bennion, Monteith & Appleby, 2000 and chapter 4) as well as the availability of long time series on planktonic diatom data (Maberly *et al.*, 1994a). A comparison of the diatom composition from phytoplankton, sediment traps and sediment cores is used here to answer three questions: (a) How faithfully do the fossil diatoms in the lake sediment (traps) reflect standing crops in the water column? (b) Are there any differences in the sedimentation for each individual species in Esthwaite Water? (c) Do the findings have any implications for diatom-based palaeolimnological reconstructions?

3.2 Methods

3.2.1 Planktonic diatom sampling

Two planktonic diatom datasets were utilized in this study: (a) a two-year planktonic diatom dataset derived from fortnightly monitoring from July 2007 to June 2009 (except for the period from July 2007 to Jan 2008 where only monthly data are available); (b) an annual average planktonic diatom dataset from the 59-year monitoring scheme (1945 to 2003) conducted by the Freshwater Biological Association and Centre for Ecology and Hydrology. These data are based on a two-litre water sample taken from the integrated water column (0-7 m) on each occasion, preserved with Lugol's iodine and kept in the dark at 4 °C until they were counted using an inverted microscope (Lund, Kipling & Cren, 1958).

3.2.2 Sediment trap installation and retrieval

A sediment trap with three separate black plastic tubes was installed above the lake bottom in the deepest part of Esthwaite Water on July 1st 2007. Collecting cylinders were constructed from PVC tubing with an aspect ratio of 5:1 in order to avoid loss of collected sediment. An anchor weight was placed on the lake bottom via a rope which in turn was tied to a subsurface buoy, and marked by another buoy tied to a second rope (modified from the method of Horn & Horn, 1990). The trap was retrieved approximately every 3 months (except for one sample which was after 6 months during September 2008 to March 2009) until 23 June 2009, according to the diatom growing seasons as defined by the average cell concentrations calculated from the 59-year long-term record (see Fig. 6.5 in chapter 6).

3.2.3 Diatom assemblages from surface sediments and sediment cores

Surface sediment samples were collected near to the sediment trap using a mini-Mackereth piston corer (Mackereth, 1969) on 27th June 2009, at the end of the two-year planktonic diatom collection period. Assuming that sediment accumulation rates (SAR) were similar to those of a former core ESTH7, which was taken in 2006 with an average SAR of 0.8 cm year^{-1} for the uppermost 2 cm, the top 2.5 cm of the new core was expected to represent approximately the sedimentation in the last two or three years. The new core was sliced at an interval of 0.25 cm for further diatom analysis. Five samples (0.25, 0.75, 1.25, 1.75, 2.25 cm) were subsequently analysed.

For data comparison over a longer timescale (59 years), cores ESTH1 and ESTH7 were used. Both cores were dated using ^{210}Pb and ^{137}Cs analysis (see chapter 4 for further details on core chronology). Based on higher sediment accumulation rates in the upper part of the core ESTH1 and following the calibration of overlapping sections representing the same time periods in both cores, the upper 17 cm of ESTH1 was used to represent the diatoms deposited in the period 1945-1993 and the upper 8.5 cm of ESTH7 was used to represent the diatoms deposited during 1993-2006.

3.2.4 Diatom slide preparation and counting

Each two-litre water sample collected during the two-year monitoring period was concentrated to 5 ml. Subsequently 1 ml of concentrate and *c.a.* 0.1 g wet mud from each trap and sediment sample were prepared using standard methods (Battarbee *et al.*, 2001). A known amount of microspheres was added to the samples to allow calculation of diatom concentrations (Battarbee & Kneen, 1982), and microscope slides were prepared using Naphrax. A minimum of 300 valves were counted under oil immersion using a Leica microscope (×1000). As for the 59 year plankton records, diatoms were counted under an inverted microscope using the method proposed by Lund, Kipling & Cren (1958). The data were expressed in percentages and the annual average for each species was calculated. To calculate the daily diatom flux in the seasonal traps, the total number of diatoms in the traps was divided by the aerial area of the trap and the number of days in the trapping period. Given the occurrence of non-planktonic species in sediment traps and lake sediments, diatom data were calculated as percentages of all planktonic species.

3.2.5 Data analysis

A threefold comparison of diatom composition was conducted. Firstly, diatom assemblages in the water column sampled between July 2007 and June 2009 were compared with those in the seasonal sediment traps collected over the same time period. Secondly, the recent (the past 1-2 year) sedimentary diatoms from the short sediment core were compared with those from the water column and the sediment traps. To reveal their similarity, a detrended correspondence analysis (DCA) of planktonic diatom data from the two year monitoring record was implemented, with samples from the sediment traps and surface sediments included as passive samples. DCA was implemented using the computer program CANOCO 4.5 (ter Braak & Smilauer, 2002). Meanwhile, the "expected" percentages of dominant species (*Asterionella formosa*, *Aulacoseira subarctica, Aulacoseira granulata* var *angustissima* and *Fragilaria crotonensis*), calculated using annual maximum cell counts for each taxa in the water column, were compared directly with those in the surface samples (Battarbee *et al.* 2005). Thirdly, the fossil diatom assemblages (denoted as FD) in the upper section of the sediment cores, representing the diatom crops from 1945 to 2003, were compared with the planktonic diatom records from the same time period (denoted as PD). Given the considerable abundance of non-planktonic species in the FD, relative abundances were recalculated based on planktonic species for comparison with the plankton records. Compositional differences between FD and PD were measured using a squared chord distance (SCD) measure (Overpeck, Webb & Prentice, 1985):

$$d_{jk}^2 = \sum_{i=1}^{m} \left(x_{ij}^{0.5} - x_{ik}^{0.5} \right)^2 ,$$

where x_{ij} and x_{ik} is the proportion of diatom taxon i in sample j (from FD) and k (from PD) representing the same year, respectively. Unlike x_{ij}, x_{ik} is the 3-point running average smoothed value from the original PD record, since the FD record generally experiences a mixing process after its sedimentation. d_{jk}^2 is the SCD between samples j and k. The values of SCD can vary between 0 and 2, with lower values indicating more similar assemblages. Critical values of SCD were defined by taking the 5th and 10th percentile of the matrix of squared chord distances among all PD samples (*cf.* Birks *et al.* 1990; Laird, Fritz & Cumming 1998), indicating good and moderate similarity, respectively.

Given the sensitivity of the diatom community to water quality change, sedimentary diatoms can potentially record changes in the epilimnetic environment as long as the fossil diatoms provide a faithful representation of the diatoms in the water column. Hence, historical epilimnetic phosphorus concentrations, reconstructed from FD using a diatom total phosphorus (TP) transfer function, were compared with measured soluble reactive phosphorus (SRP) concentrations to validate the diatom representativity. January SRP is used for comparison with DI-TP because it is widely regarded as a good descriptor of lake nutrient status, given the high seasonal variability of nutrient concentrations in the water column (Sutcliffe *et al.*, 1982; Bennion & Smith, 2000). The DI-TP transfer function was based on a Northwest European calibration set of 152 lakes and has been shown to have high predictive ability (Bennion, Juggins & Anderson, 1996; Bennion *et al.*, 2005). The quantitative reconstruction of TP was performed online using the European Diatom Database (EDDI, http://craticula.ncl.ac.uk/Eddi/jsp/index.jsp).

3.3 Results and discussion

3.3.1 Diatom composition in the two-year monitoring dataset and seasonal trap samples

The percentages and concentrations of the dominant planktonic diatoms in the two year monitoring series were described in detail in chapter 2. The composition of planktonic diatoms showed a strong seasonal pattern with *A. formosa*, *A. subarctica* and *F. crotonensis* being the dominant species (Fig. 3.1). The concentration of each diatom species exhibited high intra-annual and inter-species variability. *A. formosa* and *A. subarctica* were the two most abundant species, reaching maxima of 107,800 and 56,300 cell ml^{-1} in spring 2008, respectively. In contrast, concentrations of other species were lower than 5,000 cell ml^{-1} over the monitoring period (Fig. 3.1).

The diatom composition in the sediment traps exhibited similar seasonality to that of the plankton samples (Fig. 3.1). *F. crotonensis* dominated in the summer (mostly >70%) and *A. formosa* and *A. subarctica* dominated in the winter and spring, respectively. Periphytic species (e.g. *Achnanthidium minutissimum, Fragilaria construens* var *venter* and *Cymbella* spp) were consistently present with their total percentage ranging from 8.3% to 19.6%. Most planktonic diatom taxa were represented in similar percentages in the sediment traps to those in the phytoplankton samples, except for *A. granulata* var *angustissima* which was over-represented in the sediment traps in spring (Fig. 3.1).

In the comparison of diatom composition in the plankton and sediment traps, the seasonal traps incorporated well the major components of the diatom standing crop in the water column in each individual season (Fig. 3.1). Maximum daily diatom flux at 8.62×10^6 and 5.56×10^6 cells cm^{-2} day^{-1} in 2008 and 2009 respectively, occurred in the spring of each year in the sediment traps. Correspondingly, the highest average diatom concentrations were observed over the same periods in the water column (Fig. 3.1). The percentages of the major diatoms in the sediment traps were also comparable to those in the water column in most trapping periods. For example, *A. subarctica* dominated in the water column in winter, thus its percentage was much higher than any other species in the sediment traps at this time. However, relative diatom composition in the sediment traps was significantly affected by the abundance of the individual species, especially for those periods when two or more dominant species coexisted. For instance, in the spring of 2009, *A. formosa* occurred at relatively lower average percentages than *F. crotonensis* in the water column, but comprised ~74% of the total assemblage, compared to just 9% of *F. crotonensis* in the sediment trap. This is most likely because diatom concentrations were much higher during the period when *A. formosa* was dominant (average concentration of 17,396 cell ml^{-1}) than when *F. crotonensis* was at a peak (820 cell ml^{-1}).

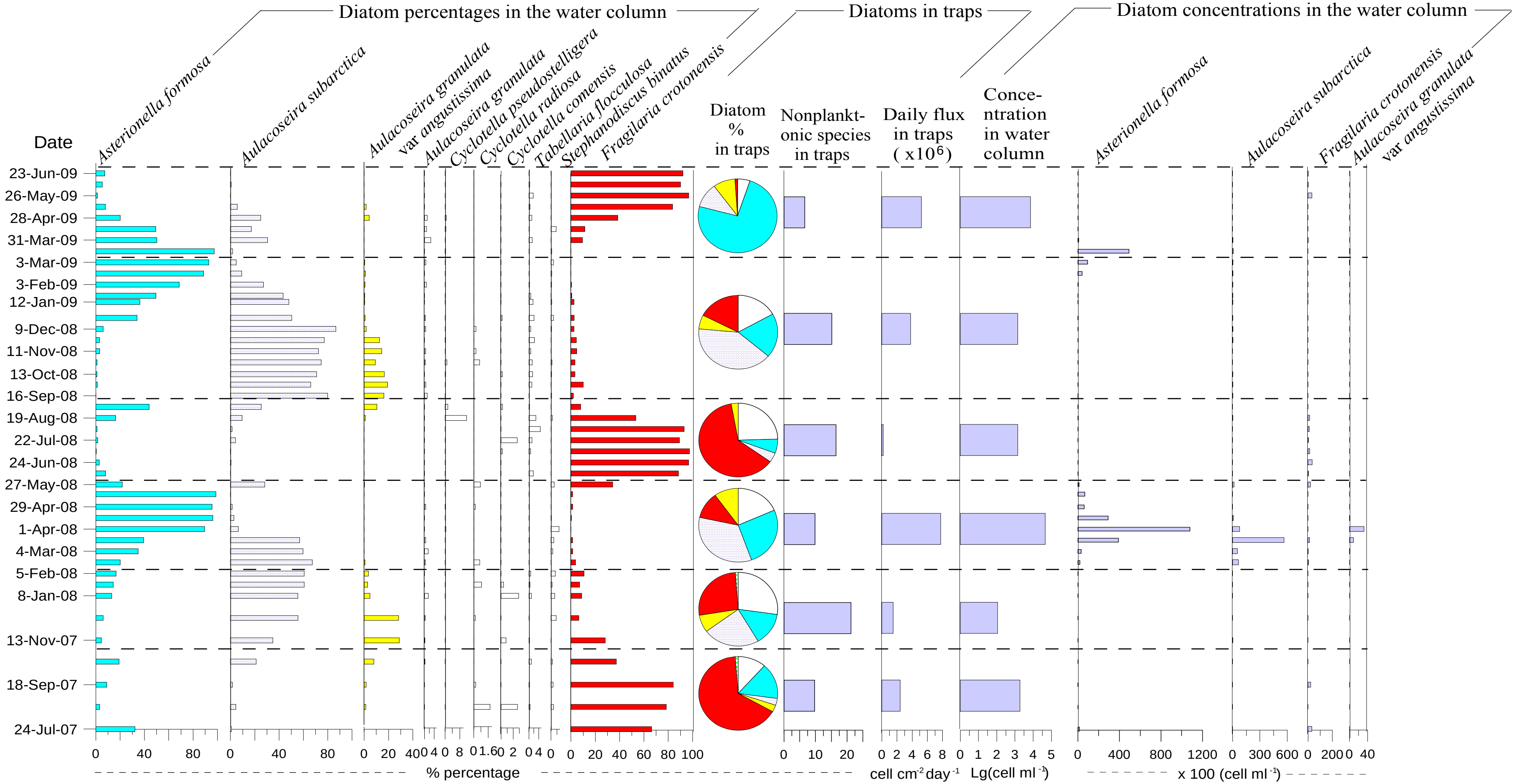


Fig. 3.1 Two-year monitoring diatom records in the water column and sediment traps in Esthwaite Water. Samples were zoned according to the trap collecting periods. Major species in the phytoplankton and traps were labelled correspondingly in same patterns, while all other species were labelled as blank.

3.3.2 Comparison of the diatoms in the surface sediments, plankton and trap samples

Diatom communities from the short sediment core exhibited similar composition in all five samples (0-2.5 cm) but high variability in the concentrations (Fig. 3.2). In all samples, the three planktonic species *A. formosa*, *A. subarctica* and *F. crotonensis* dominated (74-90% of the assemblage), with small proportions of non-planktonic species such as *A. minutissimum, Cymbella* spp and *Gomphonema* spp (9-18%). These were also the most frequent species in the plankton samples, indicating that the surface sediments faithfully record the phytoplankton crops in the water column. The maximum diatom concentration occurred in the surface sample (0.25 cm) reaching $3.60\text{x}10^9$ cells gdm^{-1}, compared to $1.34\text{-}2.03\text{x}10^9$ cells gdm^{-1} in the lower three samples.

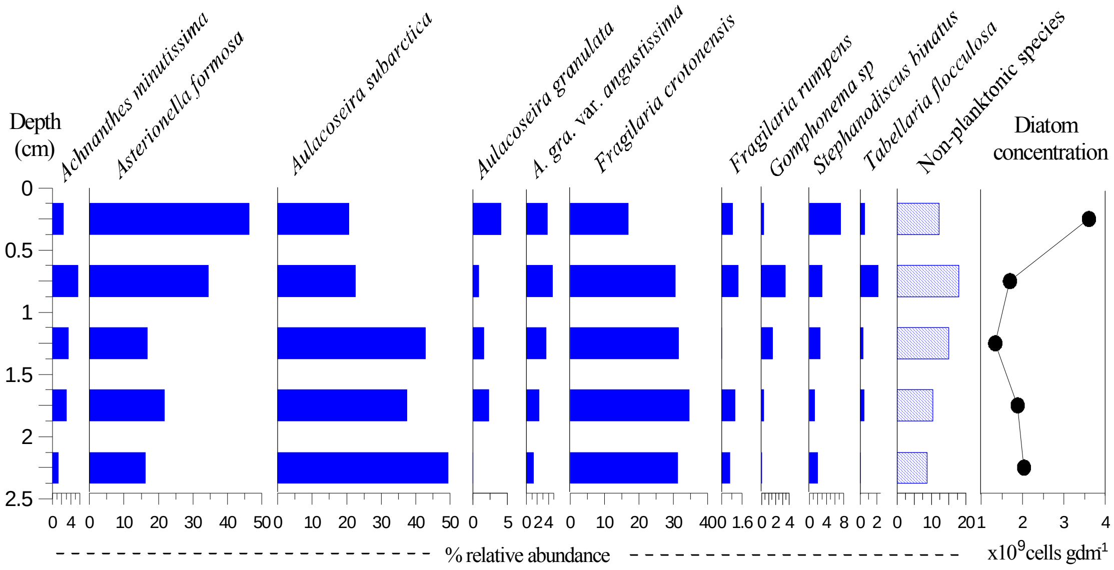


Fig. 3.2 Percentage abundances of the major taxa and the total diatom concentrations in the short sediment core taken on 23 June 2009

Differences between the "expected" (see methods) and observed percentage values in the surface sediment for major species is given in Table 3.1. The same rank order of species abundances occurred in both the water column and surface sediment samples: *A. formosa* > *A. subarctica* > *F. crotonensis* > *A. granulata* var *angustissima*, suggesting that diatom crops remained same structure when they were transferred to the lake sediment. However, *A. formosa* and *A. subarctica* were significantly underrepresented with *A. granulata* var *angustissima* and *F. crotonensis* being overrepresented in the sediment, suggesting partial losses of cells from the former species (see below). The final composition in the surface sediment will not only be greatly affected by the high variability of diatom deposition but also by the growing seasons. Sayer (2001) illustrated that diatom communities were best represented by the recently sedimented species if sampling at different seasons. Consequently, it was not possible to directly compare the plankton and core samples on an annual basis owing to uncertainties regarding the time period covered by each 0.25 cm core slice, given the high variability of sediment accumulation rates in the lake (see chapter 4).

Table 3.1 Comparison of the percentage composition of the main planktonic diatom taxa in the water column and in the surface sediment (with average percentages for all the five samples in parenthesis)

	A. formosa	*A. subarctica*	*F. crotonensis*	*A. granulata* var *angustissima*
annual average %	64.3	33.6	2.0	0.06
% in surface sediment	46.2 (27.1)	20.6 (34.5)	16.9 (28.9)	3.7 (3.1)

Ordination analysis based on the diatom percentage data from the plankton, sediment traps and surface sediments demonstrated two distinct features in terms of similarity between diatom communities (Fig. 3.3). Firstly, seasonal traps faithfully recorded the seasonal changes seen in the diatom communities in the water column, as trap samples were located close to the plankton samples collected in corresponding seasons in the ordination plot. For example, trap sample 49, representing the accumulation from 27 May 2008 to 2 September 2008, lies close to the plankton samples collected during that summer period. Secondly, the diatom communities in the surface sediments were most similar to the winter and spring trap samples collected during 13 November 2007-27 May 2008 (sample 47 and 48) and 16 September 2008-3 March 2009 (sample

50). The diatom composition in the other three trap samples exhibited greater variability when expressed as percentages due to the bloom of one dominant species, i.e. *F. crotonensis*. However, its concentration in the water column was relatively low which may result in them appearing in lower percentage abundances in the surface sediments. Overall the data indicate that the surface sediments provide a good record of the diatom communities of the lake.

3.3.3 Comparison of the 59-year planktonic diatom record and fossil diatom assemblages in the sediment core

The most abundant species in the planktonic diatom records during the period 1945-2003 were *A. formosa*, *A. subarctica* and *F. crotonensis* (Fig. 3.4). Small centric species, such as *Stephanodiscus* and *Cyclotella,* started to increase after 1976 AD. In contrast, *Tabellaria flocculosa* was present at around an average of 12% prior to 1976, but decreased to below 3% after 1976. From 1998, a new species *A. granulata* var *angustissima* appeared and has persisted at relatively high abundance over 10%.

Diatom communities in the sediment samples exhibited comparable shifts to those in the water column over the past 59 years (Fig. 3.4) and again *A. formosa*, *A. subarctica* and *F. crotonensis* were dominant (comprising over 70% of the in total assemblage). Benthic and epiphytic species contributed *c.a.* 20% to the total sedimentary assemblages prior to 1970s and *c.a.* 10% afterwards. More importantly, the sediment faithfully recorded the first appearance of *A. granulata* var *angustissima* in the late 1990s and small centric species *Stephanodiscus*/*Cyclotella* in the mid 1970s. Given the possible dating error, the sediments provide a remarkably accurate reflection of decadal-scale dynamics in diatom plankton communities. However, there was some underestimation of percentages of *A. formosa* and slight overestimation of *A. subarctica* in the sediment record.

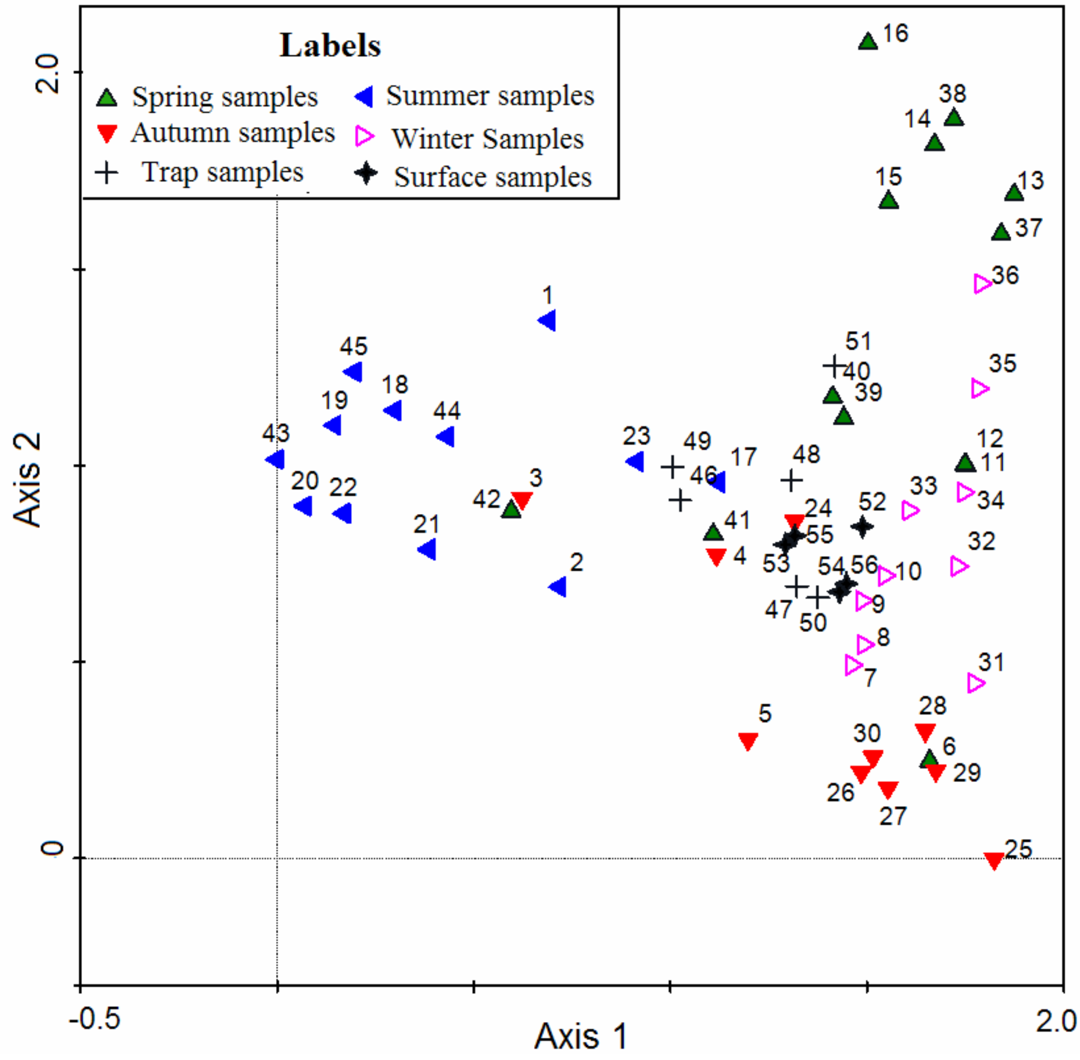


Fig. 3.3 Environment-sample bi-plot derived from DCA of relative diatom abundances, with trap diatom samples and surface sediment samples set as passive samples. Sample numbers 1-45 represent the plankton samples in chronological order, i.e. 1 to 45 denote the samples collected between 24 July 2007 and 23 June 2009. Sample numbers 46-51 represent the trap samples collected between 24 July 2007 and 23 June 2009. Sample number 52-56 represent the five sediment samples from the short sediment core.

Diatom composition dissimilarities between the planktonic and sediment records indicated that the two records matched well (Fig. 3.4). Over 70% of the fossil samples (26 out of 36 samples) exhibited good similarity (SCDs<0.081) to those in the plankton samples in corresponding years. In contrast, only 11% of the fossil samples (4 of 36 samples) had poor agreement (SCDs>0.137). These occurred between

1977-1980 and coincided with the first appearance of small eutrophic *Stephanodiscus* species and small *Cyclotella* spp in the plankton. Higher percentages of these centric species were recorded in the phytoplankton than in the fossil data indicating an underestimation in the sediment, possibly due to mixing with old sediments.

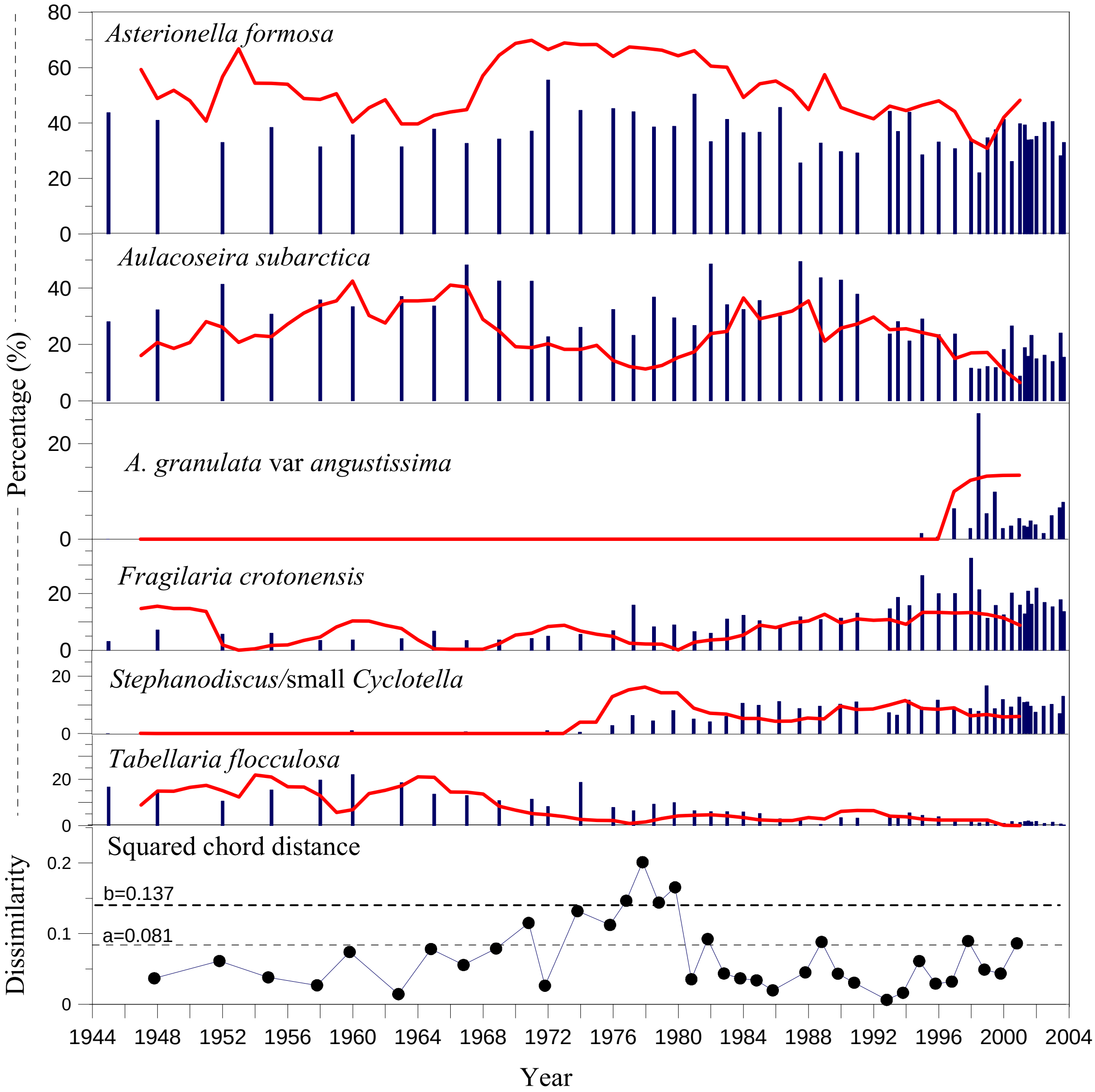


Fig. 3.4 Comparison between PD and FD for the period 1945-2003. The solid blue bars represent FD (the percentages were recalculated based on the sum of planktonic species only for each sample), while the lines represent the five-point smoothed PD. The bottom panel illustrates the diatom composition dissimilarity (expressed as squared chord distance) between the two records. Line a and b represent the critical values for good and moderate similarity, respectively.

3.3.4 Sedimentation of individual diatom species

Individual diatom taxa exhibited specific deposition characteristics, although comparisons among the three diatom records revealed good agreement at the community level. The comparison of relative abundances for the main diatom species (at least two occurrences >20%) from the water column and sediment samples (from the core and traps) is shown in Fig. 3.5. The 1:1 line is shown to allow assessment of the goodness of fit between the records. When compared with the 59-year phytoplankton record, *A. formosa* appeared to be underestimated in the sediment record; while *A. subarctica, F. crotonensis* and *T. flocculosa* were all overestimated in the sediment (circles in Fig. 3.5). The comparison between the "expected" and observed percentages (Table 3.1) also revealed that *A. formosa* was underestimated and other species such as *F. crotonensis* overestimation in the sediment record, although *A. subarctica* was underrepresented (probably this observation is the case when *A. subarctica* was underrepresented in Fig. 3.5). In the comparison between the diatom percentages in the water column and sediment traps (triangles in Fig. 3.5) for the period 2007-2009, most species exhibited a reasonable match with only one or two samples deviating from the 1:1 line (Fig. 3.5). Given the large difference among the concentrations of individual species in the water column (see Fig. 3.1 and chapter 2), for example, *A. formosa* occurs in much greater concentrations than *F. crotonensis* (Fig. 3.6), percentages of the latter species in the sediment can easily be affected by the dominant species. Hence in the following discussion on diatom representativity, we will focus on the first two dominant species *A. formosa* and *A. subarctica.*

Our study shows underestimation of *A. formosa* in sediment, suggesting losses from some component of the system during diatom growth and sedimentation. Generally, diatoms in the water column suffer processes of loss including grazing by zooplankton, death and dissolution before they are incorporated into the sediments (Cameron, 1995). Diatom dissolution is one major factor influencing diatom losses (e.g. Kato *et al.*, 2003;

Ryves *et al*., 2003; Battarbee *et al.* 2005) but it seems not to be a problem in Esthwaite Water, given the relative shallow water depth and thus diatoms can quickly become incorporated into lake sediment. Esthwaite Water is a relatively shallow lake of low alkalinity, and therefore, diatoms are expected to preserve well (Colman *et al*., 1995). The sedimentary diatom analyses also exhibited good preservation for all the species. Grazing can be one important source of diatom loss. Diverse types of organisms, such as cladocerans and copepods, feed preferentially on algae including diatoms (Reynolds, 2006). *Daphnia* is one of the dominant planktonic herbivores in many lakes and the availability of food is an important factors influencing its population dynamics (McCauley & Murdoch, 1987). In Esthwaite Water, *Daphnia* numbers always increase after a 'pulse' of edible algae occurred in the lake (George & Hewitt, 2006). Phytoplankton records show that *A. formosa* increased in spring and decreased from late April (*c.a.* 16th week, Fig. 3.6). Undoubtedly this pattern is mainly controlled by nutrient availability and climatic factors such as temperature (see chapter 2). However, the continually increasing abundance of *Daphnia* from the 15th week (Fig. 3.6) may be explained by consumption of *A. formosa,* which acts as the major food source, given that it is the dominant species over that period until the summer maxima of blue-green algae (Talling, 1993) and also *A. formosa* was reported as edible for *Daphnia* (Reynolds & Wiseman, 1982; George & Hewitt, 2006). Thus heavy grazing prior to reaching the sediments may be a key explanation for the underestimated percentages of *A. formosa* in the sediment record, although more supporting cases are needed. Other species, which may have been less abundant but were able to escape the expansion period of *Daphnia*, may be overrepresentated in the sediment.

Washing out effects may also be a key factor leading to diatom losses in lakes (Jewson, Rippey & Gilmore, 1981). Diatoms stay in the epilimnetic water column during their growth period (*c.a.* 2 weeks) and sink after their death. Sedimentation rates of *A. formosa* and *A. subarctica* have been reported as less than 2 m day^{-1} (generally less 1 m day^{-1}) in the top 20 metres of lake water thus they stay in the water column for a few days (Sommer, 1984; Reynolds, 2006), indicating that they face the risk of being flushed out of the system even after populations are declining. The average annual retention time of Esthwaite Water is relatively rapid at ~90 days (Talling & Heaney, 1988). However, during periods of heavy rainfall, for example, in winter or early spring when diatoms flourish (Fig. 3.6), the amount of diatom loss by washout will increase. The rainfall in February and March, when *A. formosa* is at its high abundance in the water column, reaches 6 mm day^{-1} (Fig. 3.6) and thus washout may contribute to its underestimation in the lake sediments.

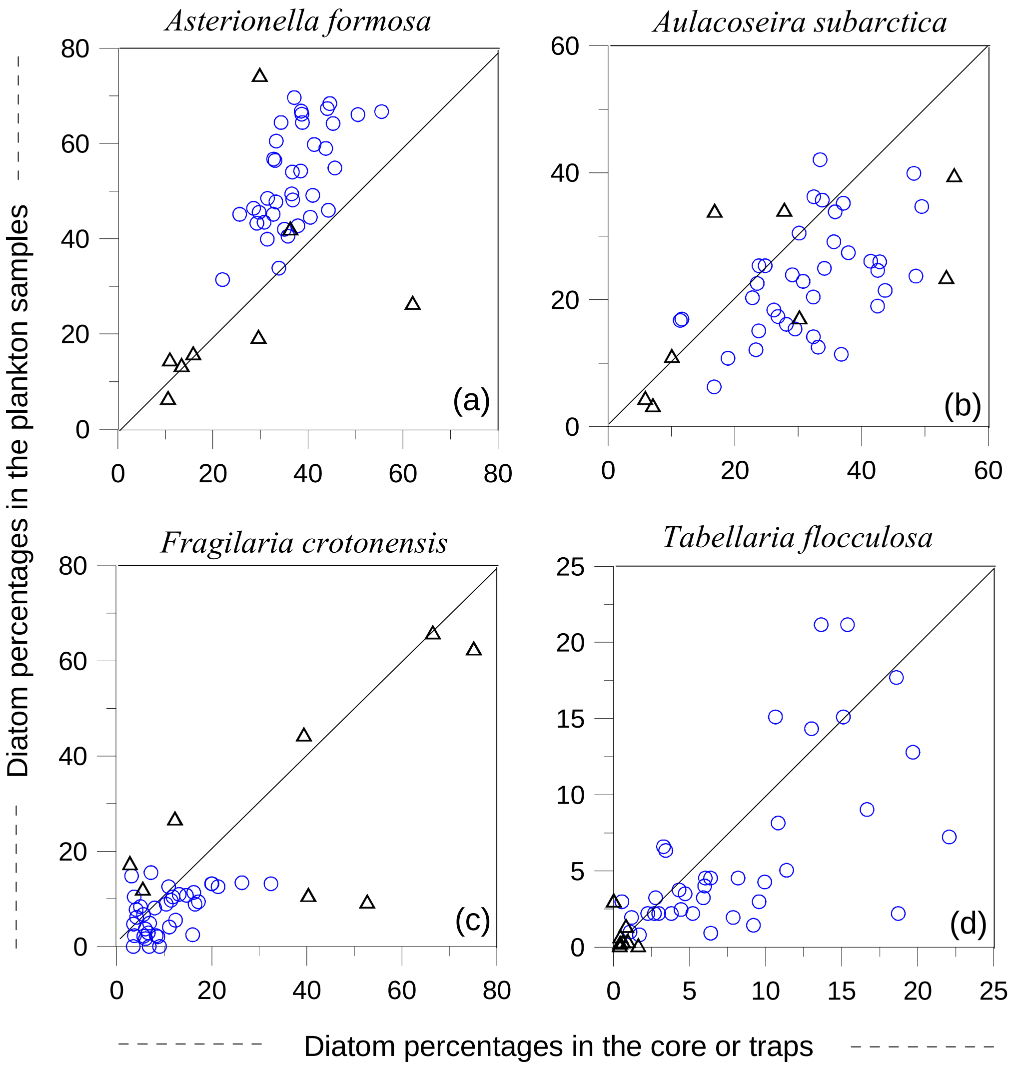


Fig. 3.5 Comparisons between percentages of the main species from the water column and sediments (including cores and traps). In each scatter plot (a to d), two comparisons of diatom percentages are presented around the expected 1:1 ratio diagonal: 1) annual average PD vs. FD, shown as circles; and 2) seasonal PD vs. diatoms in seasonal traps, shown as triangles.

Wind is another factor that can reshape the diatom assemblage, particularly in relatively shallow lakes (e.g. Taihu Lake, China, Chen *et al*., 2003). Strong winds can not only increase the vertical and horizontal spatial heterogeneity of phytoplankton but also accelerate the resuspension of lake sediment. A maximum of 19% epiphytic/benthic species were found in the sediment trap samples (Fig. 3.1), suggesting that sediment resuspension can not be ignored and that it may influence diatom representativity. Finally, the dating of the lake sediment is another potential error source when making the comparisons with the monitoring data. The coarser resolution of the sediment record may result in loss of the seasonal and annual patterns of diatom sedimentation.

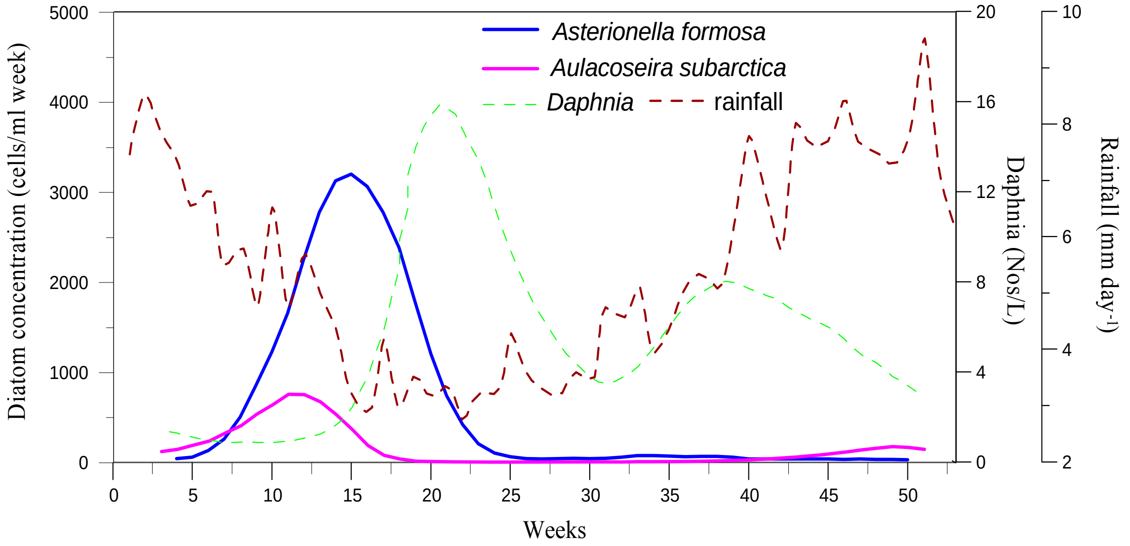


Fig. 3.6 The spline-smoothed seasonal variation in the concentration of *A. formosa*$^{(a)}$ and *A. subarctica*$^{(b)}$, numbers of *Daphnia*$^{(c)}$ and rainfall$^{(d)}$ in Esthwaite Water.

Notes: (a), (b) fortnightly average of diatom percentage data during 1945-2003; data from CEH

(c) fortnightly average between 1956 and 1972; data from George & Hewitt (2006)

(d) average weekly rainfall at Ambleside from 1965 to 2009; Data was provided by CEH and collected by Mr Bernard Tebay, Ambleside

3.3.5 Implications for palaeo-environmental reconstructions

This study illustrates that a combination of monitoring of seasonal and inter-annual variability of planktonic crops, sediment trapping, and analysis of well-dated cores provides an integrated and powerful approach to evaluate diatom representativity in sediments in the Esthwaite Water. The coherence among these different records in Esthwaite Water suggests that palaeolimnological reconstructions based on fossil diatoms preserved in the lake sediment should be generally reliable.

The diatom-inferred total phosphorus concentration (DI-TP) reconstruction exhibits good agreement with monitored winter SRP in terms of rates and magnitude of changes (Fig. 3.7). The lake remained stable with lower DI-TP concentrations (~20 µg L^{-1}) prior to 1970, which closely matches trends in the January SRP data (<5 µg L^{-1}). The DI-TP values for the period 1970-1995 showed an increasing trend, which closely parallels the monitoring record. After 1995, both the DI-TP and the monitoring records show a sharp rise in nutrient concentrations. The SRP records show a subsequent decrease since ~2003. However, this is not reflected by the DI-TP values which may be overestimated owing to the high abundance of the eutrophic species *Stephanodiscus* and *F. crotonensis* in the upper sediments (Fig. 3.4).

The good match between the trends of DI-TP and the monitoring records indicates that the fossil diatom assemblages reflect well past trends in the historical nutrient status of the lake. The close match reveals not only the robust predictive power of the diatom-TP transfer function but also the good representativity of the sedimentary diatoms.

3.4 Conclusions

The comparison of the diatom composition from the water column, sediment traps, and surface sediments over a 2-year monitoring period, showed a close agreement between the three records, indicating that the lake sediments provide a good representation of the diatom species in the water column.

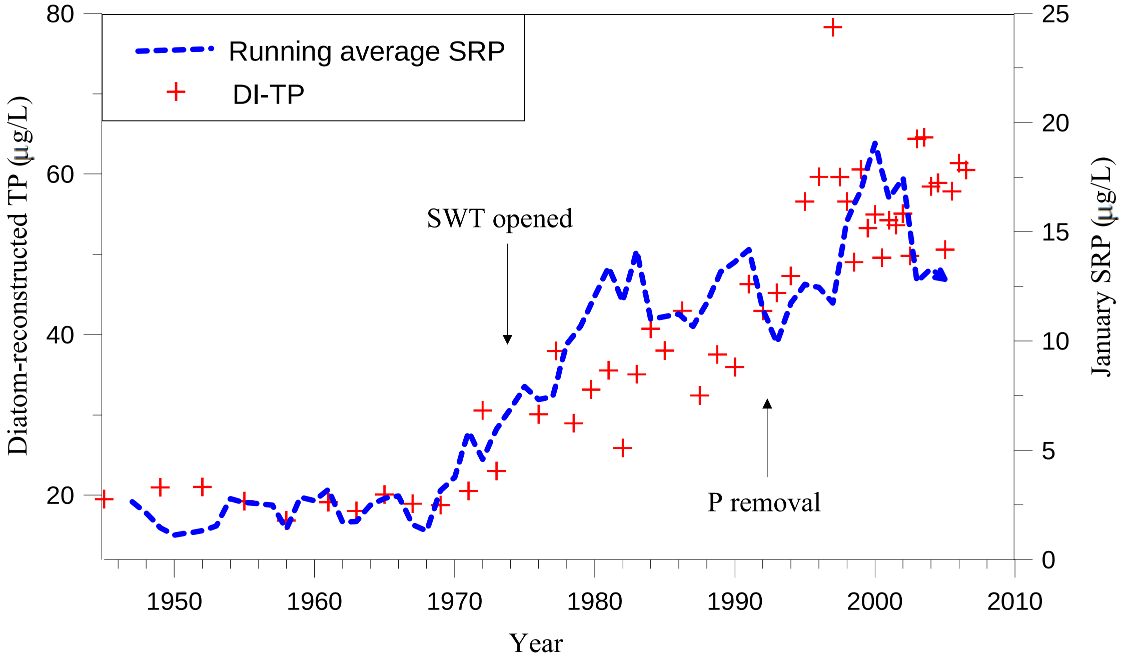


Fig. 3.7 Comparison of measured SRP (blue dashed line, three-point running average of the measured winter mean SRP) and DI-TP reconstructed TP in each sediment sample (red crosses). Data were from CEH.

The comparison between the fossil diatoms from a ^{210}Pb dated sediment core and the diatoms in a 59-year monitoring record revealed similar community structures in each set of paired samples. The dominant species in the phytoplankton records were also found in the sediments with comparable abundances, although some species were under- and others over-represented in the sediment record compared with the phytoplankton data. Representativity is likely to be affected by grazing of herbivore and climatic factors (such as rainfall and wind).

The good sedimentary diatom representativity ensures reliable palaeo-environmental reconstruction. The diatom-based TP reconstruction matched well with the long-term SRP measurements in terms of the onset, rate and magnitude of change, suggesting that the fossil diatoms recorded faithfully the past diatom flora of the lake.

Chapter 4 The inconvenient truth of sediment disturbance: how to establish a chronology for a problematic sediment core using monitoring and palaeolimnological records

4.1 Introduction

In recent decades, palaeolimnological research has developed significantly and has played an important role in developing our understanding of environment change over a variety of spatial and temporal scales (Smol, 2002; Cohen, 2003; Moser, 2004; Battarbee *et al.*, 2005a). A sound piece of palaeolimnological research requires good materials (such as undisturbed lacustrine sediment and well-preserved fossils), sophisticated analytical methods (including laboratory protocols and data analysis methods), and a reliable chronology (Birks & Birks, 2006). In particular, a well resolved chronology is important to the increasing number of studies which synthesise core data from multiple individual palaeolimnological investigations to make environmental change inferences at regional and global scales (Battarbee & Renberg, 1990; Sadler, 2004; Smol *et al.*, 2005; Enters, Kirchner & Zolitschka, 2006). For example, in climate studies, the generation of precise and accurate chronologies for proxy records of past climate change has become a key prerequisite for correlating different environmental archives, or for comparing records between hemispheres (Blockley *et al.*, 2008). Additionally, it is only possible for palaeolimnologists to determine rates of processes and fluxes of materials, and to correlate the abrupt nature of past climate change or other historical events with the sediment archives, if reliable chronologies are established (Birks & Birks, 2006; Rasmussen *et al.*, 2006).

Great progress has been made in resolving sediment core chronologies in the past three decades. Several sediment proxies, such as algal records (Haworth, 1980), spheroidal carbonaceous particles (Rose *et al.*, 1995) and tephra (Lowe, 2008) have been used to validate chronological models based on radiometric data. Much palaeolimnological work has been undertaken at a high temporal resolution by studying annually laminated sediment records (e.g. Renberg, 1981; Besonen *et al.*, 2008) or by sampling cores at finer intervals using improved corers (Glew, 1988). In addition, several statistical approaches have been developed for establishing and then refining age-depth models (Bennett, 1994; Bronk Ramsey, 1999; Bennett & Fuller, 2002; Telford, Heegaard & Birks, 2004; Heegaard, Birks & Telford, 2005).

In practice, it is common to encounter disturbed sediment cores due to external (flood, hurricane, or sediment dredging) and internal (e.g. sediment mixing, slope failure, bioturbation) disturbances. As a consequence, lake sediments can sometimes suffer from nonlinear accumulation rates, slumping events and hiatuses, which may lead to complex and incomplete core records and thus mis-interpretation (Håkanson & Jansson, 1983; Larsen & MacDonald, 1993; Bangs *et al.*, 2000; Gilbert & Lamoureux, 2004; Martin *et al.*, 2005). Although often disadvantageous, such disturbances can sometimes provide information on sediment processes, and may allow for inferences of key past environment changes e.g. floods, earthquakes, fire, or human reclamation events (Chapron *et al.*, 1999, Arnaud *et al.*, 2002; Moreno *et al.*, 2008). For example, numerous palaeolimnological studies have revealed that a reasonable chronology can be derived from multi-core comparisons so that disturbances such as slumping events can be distinguished (Tibby, 2001; Donovan & Grimm, 2007; Morellón *et al.*, 2010; Tibby *et al.*, 2010). It is recognized however that it is not always possible to retrieve multiple cores due to time and cost constraints or because the study sites are remote and not easily accessible.

In this chapter, an example of a 65.5 cm long disturbed sediment core (core ESTH7 from Esthwaite Water, UK) will be presented and the procedure for establishing a chronology for it will be discussed. Three good quality ^{14}C dates based on *Alnus glutinosa* derived leaves from the lower part of the core identified depths representive of the Medieval Warm Period (MWP, *c.a.* 900-1200 AD) and the Little Ice Age (LIA, *c.a.* 1350-1850 AD) (Broecker, 2001; Cronin *et al.*, 2003; Hunt, 2006). These two stages have been widely recognized as key periods in which to understand past climate variability (Mann, Bradley & Hughes, 1999; Mackay *et al.*, 2005; Crowley, 2000; Maasch *et al.*, 2005; Jansen *et al.*, 2007), although few ^{14}C dated cores allow these time periods to be precisely orientated due to the lack of good dating materials and measurement difficulties when ages approach the last 500 years. Thus, despite problems with sediment integrity, the sediment record from Esthwaite Water affords a rare opportunity to understand the impact of climate change and human activities on the lake ecosystem over the last 1000 years.

To establish a chronology for ESTH7, we make comparisons between multiple sediment proxies (including loss on ignition, sediment grain size, diatoms and metals) from this and two other dated sediment cores, ESTH1 and ESTH8. Furthermore, a long-term (60 year) monitoring algal record of planktonic diatom data was used to correlate key features of diatom floristic change. With these data, we aim to: a) identify the occurrence and timing of disturbance events (slumping and hiatus) in core ESTH7; b) develop a reliable age-depth model for the lake using a generalized additive model combined with existing ^{210}Pb and ^{14}C dating results; and c) evaluate the sedimentation variability in this lake and possible causes for the two identified sediment disturbances.

4.2 Study site

See the study site section on Esthwaite Water in chapter 1.

4.3 Methods

4.3.1 Sediment core extraction

The three sediment cores that are utilised in this study were all collected from the deepest part of the lake as follows: (i) ESTH1, a 86 cm core taken using a mini-Mackereth piston corer (Mackereth, 1969) on 7 June 1995 which was sliced at 0.5 cm (upper 30 cm) and 1.0 cm (below 30 cm) intervals; (ii) ESTH7, a 65.5 cm core taken using a percussion piston corer (Chambers & Cameron, 2001) on 12 April 2006 and sliced at 0.25 cm (upper 20 cm) and 0.5 cm (below 20 cm) intervals; and (iii) ESTH8, a 31 cm core taken using a mini-Mackereth piston corer on 15 August 2007 which was sliced at 0.5 cm intervals. ESTH1 was collected as part of an earlier study (Bennion *et al*., 2000) and ESTH7 and ESTH8 were collected as part of the PhD study.

4.3.2 Radiometric analysis

Sediment samples from Esthwaite Water cores ESTH7 and ESTH8 were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs, and ^{241}Am by direct gamma assay in the Bloomsbury Environmental Isotope Facility (BEIF) at University College London, using an ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. Lead-210 was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope ^{214}Pb following three weeks storage in sealed containers to allow radioactive equilibration. Caesium-137 and ^{241}Am were measured by their emissions at 662keV and 59.5keV. The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy gamma rays within the sample. ^{210}Pb chronologies were calculated using the constant rate of ^{210}Pb supply (CRS) model (Appleby & Oldfield, 1978). The same radiometric methods were applied to the earlier core ESTH1 at the University of Liverpool in 1995.

Several fragments of *A. glutinosa* leaf were extracted by washing through a 125 µm sieve from three ESTH7 sediment samples (depths of 47.25-47.5 cm, 59.25-59.75 cm, and 63.25-63.75 cm, respectively) then handpicked under a microscope (magnification ×40). The samples were AMS radiocarbon dated at the Natural Environment Research Council (NERC) Radiocarbon Laboratory in East Kilbride. ^{14}C dates were calibrated using OxCal v4.1.3 (Ramsey, 2009), and were given as calibrated years including central age and two standard deviations.

4.3.3 Loss on ignition and grain size analysis

Sediment water content was calculated after drying a known sediment mass overnight in an oven at 105°C. Loss on ignition (LOI) measurements were made after combustion in a muffle furnace at 550°C for two hours after overnight drying (Dean, 1974). Samples were cooled to room temperatures in a desiccator before reweighing.

Grain size spectra were determined using a Malvern automated laseroptical particle-size analyzer (Mastersizer-2000) after removal of organic matter by 10% H_2O_2 treatment. Median grain size (MD) was calculated as a measure of the central tendency of the different grain size distributions.

4.3.4 Trace metal analysis

Given concentrations of various metals provide abundant information on catchment soil erosion and sedimentation processes (e.g. Mackereth, 1966; Dean, 1997), metal elements including Al, Ba, Be, Ca, Co, Cr, Cu, Fe, Mn, Na, Ni, P, Pb, Sr, Ti, V, Zn, K, Mg were analyzed using standard Environment Protection Agency (USA) method 3052 (Agency, 1996). Approximately 125 mg of sediment was placed in a Teflon nitrification tank with 6.0 ml HNO_3, 0.5 ml HCl, and 3.0 ml HF. The sealed tank was then placed in a microwave oven and nitrified at 180±5 °C for 15 minutes. The residue from the tank was dissolved with 0.5 ml $HClO_4$ over a heating block at about 200 °C in a Teflon breaker. The final solution, diluted to 25 ml with deionised water, was then subjected to metal analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The accuracy of analytical determinations was established using the reference material GSD-9 (supplied by the Chinese Academy of Geological Sciences) and analytical accuracy for all elements was >95%. To highlight turnover points of metal element profiles, only those elements with obvious changes were shown and ratios of Mg/Ca and Fe/Mg were calculated.

4.3.5 Diatom analysis

Plankton samples have been collected from the deepest part of the lake since 1943 initially by Freshwater Biology Association and later by Centre of Ecology and Hydrology on a fortnightly basis (although several were monthly, Maberly *et al.*, 1994a). Integrated surface water samples (0-5 m pre-1964 and 0-7 m post-1964) were collected using a weighted plastic tube and preserved with Lugol's iodine. In the laboratory, algae in a sub-sample of the preserved samples was counted using an inverted microscope (Lund, Kipling & Cren, 1958). Annual average percentages for each species were calculated and only the diatom component of the dataset was employed in the current study.

Sedimentary diatom samples were prepared using standard techniques (Battarbee *et al.*, 2001). All samples were mounted on microscope slides using Naphrax and were observed under light microscope at ×1000 magnification. Diatom taxonomy mainly followed Krammer & Lange-Bertalot (1986, 1988, 1991a, b). Diatom data are presented as relative abundances.

Owing to difficulties in discerning small centric species (less than 10 µm in diameter) and *Stephanodiscus binatus* (more detailed features are given for this species in chapter 6) in the plankton samples under inverted microscope, their sum was calculated as "small *Stephanodiscus/Cyclotella* spp" for comparison with the sediment records.

4.3.6 Core correlation and dating model development

Given the comparable lengths (similar time ranges) of cores ESTH1 and ESTH7, they were used for most of the inter-core correlation. Two approaches were used to assess the continuity of sedimentary processes in core ESTH7. Firstly, palaeolimnological proxies including LOI, grain size, trace metal concentration, and diatom composition were correlated between cores ESTH7 and ESTH1 using a "wiggle-matching" approach (Thompson & Clark, 1989). Secondly, major species from the 59-year monitoring record of planktonic diatoms were compared with the diatom records in both sediment cores. Additionally, principal components analysis (PCA) was employed using the standardized proxy data (LOI, grain size, geochemical data, and diatom composition) to reveal the similarity among samples in core ESTH7. Samples lying in close proximity in PCA ordination space are likely to have similar sample characteristics (ter Braak & Smilauer, 2002). This method can therefore theoretically be used to track abrupt changes or inconsistencies in cores that might arise from slumping or hiatus events. PCA was performed using the software package Canoco for Windows version 4.5 (ter Braak & Smilauer, 2002).

Based on the ^{210}Pb chronologies, ^{14}C dating and the correlated points in cores ESTH1 and ESTH7, sediment accumulation rates were calculated and compared. Given the superior ^{210}Pb dating results and higher sediment accumulation rates for ESTH1, the three ^{14}C dates derived for ESTH7 were transferred to ESTH1 according to the established core correlation. The latter core was subsequently used for developing and refining an age-depth model. Based on the fixed ratio 1:2 between the sediment accumulation rates of the two sediment cores (see Table 4.2), core ESTH1 was extended to a length of 97.5 cm, since its original length did not extend back to the two earlier ^{14}C dates (1075 BP and 1160 BP).

The age-depth model was established following the method proposed by Heegaard, Birks & Telford (2005). This method estimates age-depth relationships in stratigraphic sequences by means of a generalized mixed-effect regression. The procedure uses mid-point estimates of the calibrated ages in combination with their central distributional range as the basis for estimating the fixed relationship between age and depth. One of the great advantages of this procedure is its ability to combine samples dated by different dating techniques (e.g. ^{14}C or ^{210}Pb dating), and to include layers that have specific *a priori* information, such as the uppermost core section corresponding to the date of core collection. This procedure was performed on the ^{210}Pb dating results and the three ^{14}C dating results using R 2.7.1 statistical software (Venables & Smith, 2009).

For further palaeolimnological interpretation (in Chapter 5 and 6), the above age-depth model was applied to a new integrated core ESTH0, including the upper 8.5 cm of ESTH7 (representing the period of 1993-2006 AD), the upper 30 cm of ESTH1 (representing the period of 1880-1993 AD) and 28.5-65.5 cm of ESTH7 (representing the period of 780-1880 AD).

4.4 Results

4.4.1 Radiometric analysis

In ESTH1, both total and unsupported ^{210}Pb activity in ESTH1, excluding samples from the surface and the depth of 15 cm, exhibits a rough exponential decay with depth (Fig. 4.1a, b). The ^{137}Cs measurements identify a major peak in activity at 5.25±2.5 cm likely recording fallout from the 1986 Chernobyl accident. This corroborates the very recent CRS model ^{210}Pb dates which places 1986 at ~6 cm. Although the deeper ^{137}Cs measurements were insufficient to resolve the 1963 fallout peak with any accuracy, the ^{241}Am record suggests that this feature occurs at 11.5±2 cm, in reasonable agreement with the ^{210}Pb determined level of 1963 at 14 cm (Fig. 4.1c).

In ESTH7, unsupported ^{210}Pb activity declines irregularly with depth (Fig. 4.1d, e). There is little net reduction in ^{210}Pb activity over the top 15 cm, but there is a sharp decline in the section at 9-13 cm. Unsupported ^{210}Pb activity declines rapidly from 105.48 to 8.7 Bq kg^{-1} over the depth range 24.88-26.13 cm, suggesting a discontinuous sedimentation or a substantially changed sedimentation environment in this section. The ^{137}Cs activity versus depth profile shows a similar pattern to ^{210}Pb with abrupt decreases at 9-13 cm and 24-26 cm (Fig. 4.1f). ^{241}Am was detected in

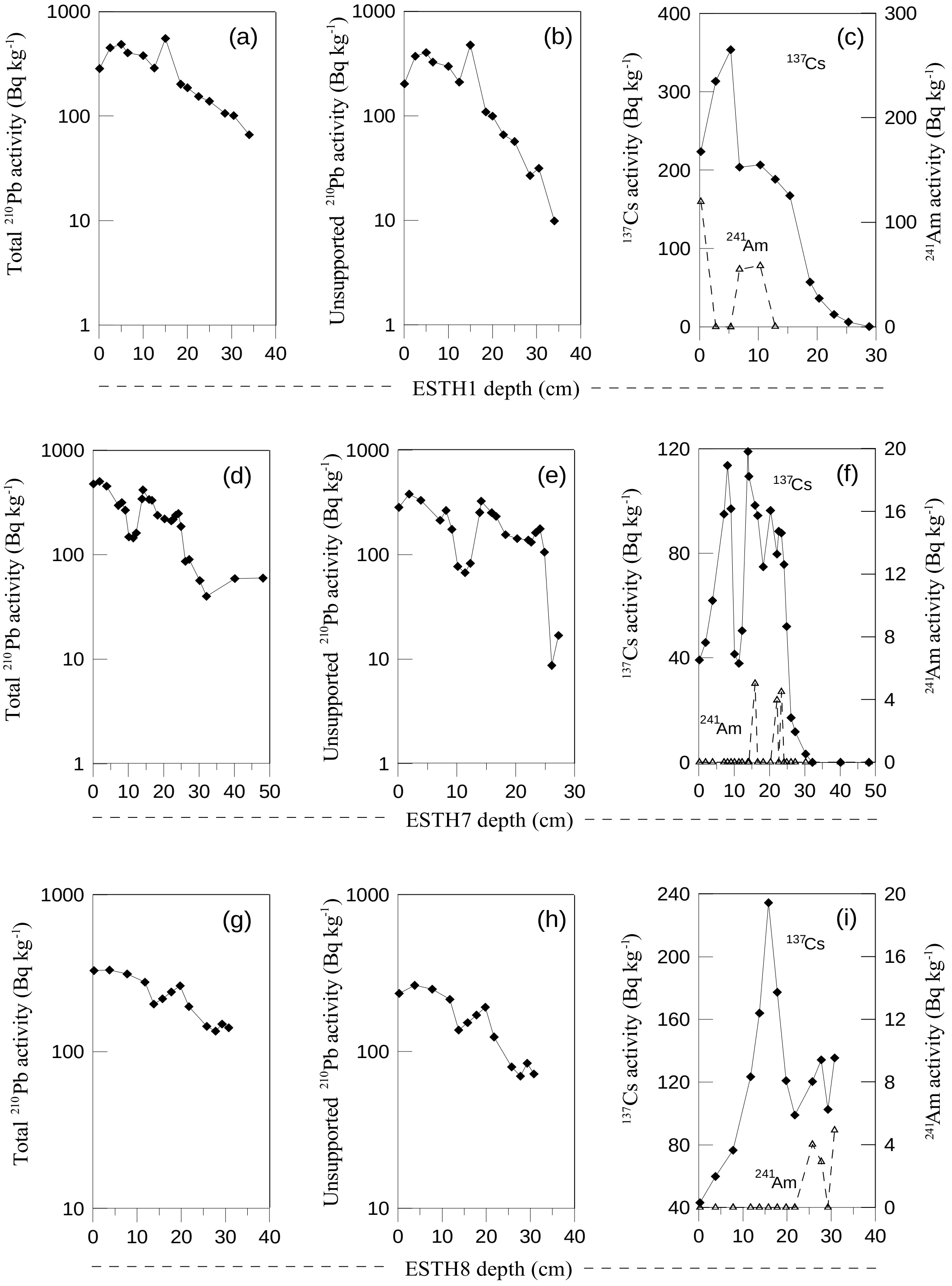


Fig. 4.1 Fallout radionuclide concentrations in cores ESTH1 (a-c), ESTH7 (d-f) and ESTH8 (g-i) from Esthwaite Water. (a), (d) and (g): total ^{210}Pb; (b), (e) and (h): unsupported ^{210}Pb; (c), (f) and (i): ^{137}Cs and ^{241}Am concentrations versus depth. Dashed lines show ^{241}Am activity. Data for ESTH1 were produced by Peter Appleby.

samples from 15.88, 20.25 and 22.13 cm, although concentrations were insufficient to resolve the 1963 fallout maximum.

Unsupported ^{210}Pb activity in ESTH8 also declines irregularly with depth (Fig. 4.1g). There is little net decline over the top 8 cm and section 13-20 cm, suggesting an increase in sediment accumulation in these sections. The ^{137}Cs activity versus depth profile shows a well-resolved peak at 15.75 cm and a less well-resolved wide peak at 25.75 cm, which are assumed to be represented the 1986 Chernobyl accident and the 1963 fallout maximum from the atmospheric testing of nuclear weapons, respectively. The latter feature is confirmed by detectable ^{241}Am (Fig. 4.1i).

Given the variable sediment accumulation rates in the lake, ^{210}Pb chronologies were calculated using the constant rate of ^{210}Pb supply (CRS) model for all cores. The depth-age models of all three cores are shown in Fig. 4.2. In ESTH1, the mean accumulation rates are relatively stable with an average of 0.038 g cm^{-2} y^{-1} prior to the 1960s, compared with higher values of ~0.062 g cm^{-2} y^{-1} after the 1960s. For ESTH8, sediment accumulation rates also exhibit a major change in the 1960s but are higher than ESTH1: 0.075 g cm^{-2} y^{-1} and 0.097 g cm^{-2} y^{-1}, average accumulation rates before and after the 1960s, respectively (Fig. 4.2). For ESTH7, ^{210}Pb data from only the upper 8 cm were used to ascribe dates due to the discontinuities described above. These are discussed further below.

The three AMS dates based on *A. glutinosa* leaves (Fig. 4.3) were converted to calendar years (Table 4.1) using the computer program OxCal v 4.1.3 (Ramsey, 2009). The calendar age used for developing the age-depth model was the mean of the calendar BP age range of the 95.4% area range with the highest probability. Dates were calibrated to 636 B.P, 1075 B.P and 1160 B.P for samples at 47.25-47.5, 59.25-59.75 and 63.25-63.75 cm, respectively (Table 4.1). The results give average sediment accumulation rates for 47.25-59.75 and 59.75-63.75 cm of 0.27 and 0.47 mm year^{-1}, respectively.

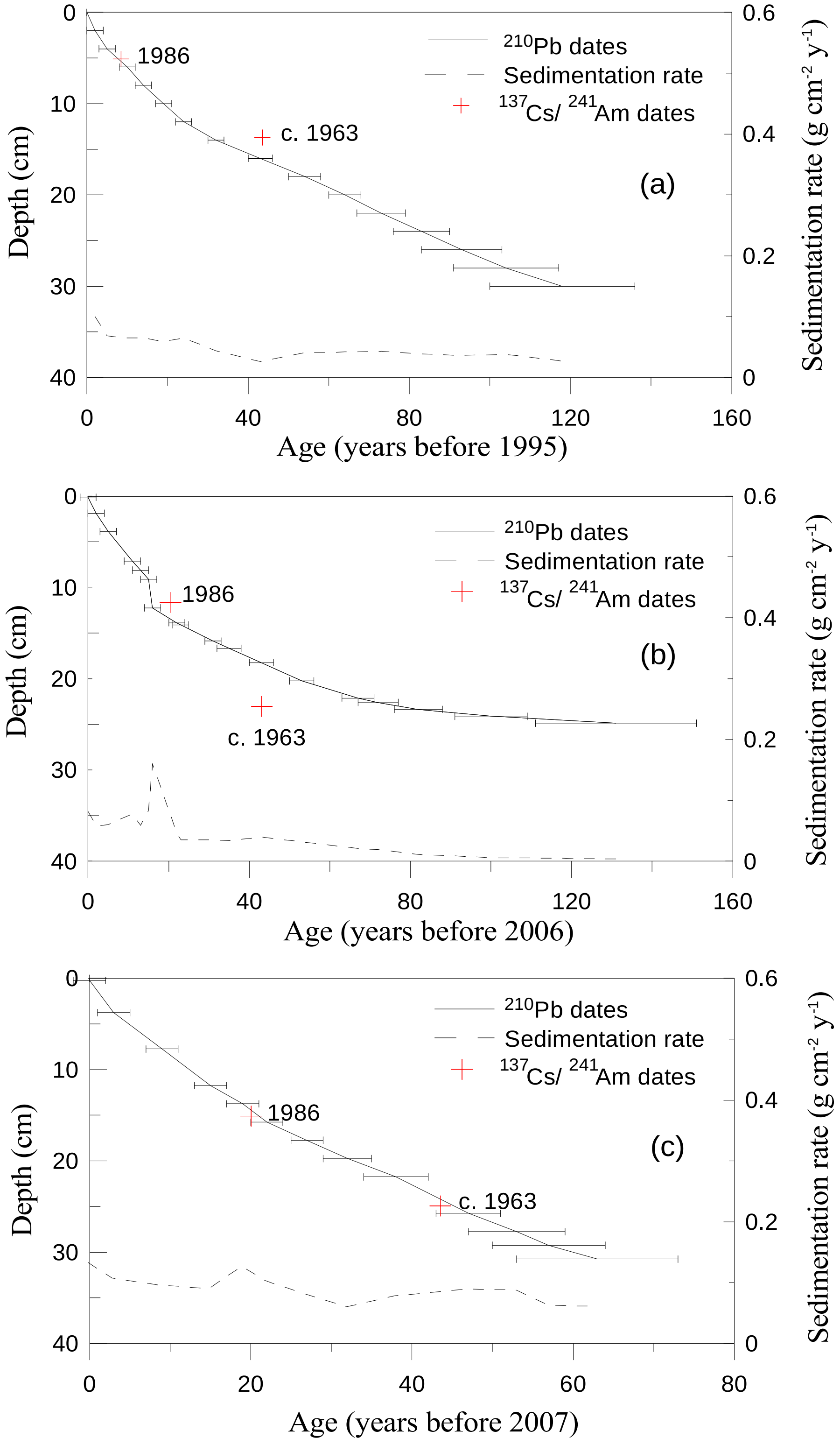


Fig. 4.2 Radiometric chronology of cores ESTH1 (a), ESTH7 (b) and ESTH8 (c).

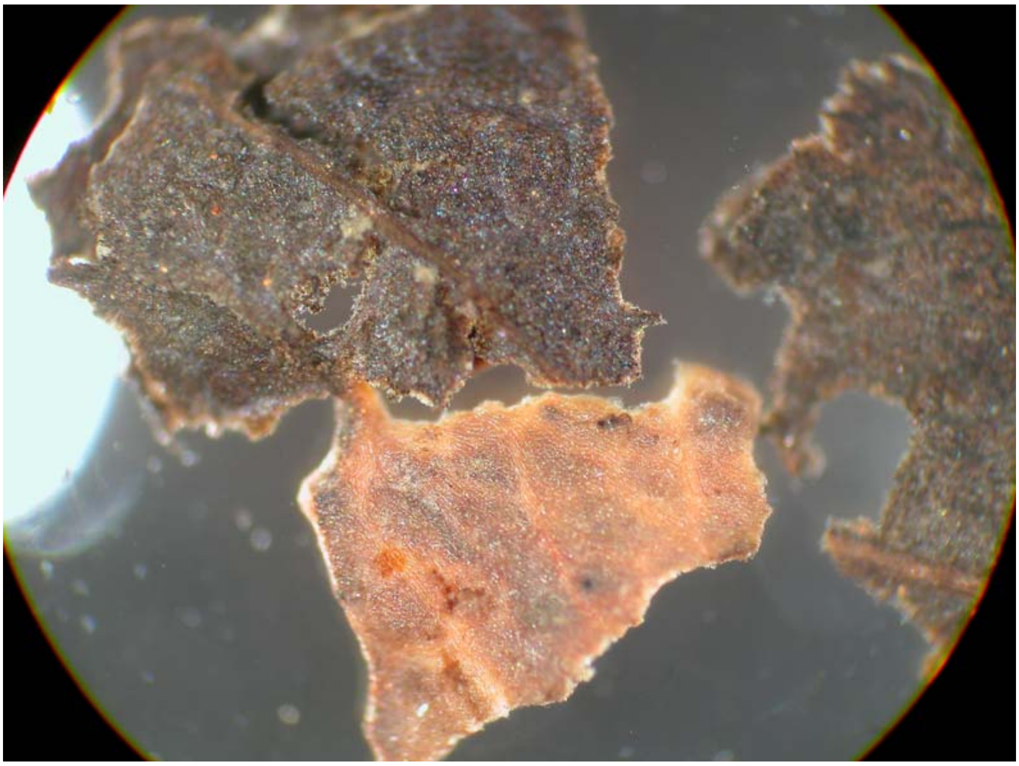


Fig. 4.3 Fragments of alder (*Alnus glutinosa*) picked from core ESTH7 for AMS ^{14}C dating.

Table 4.1 Three radiocarbon AMS dates derived from leaf fragments of *A. glutinosa* for core ESTH7.

* 2σ limits indicate 95.4% confidence interval for each sample.

Sample depth (cm)	Lab code	Conventional Radiocarbon Age (years BP ± 1σ)	Calendar years BP (2σ limits)
47.25-47.5	SUERC-23848	687±35	636 (687-586)
59.25-59.75	SUERC-23761	1164±38	1075 (1176- 975)
63.25-63.75	SUERC-26406	1226±35	1160 (1270-1050)

4.4.2 Comparison of LOI and grain size profiles

The LOI profiles of ESTH7 and ESTH1 match well (Fig. 4.4 a), suggesting good potential for core correlation. Grain size profiles also show similar trends (Fig. 4.4 b), although the link is not as clear as for LOI profiles. Several "peaks" and "valleys" were linked across the two cores by the "wiggle-matching" method. However, one feature that stands out as different in ESTH7 is an abrupt decrease in LOI values within the section 9.5-13 cm (as marked in Fig. 4.4a). The average LOI for this section is 21.9%, significantly lower than values in neighbouring layers, all of which are over 23.5%. This sharp decrease is consistent with the occurrence of a slumping event as the decline in LOI values is not seen in ESTH1. It is also coincident with the sharp declines observed in the radiometric activities of ^{210}Pb and ^{137}Cs in this section (Fig. 4.1 b-d).

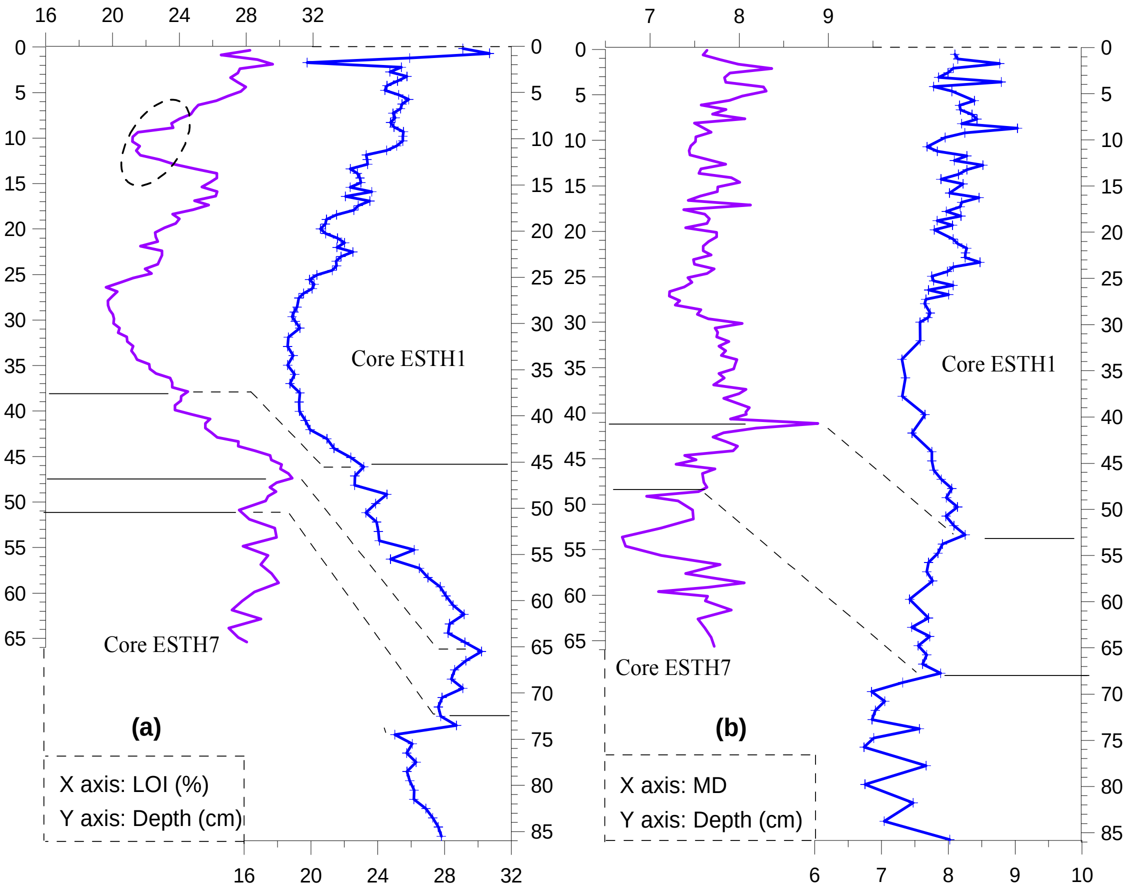
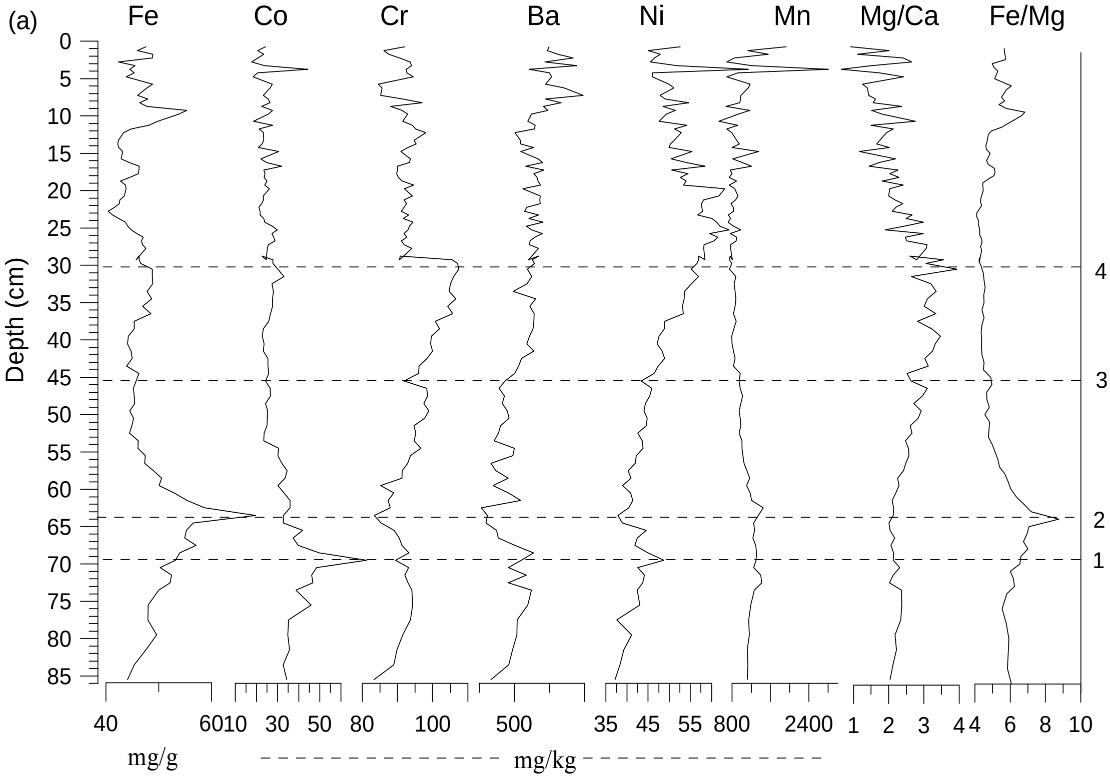


Fig. 4.4 Profiles of (a) organic matter (LOI) and (b) median grain size (MD) for cores ESTH1 and ESTH7. The dashed ellipse in (a) represents the slumping section and dashed lines indicate correlative features between the two cores

4.4.3 Comparison of metal concentrations

Vertical profiles of several selected metals and ratios of Mg/Ca and Fe/Mg in ESTH1 and ESTH7 are given in Fig. 4.5. Their distributions all have sharp peaks or valleys that are conducive to inter-comparison and four corresponding features were identified: 1) peaks in Co, Ni and Ba at depths of 69.5 cm and 49.5 cm in ESTH1 and ESTH7, respectively; 2) a peak in Fe, along with reductions in Ba, Cr, Ni and Mn, at depths of 63.5 cm and 46.5 cm in ESTH1 and ESTH7, respectively; 3) dips in concentrations of Cr, Ni and Mg/Ca at depths of 45.5 cm and 38 cm in ESTH1 and ESTH7, respectively; 4) abrupt changes in concentrations of Cr, Ni, Mn, Mg/Ca and Fe/Mg at depths of 30 cm and 28.5 cm in ESTH1 and ESTH7, respectively.



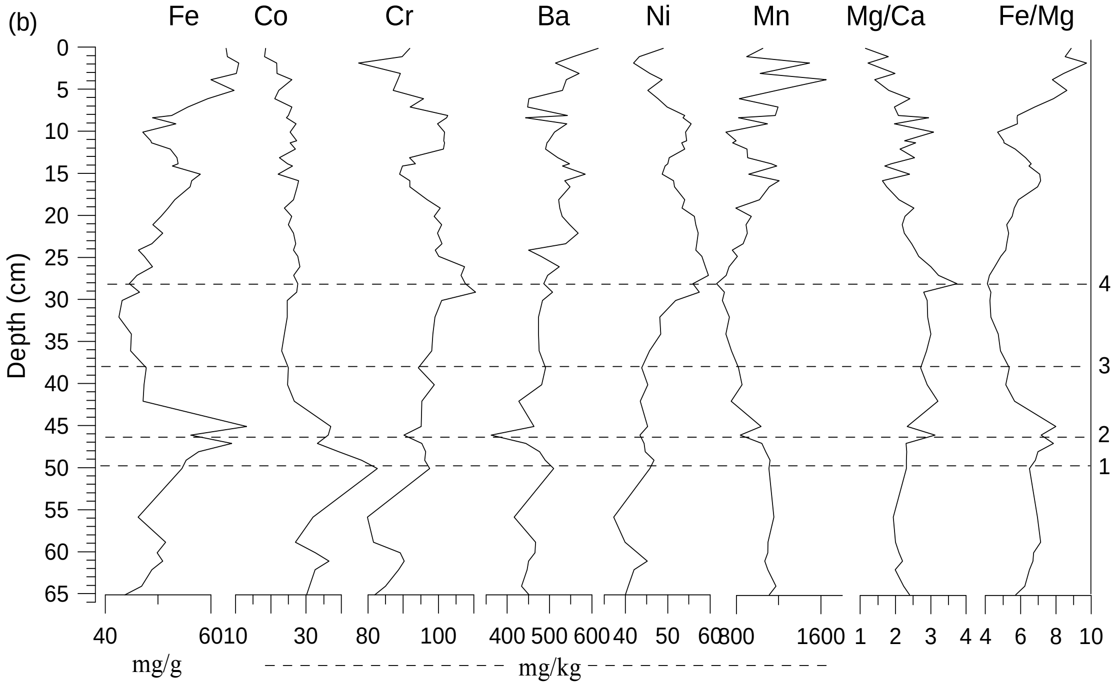


Fig. 4.5 Selected metal concentration profiles for cores ESTH1 (a) and ESTH7 (b). Dashed lines indicate correlative features 1, 2, 3 and 4.

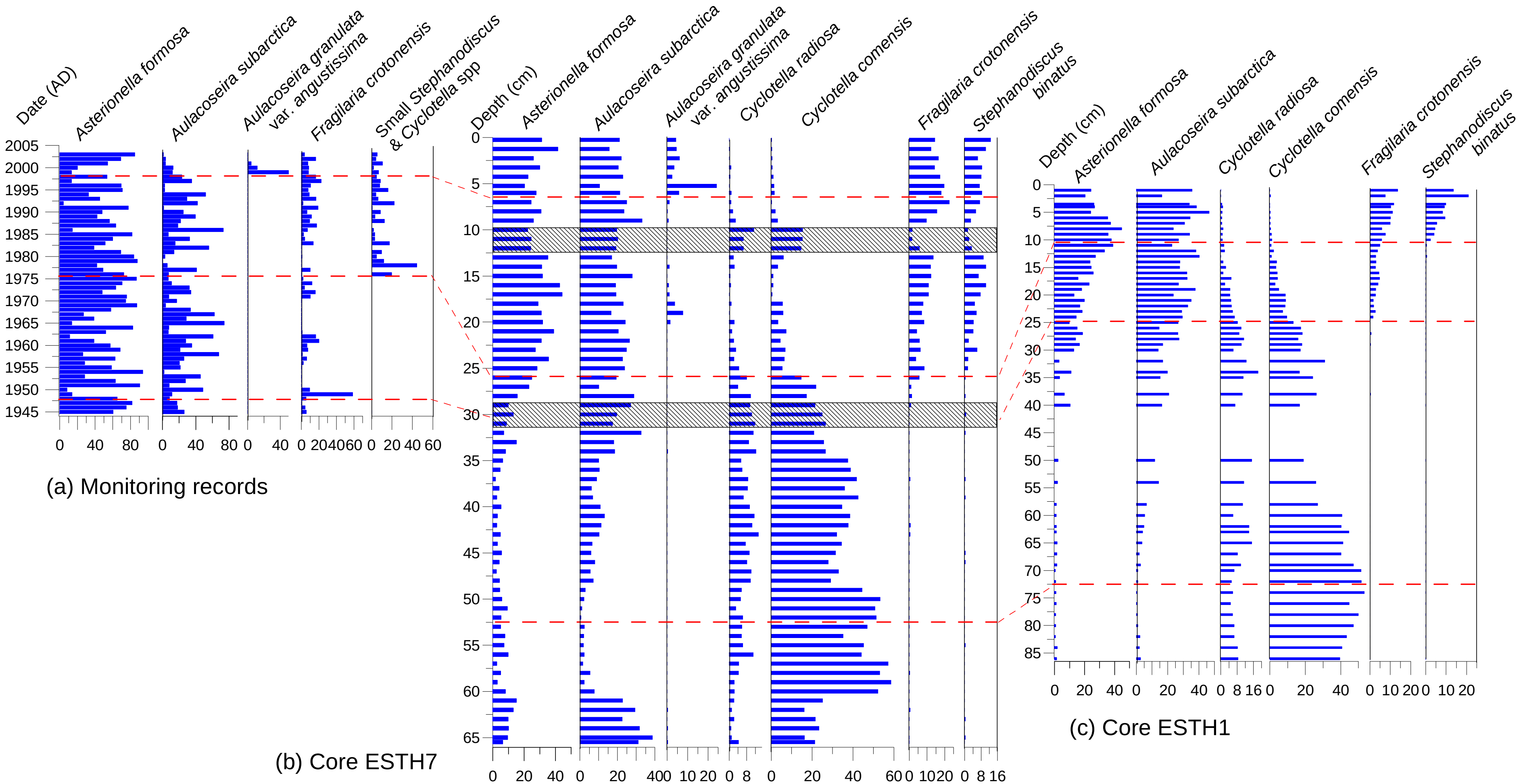
In addition to similarities in the elemental data, coherence of sediment accumulation rates was also evident in the lower part of the two cores (below 45.5 cm in ESTH1 and 38 cm in ESTH7). The depths of sediment between correlative features 1 and 2, and 2 and 3 were 6 cm and 18 cm respectively in ESTH1 and 3 cm and 9 cm, respectively in ESTH7 (Fig. 4.5). These data indicate that the sedimentation rate of ESTH1 was twice than that of ESTH7.

4.4.4 Comparison of diatom profiles

The fossil diatoms in ESTH7 exhibit two major compositional shifts (Fig. 4.6). Prior to ~60 cm, assemblages were dominated by *Aulacoseira subarctica*, above which this taxon exhibited a marked decline and *Cyclotella comensis* increased. The second major shift occurred at ~26 cm when *C. comensis* decreased and there was an expansion of taxa associated with more eutrophic waters, especially *Asterionella formosa*, *Fragilaria crotonensis* and *Stephanodiscus binatus*. In ESTH1, there was only one distinct shift at ~25 cm (~1905 AD according to the ^{210}Pb dating), similar to that at ~26 cm in ESTH7, from dominance of *C. comensis* to *A. formosa* and *F. crotonensis*. The earlier shift was not observed in ESTH1 most likely because this core does not extend as far back in time as ESTH7.

Two discrepancies, however, could be observed in the diatom stratigraphies of the two cores (Fig. 4.6). Firstly, the high percentages of *F. crotonensis* and *S. binatus* were almost synchronous in ESTH7, but in ESTH1 *S. binatus* appeared about seventy years later than *F. crotonensis* (a difference of 14 cm in terms of sediment depth). Secondly, there was a resurgence of *Achnanthidium minutissimum* (not shown here), *C. comensis*, and *Cyclotella radiosa* at the depth 9.5-13 cm in ESTH7, but in ESTH1, no such shift was observed as diatom assemblages were dominated by *F. crotonensis* and *S. binatus,* throughout the upper core.

A comparison of the dominant taxa is made here for correlation purposes (Fig. 4.6). Planktonic monitoring records reveal that small (<12 μm) *Stephanodiscus* and *Cyclotella* taxa started to appear in the lake at relatively high percentages from 1975. This change was well reflected in ESTH1 in which *S. binatus* occurred from 11 cm, dated to 1973 AD. A short-lived peak in *Aulacoseira granulata* var. *angustissima* occurred in 1999-2002 according to the monitoring record. This was well documented in ESTH7 at a depth of around 6 cm (^{210}Pb dated to 1999 AD). These two distinct community shifts provide further assistance with correlating the two cores.



(a) Monitoring records

(b) Core ESTH7

(c) Core ESTH1

Fig. 4.6 Relative abundance data of selected dominant diatom species from (a) monitoring records, (b) core ESTH7, and (c) ESTH1. Core correlations as outlined in the text are marked by dotted lines. The shadows around depths of 10 and 30 cm in ESTH7 indicate the slumping and hiatus events, respectively.

4.4.5 Comparison of multiple proxies

PCA ordination of all the sedimentary proxies reveals that samples during the suspected slumping period (samples 12-15, representing the depth 10-12.5 cm) are most similar to those which were older than 1900 AD (Fig. 4.7). The seven samples (No. 28, 30, 31, 32, 33, 52, 53), located in the selected “sample distance” circle, are closest to the “slumping” samples (Fig. 4.7). Excluding the two very old samples (No. 52 and 53), the remaining five were all deposited during 1805-1880 AD, suggesting that sediment in the “slumping” samples originated from material deposited during this era.

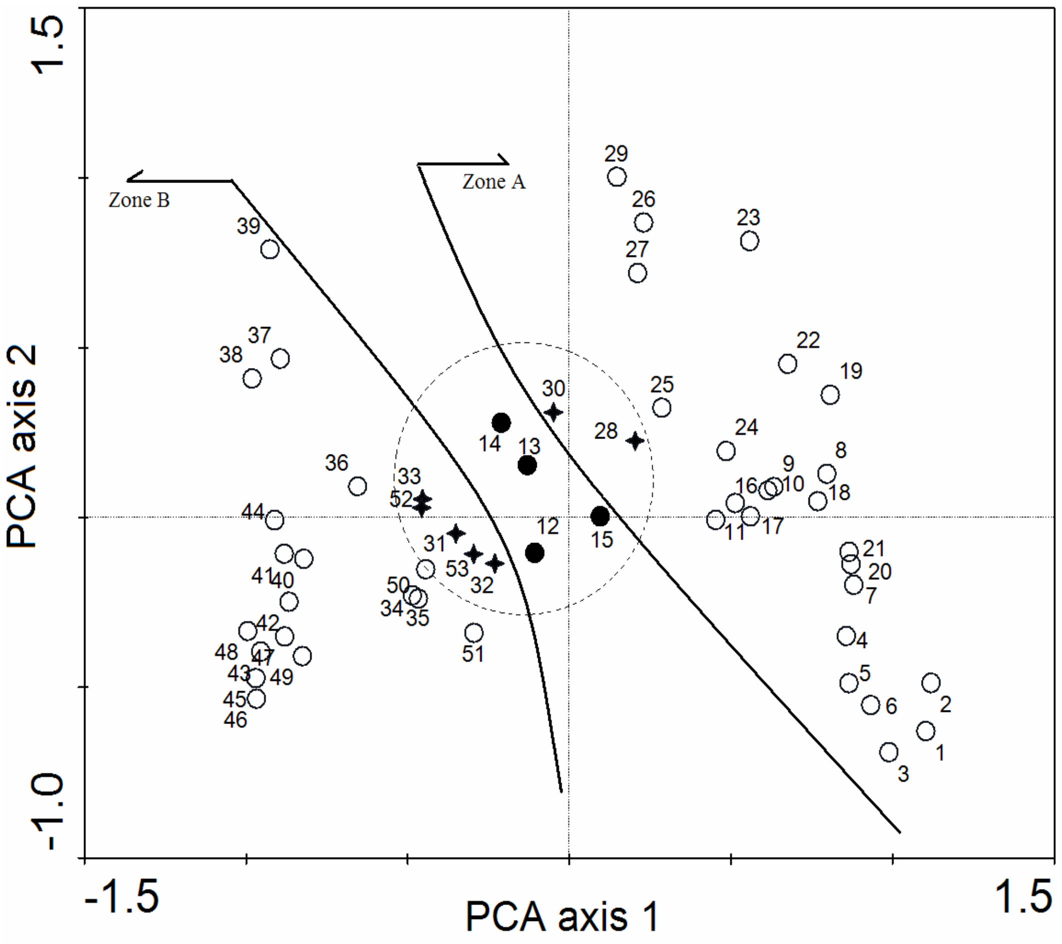


Fig. 4.7 PCA ordination of all the proxy data. Zones A and B show the samples younger or older than the 1900s, respectively. Samples 12-15 (solid circle) and the most similar samples (filled diamond) are shown in the dashed circle. Sample numbers were generated in the order of sediment depths.

4.4.6 Core correlation and chronology model development

The multi-proxy comparison conducted above has revealed several points of good temporal correlation between cores ESTH1 and ESTH7. As mentioned in section 4.4.3, the depths of corresponding layers in the two cores exhibited a fixed ratio of 1:2, indicating that sediment accumulation rates in ESTH1 were twice as high as those in ESTH7. Using this information in combination with the ^{210}Pb and ^{14}C dating, dates were calculated for each point of correlation by interpolation or extrapolation (Table 4.2). These dates were subsequently compared with the smoothed age-depth model.

A slumping and an hiatus event in ESTH7 were clearly revealed by the core comparisons. At around 11 cm in ESTH7, the diatom records (abrupt high abundance of species *C. comensis, C. radiosa, A. minutissimum*), radiometric elements (the sudden decrease of ^{210}Pb and ^{137}Cs activity), and LOI data (large dip in values) indicated that a slumping of old material occurred at around 1990. Furthermore, an hiatus at around 26 cm in ESTH7 was indicated by the unexpectedly down-core rapid disappearance of *F. crotonensis* and the chronology calculated by multi-proxy correlation. This hiatus appears to have resulted in a sediment loss covering more than 100 years (Table 4.2).

The final age-depth model was established using the ^{210}Pb data for ESTH1 and the three ^{14}C dates for ESTH7 (Fig. 4.8a). Figure 8b shows the good agreement between the inferred ages and the ^{210}Pb dates in the upper 30 cm of the record.

Table 4.2 Temporal relationship between sediment cores ESTH1 and ESTH7.

Depth in ESTH7 (cm)	Depth in ESTH1 (cm)	Evidence or by core correlation	Inferred dates by core correlation (AD)	Dates in the age-depth model (AD)
5.25	/	The appearance of high percentage of *A. granulata* var *angustissima*	1999[1]	/
14-26	0-11	Indicator species *S. binatus*	Post-1970	1973-1993
28.5	30	Mg/Ca, Cr, Ni, Mn	1877[2]	1884
38	45.5	LOI, Cr, Mg/Fe, Ca	1630[3]	1720
41	53	Grain Size	1550[3]	1614
46.5	63.5	Fe, Cr, Ba, Mn, Fe/Mg	1406[3]	1426
47.5	65.5	LOI, Grain Size	1380[4]	1389
49.5	69.5	Ba, Ni, Co	1250[3]	1303
51	72.5	LOI, diatoms	1180[3]	1216
59.5	89.5[5]	/	930[4]	906
63.5	97.5[5]	/	840[4]	818

1: Based on ^{210}Pb dating of ESTH7 and plankton monitoring data

2: Based on ^{210}Pb dating of ESTH1

3: Interpolated dates using average sediment accumulation rates

4: Results from calibrated ^{14}C dating

5: Extrapolated depth according to the sediment accumulation rate relationship between the two cores

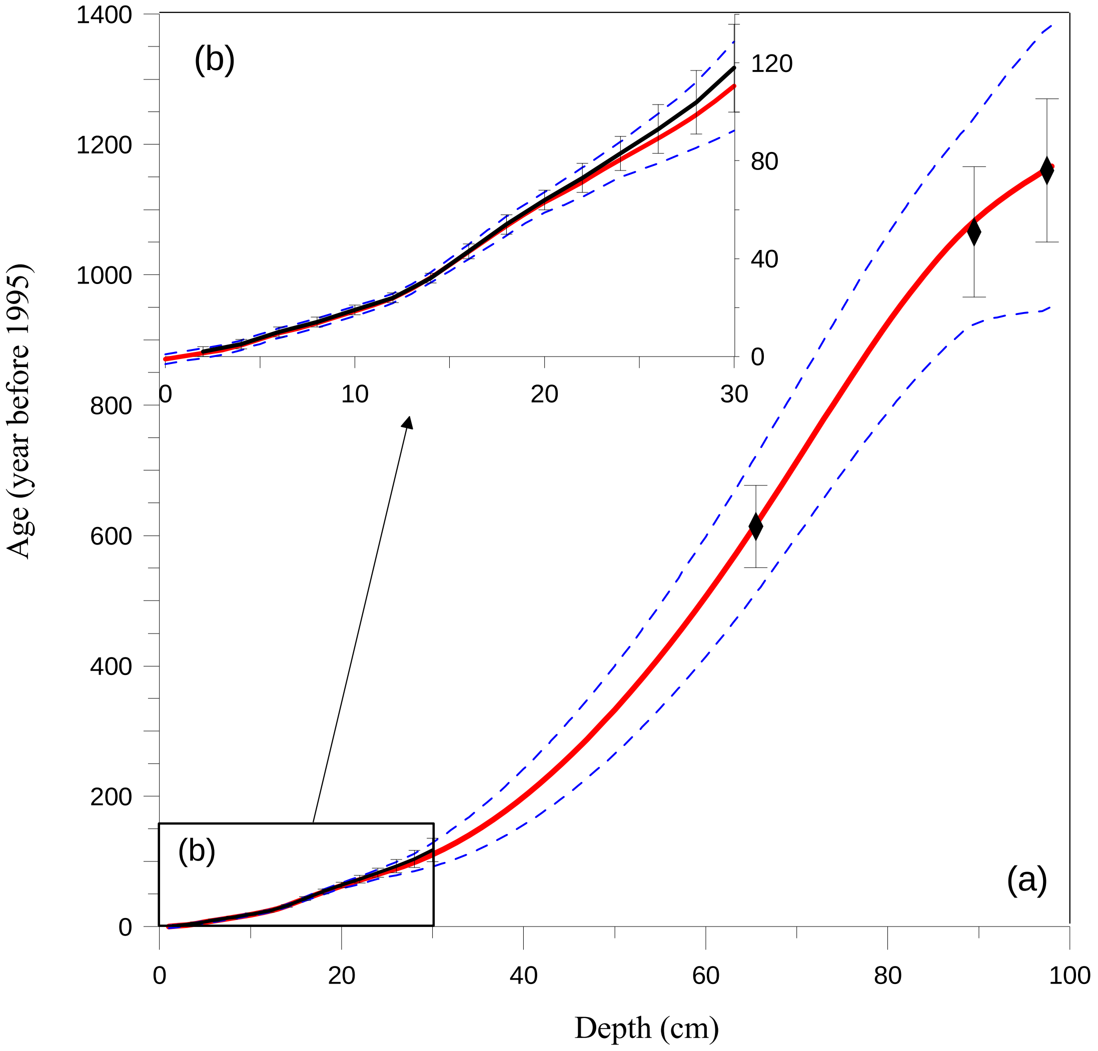


Fig. 4.8 Age-depth plot for core ESTH1 (a). Inset (b) shows the age-depth model for the period after 1880 AD based on ^{210}Pb dating analysis. The solid line in red represents the model fitted by a spline smoother and the dotted lines are the 95% confidence limits for the fitted model. The solid lines in grey and diamonds represent the ^{210}Pb and ^{14}C dates, respectively (vertical error bars are shown).

4.5 Discussion

4.5.1 Sediment discontinuities in core ESTH7

Multi-proxy comparison between cores ESTH1 and ESTH7 from Esthwaite Water indicated that both a slumping and an hiatus event was evident in ESTH7. This core was taken from the deep central area of the lake. Generally, the deepest area of the lake receives most sediment mass and can reflect well the whole lake situation

(Charles *et al.*, 1991; Smol, 2002). Theoretically, all sediment cores taken from the same lake can be related on a temporal scale, although different sediment accumulation rates often exist across the basin (e.g. Anderson, 1990; Barker *et al.*, 2005). In Esthwaite Water, existing palaeolimnological data from several cores taken over the last 15 years (ESTH1-ESTH8) from the deep central area of the lake, have exhibited close matches in LOI and diatom stratigraphies (unpublished data). However, in an earlier core described in Sanders *et al.* (1992), there was evidence for various mechanisms that may disrupt the sediment record in Esthwaite Water, namely, a broad Chernobyl ^{134}Cs peak and an earlier peak in polychlorinated biphenyls (PCB) fluxes than might be expected based on UK production dates. In that study, Sanders *et al.* (1992) concluded that post-depositional changes had occurred due to vertical mixing processes (e.g. bioturbation and molecular diffusion). Hence the palaeolimnological records of Esthwaite Water may be prone to disturbance.

PCA ordination (Fig. 4.7) based on all the sedimentary proxies of ESTH7 positioned the slumping samples alongside with those deposited around 1805-1880 AD (corresponding depth of 24.25-28.25 in ESTH7). The slumping event occurred at around 1990, according to the inter-core comparison. An hiatus occurred at around 25 cm in ESTH7. Given the relatively high abundance of the eutrophic species *Stephanodiscus binatus*, the layer 25 cm should be dated to post-1970 AD as this species was not observed in the lake plankton until this time (Fig. 4.6). Correlation of cores ESTH1 and ESTH7 suggests that this layer was dated to 1877 AD (1884 AD calculated by the mix-effect additive age-depth model). The difference between the two dates indicates that a period of *c.a.* 100 years (1870-1970 AD) is missing from the sediment record of ESTH7.

There are several possible reasons for the discontinuities observed in ESTH7. Firstly, given the small size of the lake and the steep sloping nature of the basin in the coring area, occasional sediment slumping events are likely (Larsen & MacDonald, 1993). For example, a study in a small lake (25 ha) in New York revealed that approximately

50% of the material deposited in the main basin was derived from the subaqueous slumping of material from basin slopes (Ludlam, 1974). Bennett (1986) found several slumping depositions in a small lake with an average slope of 5°. In Esthwaite Water, basin slopes near the central area are similarly steep (*c.a.* 6°, see Fig 1.2), with the water depth contour of 10 m located only about 100 m from the shore. The high slope may result in sediment focusing and thus an increased possibility of slumping in this region. Secondly, Esthwaite Water is a small lake that has been the subject of several palaeolimnological studies. Numerous sediment cores have been extracted from the lake, mostly from the deepest area (see review in Bennion, Monteith & Appleby, 2000). Coring work can potentially disturb the surrounding sediments and such disturbance should not be ignored. Thirdly, incorrect or careless sampling can result in sediment discontinuities. This can be avoided by following coring protocols and selecting coring sites with care, and is not likely to be a factor in explaining the disturbed record of ESTH7.

4.5.2 Age-depth model for core ESTH1

The ^{14}C dating based on macrofossils provides a relatively reliable chronology for the lower part of ESTH7. The selected alder leaves are less susceptible to contamination by inert carbon than their aquatic counterparts since they obtain their carbon by subaerial photosynthesis (Turney *et al.*, 2000). The dates may thus avoid hard-water effects that have been noted elsewhere (Barnekow, Possnert & Sandgren, 1998).

The age-depth model based on the mix-effect additive method presented here differs from previous age-depth estimation procedures (e.g. Boreux *et al.*, 1997; Bennett & Fuller, 2002). This method allows the integration of dating points dated by several different procedures, such as ^{14}C or ^{210}Pb dating, and also the inclusion of layers with specific dating. The only information needed is the central point of a calibrated age scale and a measurement of its uncertainty. The various inherent uncertainties of the different procedures are accounted for by a weighted regression method (Heegaard, Birks & Telford, 2005). To test the robustness of this method, another calculation based on ^{210}Pb dating and the first two ^{14}C dating results was used to develop an age-depth relationship and the third ^{14}C date (1160 BP) was used for validation purposes. Results showed that the inferred age for the third macrofossil sample was 1204.4 BP, which is within the range of the ^{14}C dated result (see Table 4.1). This consistency also mirrored the accuracy of ^{14}C dating based on the alder leaves. Furthermore, the age-depth model provides much reliable dates since it takes account of the variability of sediment accumulation rates. Due to the inherent consistency of the trends in sediment accumulation rates, the dates inferred by the model are younger than those obtained by linear interpolation; however, the two ^{14}C dates are calibrated to within *c.a.* twenty years of the older dates (Table 4.2).

4.5.3 Spatial-temporal variability of sediment accumulation rates

Sediment accumulation rates have changed significantly over the recent centuries in Esthwaite Water. The average mass sediment accumulation rates (MSAR) in ESTH1 were <0.04 g cm^{-2} year^{-1} prior to 1960 but increased to >0.06 g cm^{-2} year^{-1} after 1960 (Fig. 4.9). Sediment accumulation rates (SAR) exhibited a similar pattern to MSAR due to the relatively stable dry bulk density of the sediment throughout the core. Higher sediment accumulation rates, particularly after 1960, might reflect increased soil erosion due to anthropogenic impacts in the catchment. Indeed earlier palaeoecological work conducted by Franks (1956) revealed the ratio of tree to non-tree pollen to be negatively associated with the soil erosion rate, indicating that increased intensity of erosion was probably brought about by diminishing tree cover.

SAR in Esthwaite Water exhibit high spatial variability, even in cores taken from the same area. The SARs derived in this study are, however, comparable with several existing sediment cores taken from Esthwaite Water. For example, a long core, taken from the deepest area of the lake in the 1950s, had average sedimentation rates of 0.2-0.4 mm year^{-1} (Mackereth, 1966) and based on the three ^{14}C dates, the SARs in ESTH7 are 0.38 mm year^{-1}, 0.27 mm year^{-1}, and 0.51 mm year^{-1} for the zones of 28.5-47.5 cm, 47.5-59.5 cm, and 59.5-63.5 cm, respectively. However, the SARs of

ESTH1 and ESTH8 are twice and four times as high as those in core ESTH7, respectively. Whilst there are many studies comparing sediment processes for multiple cores from a single basin (e.g. Anderson, Korsman & Renberg, 1994; Rose & Harlock, 1999; Tibby, 2001), it is seldom that such large differences in SAR are reported for cores taken from the same area of a lake. Given the good agreement in the Esthwaite Water profiles of the palaeolimnological proxies in various cores over time, the sediment processes occurring in the coring area appear to be coherent. Therefore the differences in sedimentation rates most likely result from the morphology of the lake basin, with its steep slopes.

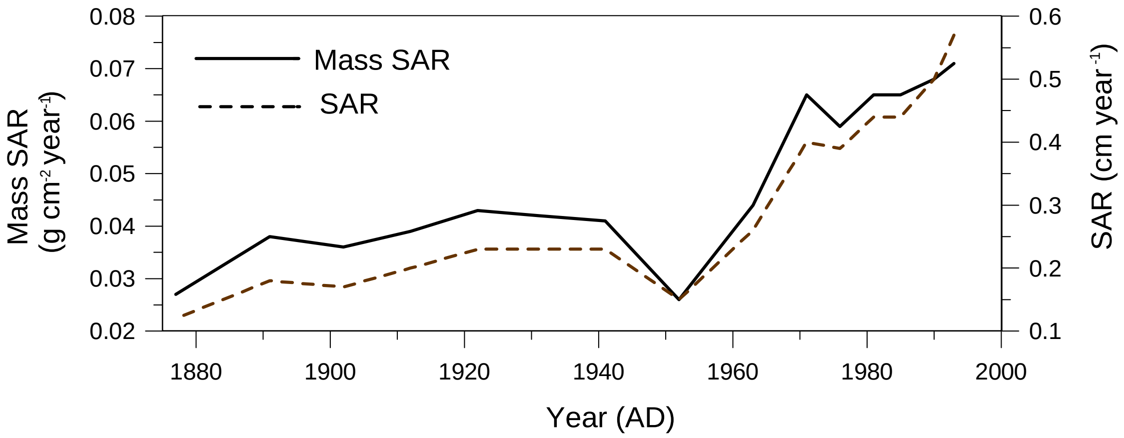


Fig. 4.9 Sediment accumulation rates of core ESTH1 since 1880 AD.

4.5.4 Implications for palaeolimnological work

This study illustrates that large differences in sediment integrity and sediment accumulation rates occur in different cores from the same lake, even from the same area of a lake. Consequently, great care is required in selecting suitable coring sites for palaeolimnological studies. Ideally, the point of sediment collection should represent, both quantitatively and qualitatively and as far as possible, an "average" accumulation of materials for the entire basin (Smol, 2002). This is the most important assumption for palaeolimnological studies. However, limited studies have been conducted to test this prior to detailed proxy analysis, which is normally based on one or two cores. Our findings suggest that this assumption is under risk not only for large, deep lakes with complicated coastlines (e.g. Lake Baikal, Bangs *et al.*, 2000), but also for small lakes.

There are no fixed guidelines for coring site selection, as lake morphometry varies from site to site. Nevertheless, this study demonstrates that coring sites located close to steep morphometric gradients should be avoided. Examination of available morphometric data and maps, and or collection of bathymetric data prior to coring is therefore essential (Smol, 2002).

An effective solution for coping with a disturbed sediment core was illustrated in this study. Multi-proxy comparison among different cores (ESTH1, ESTH7 and ESTH8), and with long-term phytoplankton records, was used to define the occurrence and timing of sediment disturbance, in this case a slumping and an hiatus event. Lake basins are natural sediment traps and hence all environmental signals, even those marking disturbance, are incorporated into the sediment. Consequently, a range of contemporary and palaeolimnological records, including existing monitoring data, sediment stratigraphy, episodic events and other anthropogenic time markers can all provide valuable information to aid our understanding of sediment processes.

4. 6 Conclusions

This study reveals how it is possible to use monitoring and palaeolimnological records to resolve the dating puzzle for a disturbed sediment core in Esthwaite Water. Using the “wiggle-matching” method, sedimentary proxies in cores ESTH1 and ESTH7 were temporally correlated in terms of the ^{210}Pb and ^{14}C dates. However, a slumping and an hiatus event were detected in core ESTH7 by the multiple comparisons. The data were used to establish an age-depth model for the lake over the past 1200 years by means of the generalized mixed-effect method.

Information on the sediment discontinuities were obtained by the multi-core correlation and resulting chronology. PCA ordination based on the sedimentary proxies revealed that the slumping material in the core originated from sediment deposited in around 1805-1880 AD. The hiatus resulted in the loss of *c.a.* 100 years of material, from 1870 to 1970, according to the inferred dates.

The three cores taken from the same area of the deep basin exhibited high variability in sedimentation rates with one core having rates twice as fast and another rates four times as fast as the core with the lowest accumulation rates. This study demonstrates that considerable heterogeneity in sediment accumulation rates can occur in the deep basins of even relatively small lakes and suggests that great care is needed when selecting coring sites for palaeolimnological studies.

Chapter 5 Nutrients provide a stronger control than climate on inter-annual diatom dynamics in Esthwaite Water: evidence from monitoring and palaeolimnological records over the past 60 years

5.1 Introduction

Lakes are important resources for humans, not only for supplying drinking water, but also for supporting other human activities such as agriculture, industry and tourism. Nevertheless lakes face a variety of environmental pressures which greatly threaten their ecological integrity (Vorosmarty *et al.*, 2000). Growing evidence has shown that lakes have undergone substantial deviations from pristine conditions over the past few centuries (e.g. Bennion, Fluin & Simpson, 2004; Taylor *et al.*, 2006; Bjerring *et al.*, 2008). One key pressure that is responsible for observed changes is eutrophication and this has received wide attention and continues to dominate the science and policy agenda (Bennion & Battarbee, 2007). Lakes have also experienced serious pressure from climate change which in recent decades has proceeded at a rate beyond historical natural variability (IPCC, 2007; Battarbee & Binney, 2008). The changing climate may alter the structure and function of aquatic ecosystems directly, but may also exacerbate other environmental pressures such as eutrophication included (George, Hurley & Hewitt, 2007; Whitehead *et al.*, 2009; Kernan & Battarbee, 2010).

For the purposes of restoration and lake management, a knowledge of how climate change (current and future) affects lake ecosystems and how it may interfere with nutrient dynamics is required (Jeppesen *et al.*, 2010). To decipher the confounding effects of climate and nutrient factors on lake ecosystems, long-term monitoring datasets including ecological communities and environmental variables are needed. But such records are rare or may lack consistency in methodology over different monitoring periods (Blenckner, 2005). From this point of view, palaeolimnological records can be used to augment relatively short observed records to infer historical changes in lake ecosystems over longer timescales of several centuries or more (Smol & Cumming, 2000; Battarbee *et al.*, 2005a); however, they lack direct records of historical climate and nutrient changes and may also lack good chronological resolution. Given the clear pros and cons of monitoring and palaeolimnological records, their integration potentially provides more comprehensive and suitable data to conduct research on separating climate and nutrient effects on lake ecosystems (Battarbee *et al.*, 2005a).

Esthwaite Water is a well-studied site for which not only a long-term high-resolution monitoring record but also numerous palaeo-environmental studies based on sediment cores have been undertaken (see chapter 1). A monitoring programme, initiated by the Freshwater Biology Association from 1943, offers a rare long-term and detailed record of key climate and nutrient related variables and biological communities (Maberly *et al.*, 1994a). Importantly, this monitoring record covers both oligotrophic (prior to 1970s) and eutrophication phases (post 1970s), whereas most other monitoring records only capture the nutrient enrichment phases (Battarbee *et al.*, 2005a). Consequently, this valuable record allows a direct comparison of the responses to climate forcing under different trophic conditions.

Given the complex interactions among environmental variables, statistical approaches have recently been developed to disentangle their relative effects. For example, variance partitioning (Borcard, Legendre & Drapeau, 1992) is used frequently to identify the major forcing variables and their relative effects on aquatic ecosystems over different spatio-temperal scales (e.g. Lotter & Birks, 1997; Hall *et al.*, 1999; Quinlan *et al.*, 2002; Bradshaw, Rasmussen & Odgaard, 2005; Kernan *et al.*, 2009). This method, however, can only output the total effect of the various covariates over the time period of interest, precluding answering questions about when and where the various covariates may be driving change in the response variable(s) (Simpson & Anderson, 2009). To overcome this, Simpson & Anderson (2009) presented a innovative study by using a flexible and powerful statistical tool, additive modeling

(Wood, 2006) to elucidate the critical questions of how much, and when, do the confounding factors affect the lake ecosystems (taking Kassjön, northern Sweden, and Loch Coire Fionnaraich, northwest Scotland as examples).

By combining the high-resolution diatom records from a sediment core and the existing long-term monitoring database in Esthwaite Water, this chapter will employ both redundancy analysis (RDA, one form of variance partitioning) and additive models to determine how climate and nutrient have affected the lake ecosystem over the period 1945-2004. First, RDA will be used to identify the major factors driving diatom community changes and to eliminate insignificant and redundant collinear variables. Additionally, the independent effect of each factor on diatom compositions over the whole period will be separated by RDA. Then, an additive model will be employed to present the detailed cause and consequence information of how much, and when, do the major factors (selected by RDA) affect the lake ecosystems. Diatoms were selected since they have been widely used to indicate trophic changes (e.g. Sayer & Roberts, 2001; Bradshaw *et al.*, 2002; Bennion, Fluin & Simpson, 2004; Werner & Smol, 2005; Yang *et al.*, 2008) or climate-induced changes in lakes such as temperature, extent of ice cover, stratification patterns, water depth and salinity change (Smol & Cumming, 2000; Battarbee, 2000; Mackay, 2007). They can, therefore, act as useful indicators of ecological change driven by both climate and nutrients.

5.2 Methods

5.2.1 Site description

Esthwaite Water, UK (N 54°21.56', W 002°59.15') is a small lake with maximum and mean depths of 15.5 m and 4.3 m respectively. It is located in Cumbria, North-West England, where climate is significantly affected by fluctuations in the atmospheric pressure gradient, known as the North Atlantic Oscillation (NAO) (e.g. George, Maberly & Hewitt, 2004). The small catchment (17 km^2) of Esthwaite Water has a distinctive feature of high rainfall, reaching an annual average amount of 1000 mm. The lake water has a short residence time of *c.a.* 90 days and stratifies from around late April to early October (Maberly *et al.*, 1994a).

Currently Esthwaite Water is a eutrophic lake with a TP concentration of 28 $\mu g\ L^{-1}$ (mean of fortnightly data collected in 2008), and in recent decades blue-green algae bloomed frequently. Nutrient loading to Esthwaite Water increased rapidly in the 1970s when a new sewage works was opened discharging treated effluent into the main inflow (Talling & Heaney, 1988). Nutrient inputs continued to increase with the establishment of a fish farm (for rainbow trout) in the southern basin and the consequent introduction of waste from cages to the system after 1981. From 1986 the phosphorus input from sewage was reduced by tertiary chemical treatment (Talling, 1999). Nevertheless, intensive human activities, particularly industry and tourism in the catchment, have continued to exert pressure on the lake system in recent decades.

5.2.2 Long-term monitoring

Long-term monitoring at Esthwaite Water has involved fortnightly water sample collection for the analysis of physico-chemical and biological parameters from 1943 to the current day. Integrated surface water samples (0-5 m from 1943 to 1964, 0-7 m from 1964 afterwards) were collected using a weighted plastic tube (Lund, 1949). Chemical properties including soluble reactive phosphorus (SRP), nitrate (NO_3-N), and SiO_2 were measured according to standard methods (Sutcliffe *et al.* 1982 and Heaney *et al.* 1988). Mean January (mid-winter) SRP concentration was used to indicate nutrient availability in this study because January SRP has been shown to provide the best measure of nutrient enrichment in the lake (Sutcliffe *et al.*, 1982; Talling & Heaney, 1988).

Meteorological data used in this study, including air temperature (AirT) and rainfall, were obtained from two weather stations in the village of Ambleside, which is within 10 km of Esthwaite Water. The first station was operated between 1931 and 1970 and the second from 1965 to 2000. The two records were combined to form a harmonised time-series from 1945 to 2004 by taking average values for the period of overlapping measurements. Given that the NAO index is a good descriptor of regional climate forcing, winter and annual NAO index values (denoted as WNAO and ANAO, respectively) were obtained from the web site maintained by the U.S. National Centre for Atmospheric Research (http://www.cgd.ucar.edu/cas/jhurrell/indices.html) for further analysis.

5.2.3 Extraction and integration of sediment cores

Two sediment cores were taken from the deepest area (~15 m) of Esthwaite Water as follows: (i) ESTH1, a 86 cm core was collected using a mini-Mackereth piston corer (Mackereth, 1969) in June 1995; (ii) the core ESTH7, a 65 cm core was collected using a percussion piston corer (Chambers & Cameron, 2001) in April 2006. ESTH1 was sliced at 0.5 cm throughout and ESTH7 was sliced at 0.25 cm in the top 30 cm and 0.5 cm intervals below 30 cm. Samples were subsequently stored in polyethylene bags at 4°C in the dark.

Both cores were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay using ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector (Appleby & Oldfield, 1978). Details of the chronology are discussed in chapter 4. Given the higher sediment accumulation rates for ESTH1 than ESTH7 during 1945 to 1991 and the consistency in the diatom records of the two cores, sediment material representing the accumulation period 1993-2004 in ESTH7 (2.5-8.5 cm) was integrated with ESTH1 to obtain diatom records over the entire period represented by the monitoring data.

5.2.4 Diatom analysis

Preparation of diatom samples followed standard techniques (Battarbee *et al.*, 2001). A minimum of 300 diatom valves were enumerated for each sample. Diatom identification followed Krammer & Lange-Bertalot (1986, 1988, 1991a, b) and Håkansson & Kling (1990). The fossil diatom data were expressed as percentages and zoned using ZONE version 1.2 (Lotter & Juggins, 1991). Diatom percentages were averaged where multiple samples for the same year were presented.

5.2.5 Ordination

Patterns of diatom community change were summarized using principal components analysis (PCA) of relative abundance data after Hellinger transformations (Legendre & Gallagher, 2001). The first two PCA axes were identified as explaining significant proportions of the variance in the species data when compared to the broken stick (null) distribution (Jackson, 1993). The scores of the two axes were retained as dependent variables for subsequent modelling.

Environmental variables SRP, NO_3-N, SiO_2, Si/P, N/P, Si/N, Air Temp, Rainfall, Winter NAO index and Annual NAO index were transformed (log(x+1) for NO_3-N and SiO_2 and square-rooted transformation for all others) prior to RDA analysis. Time was also square-rooted transformed and was setted as covariable when performing RDA. After removing redundant environmental variables (indicated by variance inflation factors above 20) by a primary RDA, a forward manual selection RDA and Monte Carlo permutation tests identified a minimal subset of environmental variables that explained significant proportions ($p<0.05$) of the variations in the species data. Partial RDA was performed on the dataset to partition the variance explained by each variable into a number of independent components (Borcard, Legendre & Drapeau, 1992). RDA analyses were implemented in the computer program CANOCO 4.5 (ter Braak & Smilauer, 2002).

5.2.6 Additive mixed models

Generalized additive model (GAM) is a non-parametric regression in which the sum of regression coefficients x explanatory variables of a linear regression is replaced by a sum of unspecified smooth functions of the explanatory variables (Hastie & Tibshirani, 1990). Here an additive mixed model (AMM), a specific form of GAM, was used (Wood, 2006; Simpson & Anderson, 2009). AMM contains both fixed and random effects. The former is the standard representation of variables in a linear model, such as the effects of a treatment variable or explanatory variable on the response. Grouping structures may lead to additional sources of variability in the data, which are penalized using a random effect. The random effects component is assumed to be normally distributed. Formally, an AMM can be stated as:

$$y_i = \mathbf{X}_i\boldsymbol{\beta} + \sum_{j=1}^{k} f_j(x_{ji}) + \mathbf{Z}_i\mathbf{b} + \varepsilon_i$$

where y_i is the dependent variable, $\mathbf{X}_i$ is the ith row of the model matrix of fixed effects, $\boldsymbol{\beta}$ is a vector of fixed parameters, f_j (x_{ji}) is a centered smooth function of the jth explanatory variable, i =1, ..., n, is the number of observations, $\mathbf{Z}_i$ is the ith row of the model matrix of random effects and **b** is a vector of random effects coefficients, which are assumed to be normally distributed. The errors, ε_i, are assumed to have a Gaussian distribution.

A series of AMMs as well as GAMs, containing single variable and then their combination as predictor variables, were employed to model the changes of the scores of the first two PCA axis. The optimal degree of smoothing f_j was decided by automatic selection using generalized cross-validation (Hastie & Tibshirani, 1990). *p*-values based on analysis of variance *(*ANOVA*)*, F-ratio tests and Chi-squared tests were used to evaluate the significance of each additional factor. Akaike's Information Criterion (AIC) and an adjusted coefficient of determination (R^2_{adjust}) were used to select the best model (with minimum AIC and highest R^2_{adjust}). Residuals were tested for temporal autocorrelation and, where this existed, continuous order 1 autoregressive correlation structures (CAR1) were used to cope with irregularly sampled data (Simpson & Anderson, 2009).

Both the PCA and AMMs were performed with the R statistical software (R Development Core Team, 2009) using the vegan package (Oksanen *et al.*, 2008) and mgcv package (Wood, 2006) for R, respectively.

5.3 Results

5.3.1 Monitoring records of climate and nutrients

Changes in the major water chemical and climatic parameters over the 60-year time series are illustrated in Fig. 5.1 a-f. Both air temperature and the annual NAO index exhibited high variability, with decreasing trends prior to 1987 and relatively higher values after 1987. Average temperatures for the two periods were 8.65 and 9.27 °C, respectively, indicating an overall warming trend over the monitoring period. Average annual rainfall did not show high variability over the monitoring period, but an exceptional high amount of rainfall was observed in both 1954 and 2000. There was no relationship ($r^2=0.005$, $p>0.1$) between annual rainfall and the NAO index.

Both SRP and NO_3-N remained low before 1970, with average values of 2 $\mu g\ L^{-1}$ and 467 $\mu g\ L^{-1}$, respectively. After 1970, particularly after 1976, increased trends were observed in both nutrients, with average values of 12 $\mu g\ L^{-1}$ and 797 $\mu g\ L^{-1}$ respectively for the period 1970-2004. Silicate (SiO_2) changed little over the monitoring period, with the exception of two silicon exhaustion years (in 1953 and 1993) and one peak value of 3,900 $\mu g\ L^{-1}$ in 1954.

5.3.2 Sedimentary diatom records

Overall, 116 diatom taxa were identified in the sediment core (only the main species are shown in Fig. 5.2 and see full species with relative abundances >2% at least in one sample in Appendix II). Diatom assemblages were dominated by planktonic taxa and showed a typical succession found in many eutrophic lakes. The diatom stratigraphy was divided into two zones. In zone I (prior to 1976), *Asterionella formosa* and *Aulacoseira subarctica* were the dominant species, with average relative abundances of 28% in both cases. Other species typically found in relatively nutrient-poor waters, *Tabellaria flocculosa* and *Achnanthidium minutissimum*, were present with abundances around 10%. *Fragilaria crotonensis*, *Cyclotella comensis* and *Cyclotella radiosa* were also present but with low abundances around 5%. A major shift occurred around 1976 (zone II), with an expansion of taxa associated with more productive waters, such as *A. formosa*, *F. crotonensis* and *Stephanodiscus binatus*. Correspondingly, formerly abundant species such as *T. flocculosa* and *A. minutissimum* gradually declined. Zone II was subdivided into two subzones IIa (1976-1996) and IIb (1996-2005), due to substantial expansion of *Aulacoseira granulata* and its subspecies *A. granulata* var. *angustissima* from ~1996.

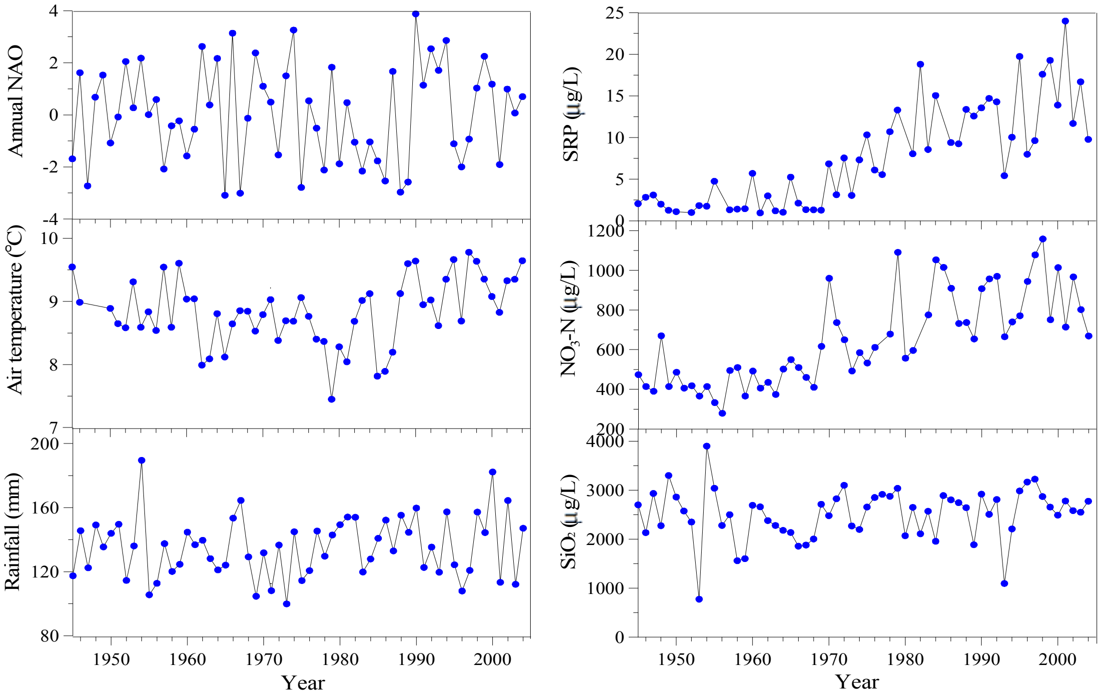


Fig. 5.1 Annual averages for climatic (a-c) and January nutrient (d-f) variables over the monitoring period in Esthwaite Water, respectively

Comparison with a broken stick distribution revealed that the first two axes of PCA summarised diatom community changes well (Fig. 5.2). Axis 1, with a distinct shift in sample scores at around 1976, accounted for 50% of the diatom variance. The scores of axis one were relatively stable prior to 1976 but increased gradually up the core, reflecting the progressive turnover in the assemblages. Axis 2 accounted for 16% of the diatom variance and exhibited higher variability than axis 1 and an obvious decrease after 1985. Only these two PCA axes were included in the AMM analysis, since subsequent axes explained no more variance than expected under the null model.

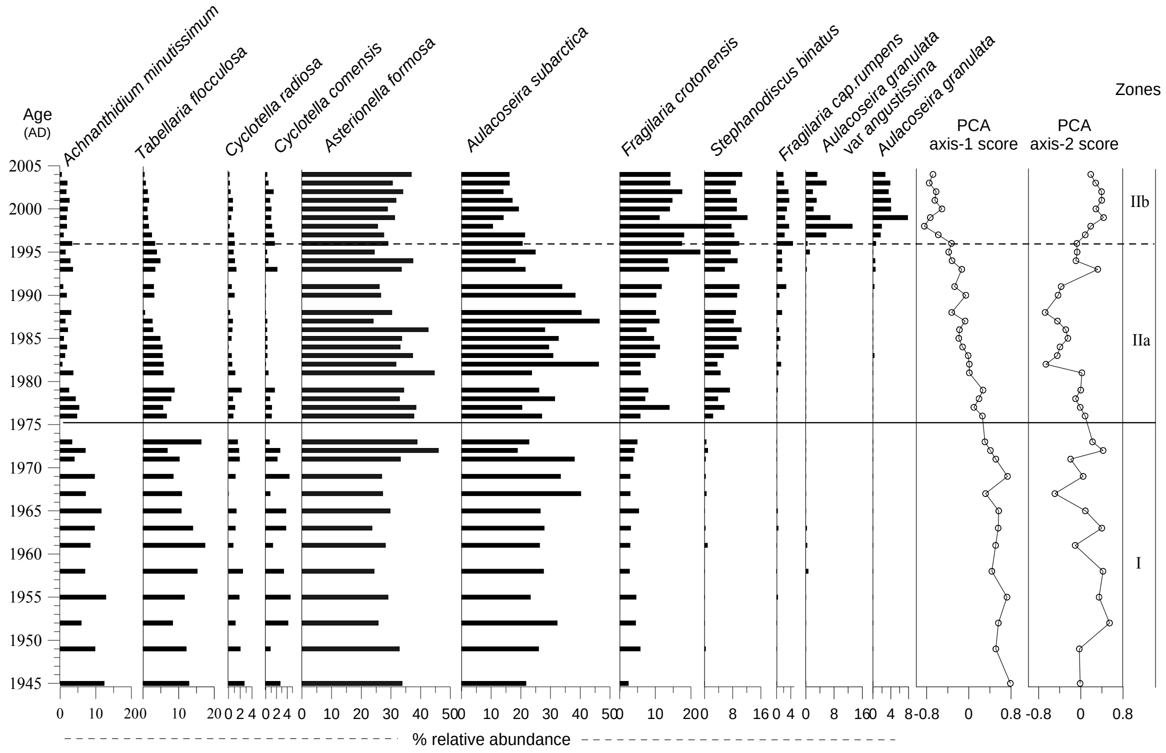


Fig. 5.2 Diatom assemblage changes over the past 60 years in core ESTH0 from Esthwaite Water. Diatom data are expressed as % relative abundance and PCA axis 1 and 2 sample scores are shown. Zones of major compositional change are indicated by horizontal lines with dash lines for subzones.

5.3.3 Redundancy analysis

The RDA ordination biplot of samples and environmental variables (VIFs <20) shows that several variables exhibit considerable collinearity (Fig. 5.3a). Three groups of closely related environmental variables were detected. Nutrient factors SRP, NO_3-N and SiO_2 were correlated with each other, all of which were highly correlated with axis 1. The paired climate factors, air temperature with annual NAO and rainfall with winter NAO, were the other two groups, explaining a considerable amount of diatom variance. Samples from the two zones defined in Fig. 5.2 were separated along the environmental gradients, with zone I samples negatively correlated with the nutrient variables. In contrast, zone II samples were generally positively correlated with nutrients across the whole range of climate conditions. The sample representing the sediment in 1972, fell into zone II due to its high abundance of *A. formosa.*

Given the colinearity among variables illustrated in Fig. 5.3a, a forward manual selection RDA, with Monte Carlo permutation tests, revealed that SRP and AirT jointly explained 32% of the diatom variance, compared to 41% for all variables. Partial RDAs undertaken using SRP and AirT illustrated the amount of variation explained independently by each component (Fig. 5.3b). SRP was the most important variable and significantly explained 22% of diatom variance, while AirT explained 8%. The interaction between SRP and AirT, however, was weak, explaining only 2% of the diatom data.

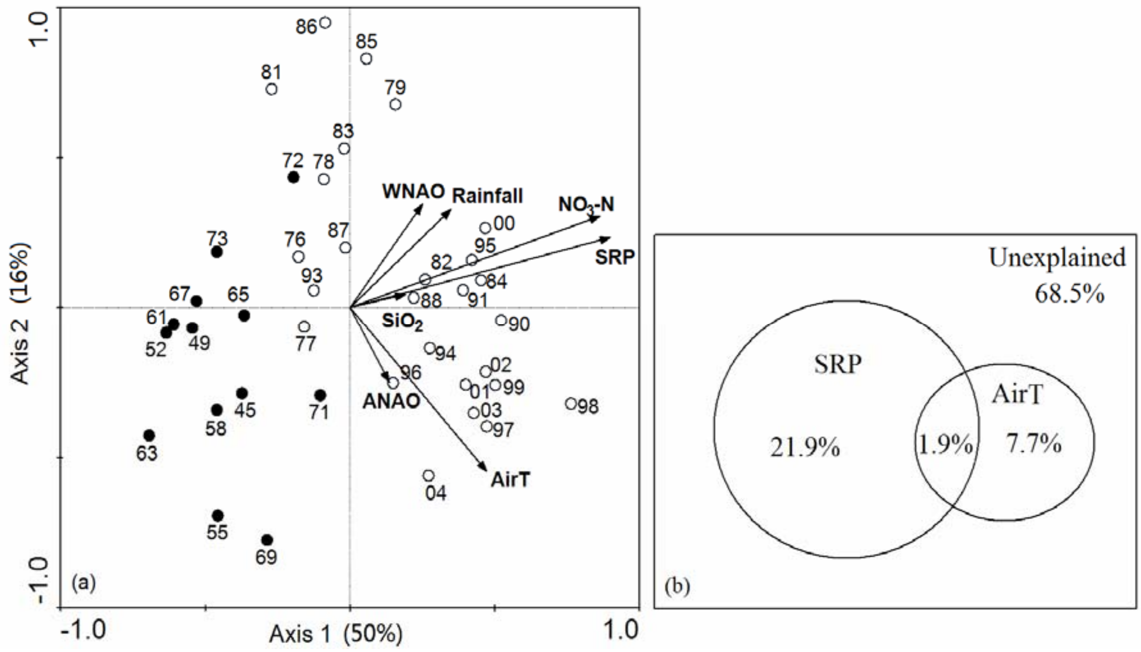


Fig. 5.3 (a) Ordination biplot showing environmental variables and samples plotted against RDA axes 1 and 2 for 60 year sedimentary diatom record. Samples are labelled with the last two numbers of their dates The amount of diatom variance explained by two axes were shown in numbers in parenthesises. (b) Variance partitioning of diatom composition, explained by SRP and AirT. See methods for the abbreviations of environmental variables.

5.3.4 Additive mixed models

A series of AMMs including smooth functions of SRP and AirT as the single variate (or covariate) were fitted to both sets of axis scores, with and without a CAR(1) correlation structure. The AIC and R^2_{adjust} values for modelling the PCA axis 1 scores (denoted as PCAS1) with SRP and AirT together (with values of 18.074 and 0.704, respectively) exhibited significant improvement on those models with only the single variable SRP (21.510 and 0.623) and AirT (51.277 and 0.158). Consequently, the final model selected both SRP and AirT as predictors. The results showed that SRP and AirT did not significantly ($p>0.05$) model the PCA axis 2 scores (denoted as PCAS2) when modeled either solely or together (Table 5.1). Given the limited diatom variance explained by PCA axis 2, modeling was focused on PCAS1 only. No significant difference was observed between the results of the statistical tests of generalized additive models and additive mixed models.

Table 5.1 Model summary for the additive mixed model fitted to diatom PCA axis 1 and 2 scores.

	PCA axis 1			**PCA axis 2**		
Variable	edf*	F	*p*-value	edf*	F	*p*-value
SRP	2.57	31.7	1.92E-9	1	0.29	0.58
Air Temperature	1	7.68	0.008	1	0.00	0.97

* edf refers to effective degrees of freedom

The final AMM fitted to PCAS1 includes a significant smooth term for SRP ($p<0.0001$) and AirT ($p<0.01$). The fitted smooth functions for SRP and AirT are shown in Fig. 5.4. The fitted relationship between PCAS1 and SRP is nonlinear (edf=2.57), while a linear smooth function was used for AirT (edf=1). The values of the link function for SRP increase with increasing SRP and have larger uncertainties at SRP >20 $\mu g\ L^{-1}$ (Fig. 5.4a). In contrast, the link function for AirT is much simple, exhibiting a increase trend with AirT (Fig. 5.4b). The CAR(1) error structure was not required, as assessed by a likelihood ratio test comparing AMMs with and without the structure ($p>0.1$).

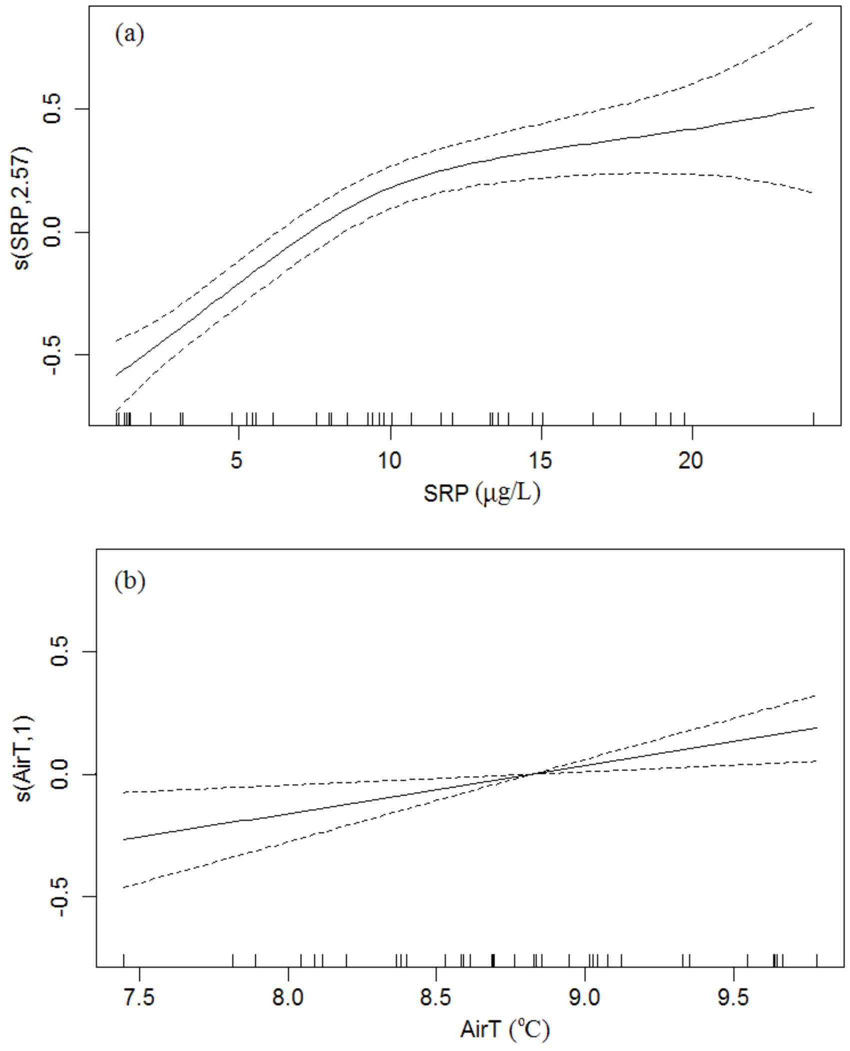


Fig. 5.4 The fitted smooth functions for SRP (a) and air temperature (b) from the final AMM for the PCAS1. The dashed lines are approximate 95% confidence intervals on the fitted functions. The tick marks inside the panels on the x-axis show the distribution of observed values for the two covariates. The numbers in brackets on the y-axis (2.57 and 1 for SRP and AirT, respectively) are the effective degrees of freedom for each smoother.

Contributions to the fitted values of the two covariates (SRP and AirT) are shown in Fig. 5.5. The contribution of SRP to fitted PCAS1 is much larger than that of AirT (Fig. 5c), which is clearly illustrated by the same *y*-scale in the two panels (Fig. 5.5a, b). A significant change occurred at around 1976 for the contribution of both SRP and AirT. Prior to 1976, SRP made a major "negative" contribution to PCAS1 (~-0.5). After this time the effect of SRP was slightly reduced but it still made a considerable "positive" contribution from 1980-2005 (0.3-0.5). AirT exhibited almost zero effect on PCAS1 prior to 1976, but afterwards there was a small contribution of around ±0.2.

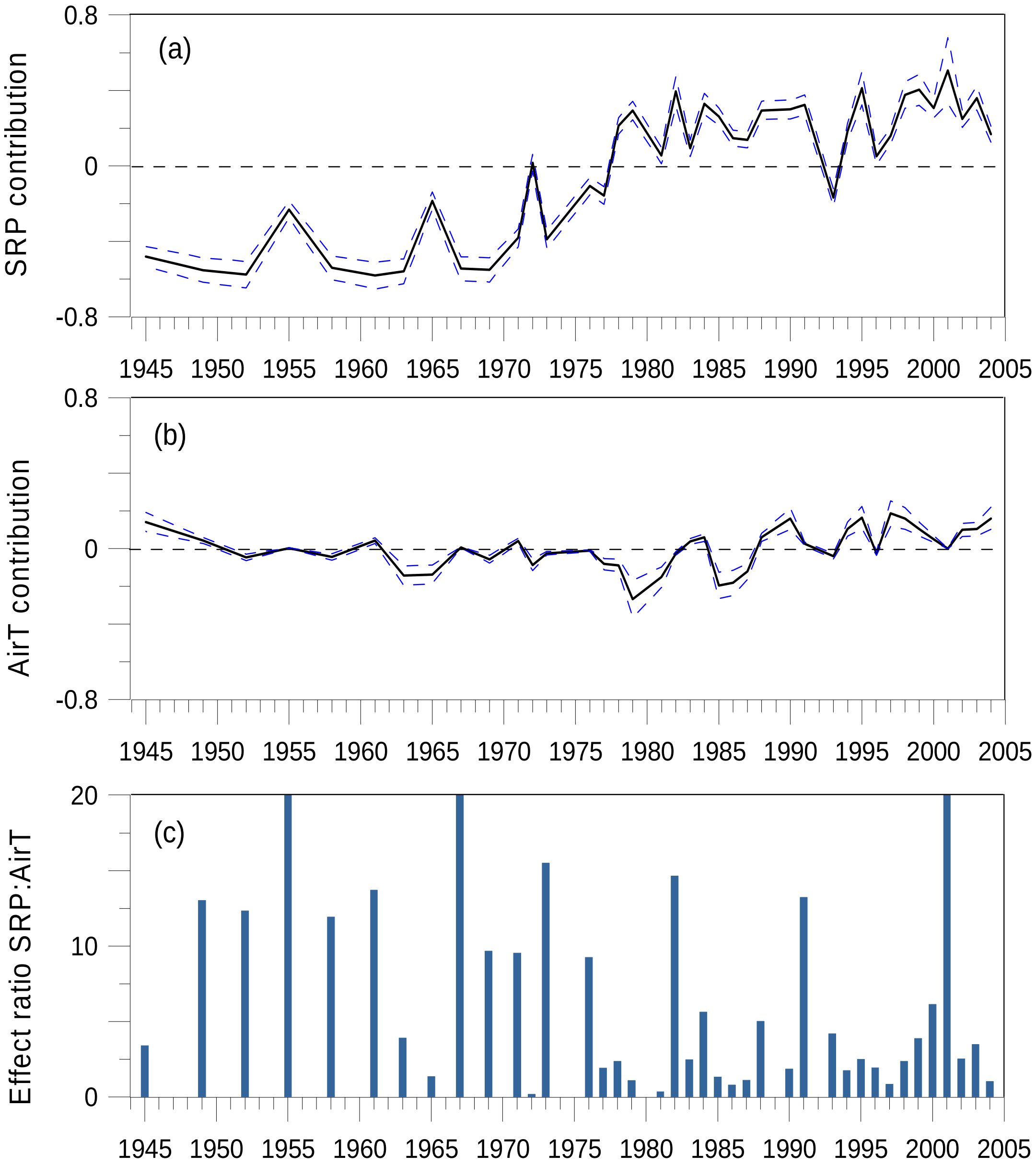


Fig. 5.5 The contribution of (a) SRP and (b) Air temperature to the fitted diatom PCA axis 1 scores. The dashed lines are approximate 95% confidence interval on the contribution. (c) Effect ratio between SRP and AirT. The three highest ratio (>100) in the year 1955, 1967 and 2001 were cut off at 20.

5.4 Discussion

5.4.1 Aquatic environmental change over the past 60 years

Similarly to many lowland lakes in Europe and North America (see review in Smith, Tilman & Nekola, 1999; Schindler, 2006; Ulén *et al.*, 2007), monitoring records of water chemistry from Esthwaite Water indicate substantial nutrient enrichment of the lake over the past 60 years (Talling & Heaney, 1988). Nutrient loading to Esthwaite Water increased rapidly after 1973 when a new sewage treatment works opened, discharging an estimated 409 kg yr^{-1} of phosphorus (TP) into Black Beck (the main inflow to the lake) (Agar *et al.*, 1988). As a consequence, measured annual mean TP concentrations increased steadily from ~25 μg L^{-1} in the mid-1970s to 30 μg L^{-1} during the 1980s and to values in excess of 30 μg L^{-1} since the late 1980s (Bennion *et al.*, 2005). Maximum concentrations of SRP (24 μg L^{-1}) and NO_3-N (1,158 μg L^{-1}) were observed in 2001 and 1998, respectively (Fig. 5.1). While improvements in wastewater treatment after 1986 have reduced point source nutrient inputs, nutrients derived from catchment runoff, a fish-farm installed in 1981 and sediment-P release have negated any potential reduction in lake nutrient concentrations (May, 1997; Bennion, Monteith & Appleby, 2000). In addition, phosphorus and nitrogen accumulation from atmospheric deposition are currently a notable source. Estimates for the atmospheric input of phosphorus (total-P analyses) and N in 1986-1988 were 56 kg P km^{-2} yr^{-1} at a site in the nearby Windermere catchment, and 3,500 kg N km^{-2} yr^{-1} in the whole Lake District area (Talling & Heaney, 1988). Current levels of nutrient deposition are expected to be higher (Tipping *et al.*, 2008).

Esthwaite Water has also experienced considerable climate change over the past 60 years. On a regional scale, the NAO is one of the most important factors affecting Esthwaite Water's physical characteristics, such as lake level, ice-out time and importantly stratification (George, Maberly & Hewitt, 2004). Under positive NAO conditions, the lake catchment has experienced milder and wetter conditions over the past 60 years. For example, the winter air temperature variations at Ambleside show that the average temperature recorded during 1940-1970 was 3.0 °C and that recorded during 1970-2000 was 3.6 °C, while the average winter rainfall recorded for these periods was 5.7 mm day^{-1} and 7.1 mm day^{-1}, respectively (George, Hurley & Hewitt, 2007). Several biological components of the lake ecosystem, particularly phytoplankton and zooplankton, have been shown to have responded to changes in weather conditions in Esthwaite Water over intra- and inter- annual timescales (George, 2000; Talling, 2003; George, Maberly & Hewitt, 2004; Jones & Elliott, 2007).

Diatoms in the core from Esthwaite Water clearly document environmental changes, particularly in lake nutrient status over the past 60 years. Oligotrophic species such as *A. minutissimum*, *T. flocculosa*, *C. comensis*, and *C. radiosa* were present during 1945-1970 when nutrient concentrations were low (average SRP 2 μg L^{-1}, Fig. 5.1). With the slight increase in SRP during 1970-1976, the abundance of the mesotrophic species *A. formosa* increased significantly. However, the main change in the diatom community occurred after ~1977, when eutrophication accelerated (average SRP 12 μg L^{-1} during 1977-2004, Fig. 5.1). Species preferring eutrophic conditions, such as *S. binatus* (Findlay *et al.*, 1998) and *F. crotonensis* started to dominate and have remained abundant in the sediment ever since. The first appearance of *A. granulata* and *A. granulata* var *angustissima* (shift from IIa to IIb) occurred from ~1996. These taxa commonly have high optima for silica and nitrate concentrations (Interlandi, Kilham & Theriot, 1999) and perform well in turbulent conditions (Kilham, Kilham & Hecky, 1986; Hötzel & Croome, 1996). They are also thermophilic species, generally associated with water temperatures in excess of 15 °C (Stoermer & Ladewski, 1976; Poulickova, 1992). Consequently, observed shifts were probably co-driven by seasonal nutrient (e.g. silica and nitrate) and climatic factors (e.g. summer temperature, wind), since annual values of these variables exhibited high variability over the period of *Aulacoseira* blooming (Fig. 5.1). For example, monitoring records showed that the second highest average summer temperature (16.1 °C) occurred in 1995 over the period 1980 to 2000, with relatively higher values after 1996 compared with the earlier period (George, Hurley & Hewitt, 2007). The increasing temperature under the high nutrient conditions probably favoured the growth of *Aulacoseira.*

5.4.2 RDA-based separation of nutrient and climate effects

RDA analysis revealed that SRP explained the largest amount of diatom variance of the measured environmental variables (22%), suggesting that this was the major driving factor of diatom community change over the 60 year dataset. PCAS1 accounted for 41% of diatom variance and was highly correlated to SRP (r=-0.753, p<0.01, n=39). NO_3-N was also highly correlated with SRP (r=0.69, p<0.01, n=39) and likely played an important subsidiary role in controlling diatom dynamics, whereas SiO_2 explained only a limited amount of diatom variance (Fig. 5.3a). Undoubtedly, all three nutrient elements are important to diatom growth in Esthwaite Water and elsewhere (Interlandi, Kilham & Theriot, 1999; Reynolds, 2006). However, their relative importance depends on supply rates and on the order in which they are consumed. Limiting nutrient elements exhibit greater importance in diatom community development. In Esthwaite Water, a two-year monitoring dataset from June 2007 to June 2009 showed that SRP was the first nutrient element to be exhausted and was the most important nutrient factor limiting diatom growth (chapter 2). Thus our inter-annual data support this finding suggesting that SRP is of considerable importance at seasonal to decadal scales in Esthwaite Water. Air temperature, explained just 8% of diatom variance, suggesting climate conditions imposed a weaker effect on diatom inter-annual change than nutrients.

5.4.3 AMM-based separation of nutrient and climate effects

The smoothing functions (Fig. 5.4) and relative contributions (Fig. 5.5) derived from AMM describe diatom responses to changes in SRP and air temperature. Given the additive nature of AMMs, these smooth functions can be shown as covariates in 3-D space (response surface, Fig. 5.6). Here PCAS1 was used to represent whole diatom community changes, since the PCAS2 explained only 16% of variance. The response surface clearly exhibits a gentle response of diatoms to changing climate and a steeper more complex response to nutrients. When SRP values were low (e.g. <6 μg L^{-1} in

1976), diatom communities changed steeply (nearly linear) with increasing SRP; while a more sluggish response occurred when SRP values were higher.

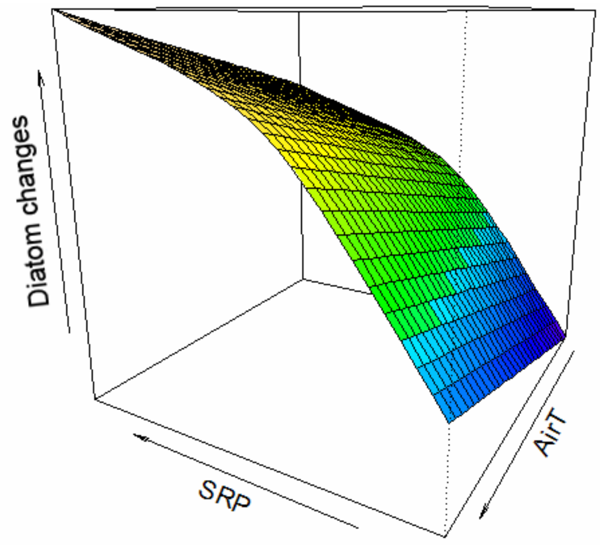


Fig. 5.6 AMM-derived covariate effects (SRP and AirT, respectively) on diatom changes in Esthwaite Water.

SRP availability was clearly more important than AirT in regulating diatom communities when SRP concentrations were low prior to 1976 (Fig. 5.5). When SRP values were low (e.g. <6 μg L^{-1} before 1976), the contribution of SRP to changes in the diatom assemblages was high. In contrast, AirT showed almost no effect on diatom communities prior to 1976 but became stronger after 1976 even through the influence of nutrients remained dominant (Fig. 5.5). The prevailing nutrient effect over the whole period (1945-2004) reflects the various stages of nutrient enrichment, all of which led to diatom community shifts. Furthermore, research has shown that diatoms show little variation in their ability to compete for nutrients across temperature gradients from 5-20 °C (van Donk & Kilham, 1990) and any change in one of the other factors (e.g. pH, nutrients) may change the diatom composition while temperature remains constant (Anderson, 2000). In Esthwaite Water, relatively moderate temperature variations were observed, for example, the monthly maximum and minimum temperature ranges were 5.4-18.7 °C and 0-10.2 °C for the period 1960-1990, respectively (data from http://www.metoffice.gov.uk/climate/uk/averages/19611990/sites/newton_rigg.html, *cf.* Fig. 1.12 in chapter 1). Thus when nutrients (particularly SRP) are in a range where they are potentially limiting the growth of diatoms, it seems that competition for nutrients, rather than climatic factors, drive the community-level shifts.

5.4.4 Synthesis: nutrient and climate effects on diatom communities

In general, climate (including temperature, rainfall, wind, solar irradiation and others) and nutrient factors have complex and interacting effects on aquatic ecosystems. For example, increasing temperatures not only lengthen the period of thermal stratification but also bring more nitrate into lakes as higher temperatures increase soil mineralization (Whitehead *et al.*, 2009). However, against a background of higher temperatures in Southern Europe, the predicted decrease in precipitation and higher evaporation will result in less runoff and, as a result, possibly lower nutrient loading to freshwaters (Jeppesen *et al.*, 2009). Thus the interaction between climate change and a change in nutrient loading may vary between different lake types (e.g. deep vs shallow lakes) and different trophic states (Huber, Adrian & Gerten, 2008). In small, shallow lakes climate can obscure or exaggerate the nutrient enrichment process, since the heat and energy is more easily transferred within the lake than in larger, deeper systems. Nevertheless, in Esthwaite Water it is interesting that the interaction between nutrient and climate factors was rather weak (just 2% in the partial RDA) in terms of their influence on diatom community changes over the 60 year period (Fig. 5.3). By contrast, at the seasonal scale, a two-year monitoring study in Esthwaite Water from July 2007 to June 2009 revealed that seasonal climatic factors (air temperature) were significantly related to nutrient factors (SRP, NO_3-N and SiO_2) and that their interaction imposed significant effects on diatom dynamics (see chapter 2).

The effects of climate and nutrients on diatom communities vary depending on the time-scale of the limnological records. In this study both the RDA and AMM model based on the annual average data revealed that climatic factors (including air temperature, rainfall, ANAO and WNAO) imposed limited effects on diatom dynamics in Esthwaite Water. However, it is undeniable that weather is one of the most important factors controlling diatom dynamics on a seasonal basis (van Donk & Kilham, 1990; Talling, 2003), a timescale normally ignored by palaeolimnologists since most sediment records have coarser resolution. Indeed, Anderson (1995) showed that seasonal-interannual oscillations in diatom plankton may be smoothed out in cores which better reflect longer-term changes (e.g. decades to millennia). This is perhaps one key reason for the limited effect of climate on diatom communities in this study. In fact, temperature, with distinct seasonal cycles but relatively stable inter-annual change, controls many fundamental properties of phytoplankton and is a key factor regulating primary production in most lakes (Reynolds, 2006). This is particularly true as nutrients become less limiting for phytoplankton. Some studies have shown climate warming to have induced forward shifts in the timing of the phytoplankton spring maximum in lakes across the northern hemisphere (Gerten & Adrian, 2000; Straile *et al.*, 2003). Indeed, in Esthwaite Water, long-term monitoring records from 1945 to 2005 also show that the timing of the spring bloom of *A. formosa* has been appearing progressively earlier (Patrick *et al.*, 2004). However, these phenological changes are not exhibited in the sediment records.

5.4.5 Combination of RDA and AMM method

RDA analysis extracted the minimum variable combination (SRP and AirT) for further AMM procedures. Given the great flexibility of AMM, it can provide an excellent fit in the presence of nonlinear relationships and significant noise in predictor variables (Hastie & Tibshirani, 1990; Wood, 2006). However, caution should be exercised to avoid over-fitting of the data, i.e., application of an overly complex model (e.g. with many degrees of freedom) to data so as to produce a good fit. Unexpected results may derive from an AMM based on a group of predictors with colinearity (Zuur *et al.*, 2009). The RDA including all the predictors illustrated the multi-colinearity of the environmental dataset (Fig. 5.3a). Consequently, a predictor selection process for complicated AMMs is generally required (Wood, 2006). This study illustrates that the forward selection RDA method offers a good solution for effective predictor selection.

5.4.6 Combination of monitoring and palaeolimnological records

Monitoring and palaeolimnological data are highly complementary and their combination makes a valuable contribution to understanding how nutrient and climate have affected the site. In general, observational time-series data are very limited both in space and time (Battarbee *et al.*, 2005a), although they provide a precious and high-resolution description of past environmental change. Palaeolimnological data extend the instrumental records and can complement monitoring data, but can also extend well beyond it, affording an important means of validating ecological hypotheses and long-term model behaviour (Anderson *et al.*, 2006, Sayer *et al.*, 2010b). In this study, both ordination analysis and modelling were carried out on diatom records from the sediment core for 1945-2004, alongside analysis of detailed planktonic diatom records for the same period (Maberly *et al.*, 1994a). Sediment records provide more comprehensive diatom habitats (including epiphytic and benthic species) than phytoplankton data and, what is much importantly, the analysis based on the 60 year dataset can be used “experimentally” to test the practicability of using the sediment record for reconstructing longer term changes. This lays the foundation for further analysis on a centennial timescale, i.e. past 200 years, a period over which reliable observational records exist, such as the Central England Temperature series.

One possible disadvantage of using palaeolimnological records to extend monitoring data is that they may suffer from taphonomic biases and occasionally from uncertain chronology (Battarbee *et al.*, 2005a). Fortunately, increasing research has demonstrated that shifts in many biological components of aquatic ecosystems can be reliably recorded in the lake sediments (see review in chapter 2). In Esthwaite Water, there was good agreement between the 59-year monitoring diatom data and corresponding fossil diatom assemblages, indicating that sediment records for this site are reliable (see chapter 2).

5.5 Conclusions

Diatom analyses of an integrated ^{210}Pb dated lake sediment core from Esthwaite Water, covering the period from 1945 to 2004, revealed that fossil diatoms exhibited distinct compositional change in response to nutrient enrichment. Prior to 1970, *Asterionella formosa* and *Aulacoseira subarctica* were the dominant species, with low abundances of *Tabellaria flocculosa*, *Achnanthidium minutissimum* and *Cyclotella comensis*. With the onset of nutrient enrichment from a local sewage treatment works in 1976, there was an expansion of *Fragilaria crotonensis* and *Stephanodiscus binatus,* species typically associated with nutrient-rich waters. *Aulacoseira granulata* appeared in the record from 1996, most likely a result of both nutrient enrichment and warmer summers.

Redundancy analysis based on fossil diatom and environmental datasets over the past 60 years revealed that the most important variable, soluble reactive phosphorus (SRP), followed by air temperature, independently explained 22% and 8% of the diatom variance, respectively. However, the interaction of these variables (2%) imposed limited effect on diatom dynamics. Results of additive mixed models showed that SRP was the most important factor controlling the diatom assemblages for the whole monitoring period. AirT had little effect on the diatom assemblages when nutrient levels were low prior to 1976, indicating that nutrients outperform climate when nutrients are inadequate for diatom growth. With the increase in nutrient availability during the eutrophication phase after 1976, climate became more important in regulating the diatom shifts, although SRP was still the major controlling factor.

The relative effects of climate and nutrients on diatom communities vary depending on the timescale of the limnological records. The RDA analysis and additive mixed model revealed that climate contributed little to diatom dynamics at an annual or decadal scale. However, on a seasonal timescale, climate has a relatively strong influence on diatom community dynamics.

The combination of monitoring and palaeolimnological records employed here offers a great opportunity to explore how nutrients and climate have affected the lake ecosystem over a range of timescales. This dual approach can potentially be extended to much longer timescales (e.g. centuries), where long-term, reliable observational records exist, such as the Central England Temperature series (see chapter 6).

Chapter 6 A multi-proxy palaeolimnological study of climate and nutrient impacts on Esthwaite Water, England over the past 1200 years

6.1 Introduction

Climate change poses one of the most severe threats to the future of human society (Fischlin *et al.*, 2007) and a growing body of evidence suggests that climate change over the last two centuries has moved beyond the range of natural variability (Houghton *et al.*, 2001; Bengtsson *et al.*, 2006; IPCC, 2007). Future climate scenarios predict that intensity of both extreme temperatures and heavy precipitation will increase in many regions of the globe (e.g. Frei *et al.*, 2006; Beniston *et al.*, 2007; Planton *et al.*, 2008; Fowler & Ekström, 2009), with profound implications for the structure and function of the biosphere. One of the key areas of concern is the degradation of the freshwater environment. Fresh waters are particularly vulnerable to climate change due to the nature of their isolation and physical fragmentation within a largely terrestrial landscape, and the pressure from human activities (e.g. the heavy exploitation for drinking water and food) (Woodward, Perkins & Brown, 2010). With declining water quality, quantity and biodiversity, an understanding of how aquatic ecosystems will respond to future climate scenarios is essential (Harrington, Woiwod & Sparks, 1999).

For a better prediction of how future climate scenarios might impact upon aquatic ecosystems, reconstructions of past climatic conditions and ecosystem responses from the pre-industrial as well as the industrial period are essential (Bertrand *et al.*, 2002; Morellón *et al.*, 2010). Both palaeoclimatic and palaeoecological studies, particularly of temperature effects, over the past millennium have received much attention (Mann, Bradley & Hughes, 1999; Crowley, 2000; Mackay *et al.*, 2003; Mackay *et al.*, 2005; Jansen *et al.*, 2007; Jones *et al.*, 2009). This period, characterized by unprecedented human activities and providing a connection between instrumental and proxy records, has been recognized as a key timeframe for understanding past climate variability (Esper, Cook & Schweingruber, 2002; Maasch *et al.*, 2005; Jones *et al.*, 2009). The three major climatic variations during the last millennium are the Medieval Warm

Period (MWP, ~1000-1300 AD) (Crowley & Lowery, 2000; Broecker, 2001; Cronin *et al.*, 2003), the Little Ice Age (LIA, ~1350-1850 AD) (Grove, 1988; Bradley & Jonest, 1993; Hunt, 2006) and recent warming since ~1850 AD. Numerous studies have revealed these special climate phases using a variety of reconstruction techniques (see review in Juckes *et al.*, 2006; Morellón *et al.*, 2010). However, based on the results from different proxies and research areas, these time periods have proved to be asynchronous globally and regionally and delineating their exact 'initiation' and 'termination' has often proved problematic and remains open to debate (Mann, Bradley & Hughes, 1998; Grove, 2001; Moberg *et al.*, 2005; Osborn & Briffa, 2006). Given this differential response pattern, more records covering the past millennium from different regions of the world are needed for further data synthesis, correlation and synoptic mapping.

To date, only a small number of studies have attempted to reconstruct climate change at a high-resolution (Jones *et al.*, 2009). In the English Lake District, there have been several Holocene-scale sediment core studies. However, many of these were undertaken prior to 1990 and had poor chronologies, often based on few radiocarbon-dates from bulk sediment (e.g. Franks, 1956, Franks; Pennington & Tutin, 1961; Oldfield, 1960; Fogg & Belcher, 1961; Round, 1961; Goulden, 1964; Pennington *et al.*, 1976; Haworth & Allen, 1984). Such dates may be influenced by unknown hard water errors and other factors that can result in erroneous ages (Olsson, 1986; Telford, Heegaard & Birks, 2004).

Esthwaite Water is a small lake located in the Windermere catchment of the English Lake District. To our knowledge, there are no existing satisfactory palaeo-records providing detailed descriptions of how climate and nutrients (human activities) impact local aquatic ecosystems during the last millennium for this catchment. In a pilot study, three ^{14}C dates based on macrofossils ensured a high-resolution chronology of a sediment core taken from the lake (see chapter 4). More importantly, numerous documentary records and long-term monitoring records exist for the lake and its catchment which can be used to help validate palaeolimnological reconstructions (see chapter 1). For example, monthly temperature records from Central England (CET, Fig. 6.1a, b) and monthly precipitation records for the central English Lake District (Fig. 6.1c) both extend back to the mid-eighteenth century, providing a rare opportunity for a direct comparison of palaeolimnological and climate data over a period of a few hundred years. Consequently, Esthwaite Water is an ideal site to explore climate variability and nutrient evolution over the past ~1200 years, with special focus on the Medieval Warm Period, the Little Ice Age and recent anthropogenic change. Combined with physico-chemical parameters such as loss on ignition (LOI), grain size, and major and trace elements, this study employs diatoms as the major proxy, because they are sensitive to both changes in climate and nutrients (Battarbee *et al.*, 2001; Stoermer & Smol, 2001). Further, good ecological information exists regarding diatom ecology and seasonality in this lake (see chapter 2 and chapter 5).

6.2 Study site

The catchment of Esthwaite Water covers approximate 17.4 km^2. The geology consists mainly of volcanic rocks, including the Borrowdale and Bannisdale series, which are hard and weather to thin soils. The main soil associations are the Bangor, Denbigh, Malvern, and Wilcocks associations. These are described as well drained or slowly permeable. The terrain is mountainous with high slopes (*cf.* slope of 30^o for Windermere catchment, see Colin, 2003). The steeper slopes with thin soils give high rates of runoff. More information on the climatic setting and water quality of Esthwaite Water can be found in chapter 1.

Similarly to most other lakes in northern and western Europe, Esthwaite Water is significantly affected by regional climate influences such as the North Atlantic Oscillation (NAO, Hurrell *et al.*, 2003). For example, George *et al.* (2004) found that the NAO index had a high correlation coefficient with lake surface and bottom temperatures, winter nitrate and dissolved reactive phosphorus. By comparison with the other two larger and deeper lake basins (Lake Windermere) in the same catchment, Esthwaite Water responds to the changing climate more sensitively (George, Maberly & Hewitt, 2004).

There has been a long history of human activity in the lake catchment (Table 6.1). For example, evidence of mining and quarrying dates back to the 12th Century (Postlethwaite, 1913). Historically, farming, in particular of sheep, has been and remains the major agricultural land use in the region. The first railway connection to

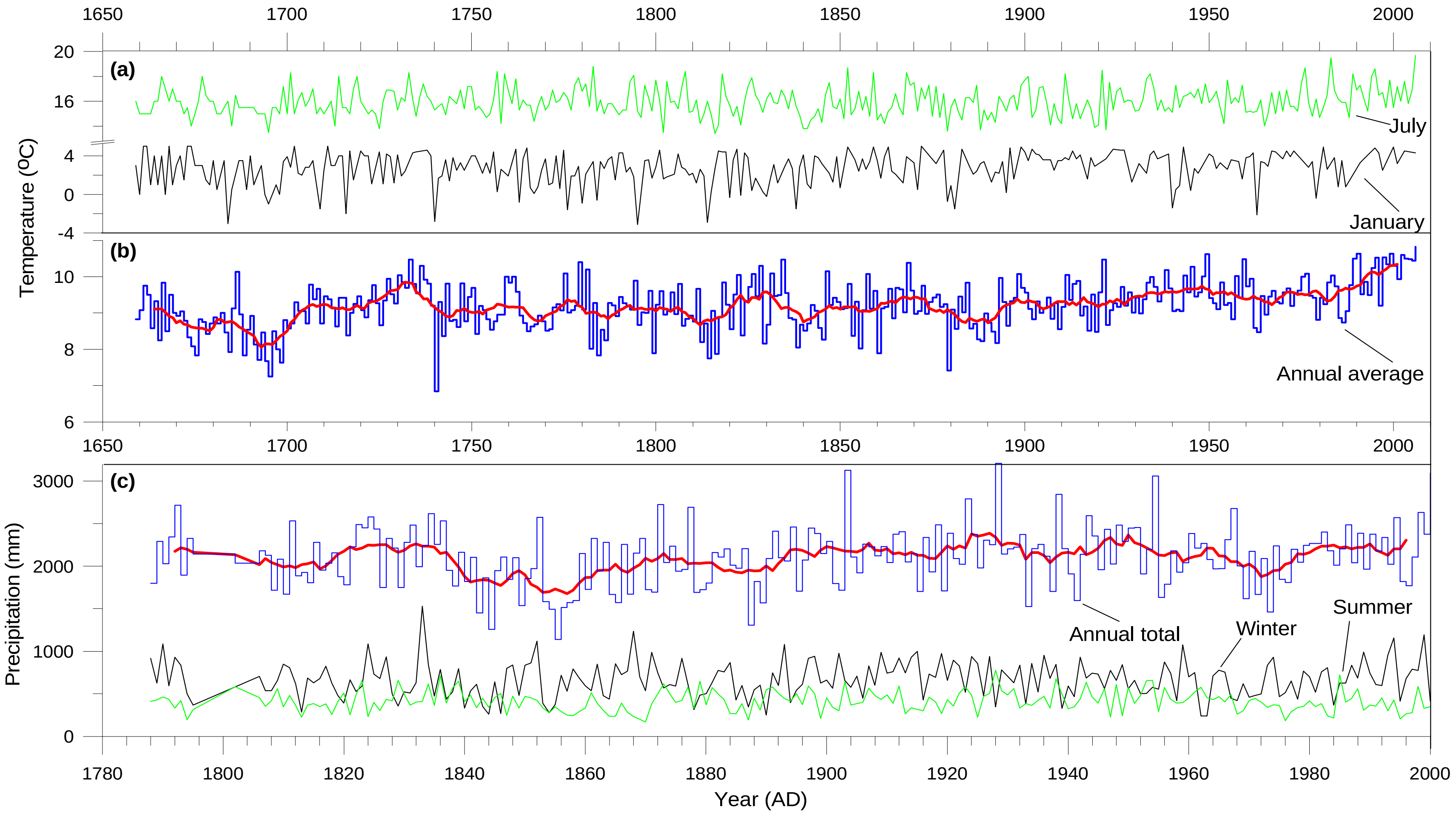


Fig. 6.1 Climate records over the past several centuries. (a) January and July temperatures from the CET record (data from the Meteorological Office); (b) annual average temperature from the CET; and (c) precipitation records for the central Lake District (data from Barker, Wilby & Borrows, 2004)

Windermere was established in 1847 and resulted in a rapid increase in the number of tourists visiting the area (Rollinson, 1967; Smyly, 1961; George, Hurley & Hewitt, 2007). More recently, Esthwaite Water has experienced eutrophication due to increasing nutrient inputs from lowland pasture in the catchment, sewage effluent from local villages and from a fish farm on the lake. This degradation has occurred over the same period as global warming such that the lake has been affected by multiple stressors.

Although several "classical" palaeolimnological studies have focused on the Holocene vegetation history of the Esthwaite Water catchment (Franks, 1956; Franks, Pennington & Tutin, 1961; Pennington, 1970, Pearsall & Pennington, 1947; Pennington & Tutin, 1964, Pearsall & Pennington, 1973; Pennington, 1975), the late Holocene period, particularly for the past two millennias, is poorly understood. Recently, a high-resolution pollen analysis was conducted for Hulleter Moss in south Cumbria (Coombes, Chiverrell & Barber, 2009). Hulleter Moss (W3°01.27', N54°11.99') is within the Rusland Valley (see Fig. 1.2 in chapter 1), which is less than 10 km from Esthwaite Water (W2°59.15', N54°21.56') within the same catchment. A comparison of pollen composition from the Esthwaite Water core of Franks, Pennington & Tutin (1961) and the Hulleter Moss core of Coombes, Chiverrell & Barber (2009) revealed a similar assemblage of *Betula, Quercus, Pinus, Alnus* and other herb species in the early twentieth century. Therefore, pollen records from Hulleter Moss offer a good foundation for the interpretation of palaeolimnological records in Esthwaite Water (see Fig. 6.2).

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Table 6.1 Historical records of human activity and land-use for the Esthwaite Water catchment and the English Lake District (LD). Information source: [*] Macan, 1970; [★] Rollinson, 1967; [Θ] Pearsall & Pennington, 1947; [§] Bouch & Jones, 1961); [Ψ] Marshall & Davies-Shiel, 1971; [+] http://www.dfmrt.org.uk; [※] Grove, 1988; [Φ] Horrox, 1994

Age	**Human activity and land-use record**
20th century	● fish cages were introduced in 1981 and removed in 2009 ● Continued expansion of tourism facilities such as hotels, boating *et al.* ● Sewage treatment works opened in Hawkshead in Esthwaite Water catchment in 1973 and was improved by tertiary chemical treatment in 1986 ● In 1960s the last iron ore workings at Hodbarrow was closed, the steelworks at Barrow closed in 1984 and the last iron furnace, Cairds of Barrow closed in 1990[Ψ] ● The LD became a National Park in 1951
19th century	● Railways reached Kendal (1846) and Windermere (1847), leading to the expansion of tourists. ● In the mid-1800's blast furnaces began using imported coke as fuel. The sleepy fishing villages of Barrow and Millom soon became towns based on iron production[+] ● Population increased in 19th century, e.g. Between 1800 and 1831, an increase of 36% was recorded (from 17,887 to 24,311) in Furness and Cartmel. Greater development of textile manufactures, mining, ironworking and shipping was already manifest by 1830 in the LD catchment[§] ● More gunpowder plants producing for mining work were established in Elterwater (1824) Black Beck and rural Furness (1860) [Ψ]
18th century	● In 1778, Father Thomas West wrote A Guide to the Lakes, which started the era of true tourism in the LD[*] ● The first gunpowder works was built in south of Kendal on the river Kent in 1764, followed by others near Basingill (1790) and Lowwood in Furness in 1799[Ψ] ● Agriculture remained backward until the late 18th and early 19th century[★] ● Iron melting technique was improved in the early 1700s[§] ● Kendal became a centre of several textile manufacture[§] ● After 1750 there were improved roads under turnpike trusts[§] ● Since 1750 there was large-scale amenity planting and woodland conservation in the LD, although grazing continued to expand[Θ]
17th century	● The largest forge was removed to Bunawe because it was no longer possible to obtain charcoal in the LD, suggesting that deforestation reached its greatest extent[Θ] ● A large company, Lead Miners in England and Wales, was established in 1693 and lead exploitation of Cumberland started to flourish[§]
16th century	● Plague occurred in Hawkshead 1577 and larger plague in Newton Rigg 1587 and 1596[§] ● A survey in 1567 showed denudation of 233 acres in Low Furness and 4090 in Furness Fells. By 1650 the low Furness woods had almost disappeared[§] ● Mining expanded: the Society of Mines Royal was established with rights over all the minerals in the LD, indicating large-scale operations in the LD[§,*]
14th century	● Black death reached England in June 1348, leading a decrease of 1/3-1/2 of the population. By the end of 1350 the Black Death had subsided, but it never really died out in England until the late 17th century when England became largely free of serious plague epidemics[Φ] ●Scottish poured into northern Cumbria and the raiding continued throughout the 14th century, which resulted in devastation of the countryside and population decrease[★]
13th century	● Famines in England in 1272, 1277, 1283, 1292 and 1311. Years between 1314-1319 saw harvests fail in nearly every part of Europe[※] ● Forest areas diminished and more and more land was brought into cultivation. King Henry III sent orders that all woodland should be deforested[★] ● Charcoal burning was flourishing[★]
11th-12th century	● Norman barons divided up and Abbeys were built across the whole LD and promoted sheep-farming, which lead to further removal of woodland for pasture; monks started smelting iron ore which led to further pressure on the woods[*] ● Big market towns appeared in 1189 AD at Kendal[★]
9th-10th century	● Norse came to Cumbria, clearing the woods and settling, and spread in the LD[Θ,*] ● Norse colonization, with a mode of life based largely on sheep, which resulted in an intensification of sheep-grazing[Θ]
7th-8th century	● Anglian colonization period which has been suggested by place names in Cumberland and Lancashire for King Aethelfrith

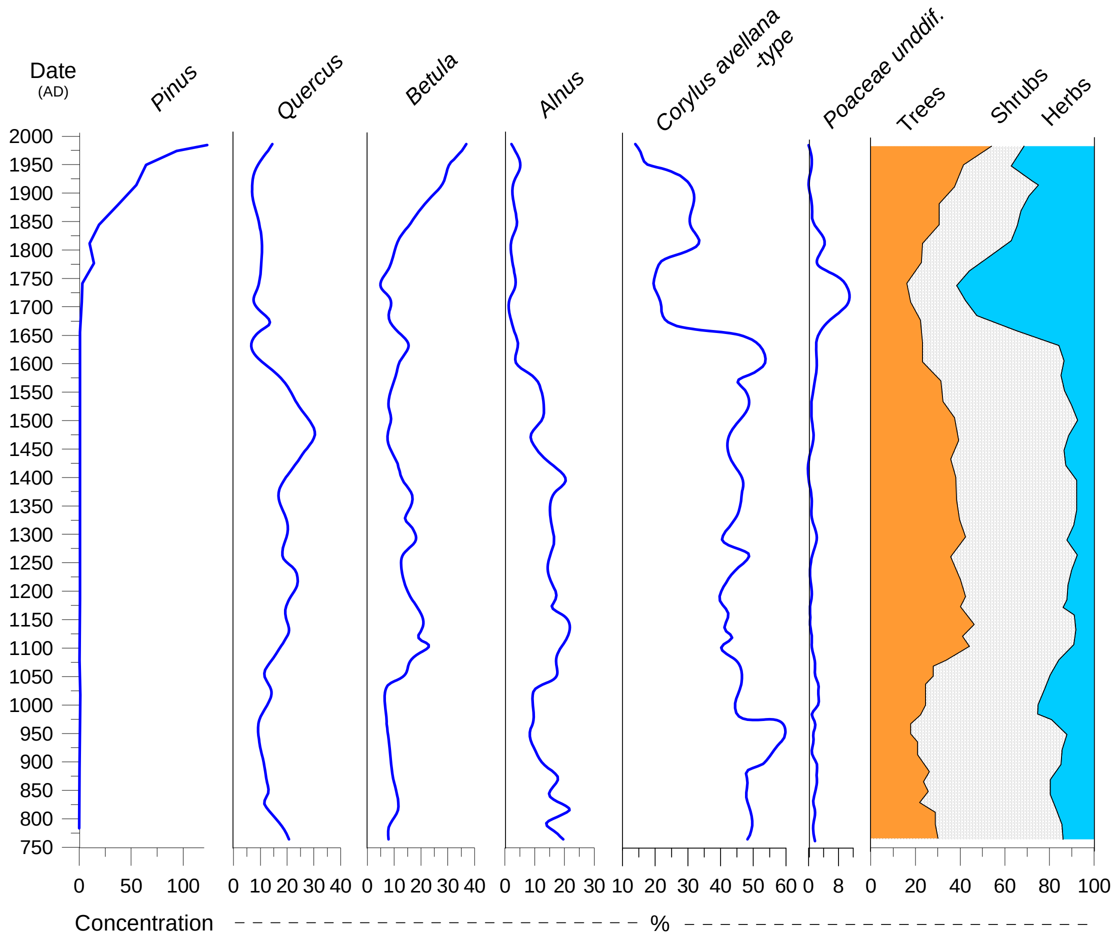

Fig. 6.2 Stratigraphic patterns of selected pollen taxa from Hulleter Moss over the past 1200 years. Data were obtained from Coombes, Chiverrell & Barber (2009) and curves have been spline-smoothed.

6.3 Methods

6.3.1 Sample collection and laboratory analysis

Sediment coring, subsampling, dating, and the methods used for palaeolimnological analyses including chronology, LOI, grain size, element concentrations, and diatom analysis, are described in chapter 4. The final combined core, ESTH0, was used to produce stratigraphies for all the proxies (see chapter 4). To account for sediment compaction and to interpret past patterns of sediment accumulation, dry density ($Density_{dry}$) and sediment accumulation rate (SAR) were calculated using the following equation:

$$Density_{dry} = Density_{wet} * \mathrm{DW} \quad \text{and} \quad \mathrm{SAR} = \mathrm{SR} * Density_{dry}$$

Where $Density_{wet}$, DW (%) and SR are sediment wet density, dry weight and sedimentation rate (cm year^{-1}), respectively. Given the difference of SARs of three cores, caution is needed when making comparisons between them.

Diatom accumulation rates (DAR) and sedimentary element fluxes (EF) were calculated as:

$$\text{DAR} = (\text{Diatom concentration})*\text{SAR}$$

$$\text{EF} = (\text{Element concentration})*\text{SAR}$$

The units of diatom concentration, DAR and EF are cells g^{-1} dry mass (cells gdm^{-1}), cells cm^{-2} $year^{-1}$ and µg cm^{-2} $year^{-1}$, respectively.

To confirm identification of the small centric diatom species (mainly for *Stephanodiscus*), several surface samples were selected for Scanning Electron Microscope (SEM) analysis. After the treatment of samples using standard procedures for sedimentary diatoms (see chapter 4), a 1 ml liquid subsample was pippeted onto a glass coverslip, affixed to an aluminium stub and sprayed with gold-palladium. The SEM used was a Jeol JSM-6480LV high-performance, variable pressure analytical SEM in the Department of Earth Sciences at University College London. Terminology for describing diatom morphological features in the centric diatoms follows Ross *et al.* (1979).

To improve interpretation of the diatom stratigraphy, a 59-year contemporary monitoring series of planktonic diatoms (as described in chapter 3, 4 and 5) was used to infer the diatom seasonal dynamics in the lake. The average concentrations of the main species *Asterionella formosa*, *Aulacoseira subarctica*, *Stephanodiscus binatus*, *Fragilaria crotonensis*, *Tabellaria flocculosa*, and *Aulacoseira granulata* var *angustissima*, were calculated. Given the particularly high occurrence of *Cyclotella comensis* in the core, but limited occurrence in the modern phytoplankton of Esthwaite Water, another long-term monitoring record collected from a nearby lake (Derwent Water) was used to reveal the seasonality and environmental preferences of this taxon. Derwent Water (N54°35', W3°09') has a surface area of ~5.2 km^2 and an average depth of ~5.5 m deep. Currently it is oligotrophic with average annual soluble reactive phosphorus (SRP) concentrations of below 1 µg L^{-1}. Water samples were collected and treated for diatom analysis following standard methods (see chapter 2). The data for Derwent Water, including SRP, surface temperature and concentrations of *C. comensis* in the water column, were extracted from a fortnightly monitoring record spanning 22-June-1993 to 18-December-2008 (data from CEH).

6.3.2 Numerical analysis

To understand the ecological preference of *C. comensis*, its response to nutrients (SRP) and climate (water temperature) was analyzed. Its seasonal distribution was explored based on monthly averages of count data for the whole monitoring period. Given the large number of zeros and high variance in the count data, traditional regression techniques (e.g. least-squares, maximum likelihood regression) are suboptimal even when both datasets are transformed. Thus the data were transformed to presence/ absence (0 and 1, respectively). Those samples with *C. comensis* concentrations <5 cell ml^{-1} were regarded as "absent" to avoid the influence of dead valves brought into the water column from the sediment. A logistic regression (Crawley, 2002) based on the presence/absence data with a binomial error distribution was performed as follows:

$$p = 1/(1+\exp(-(\beta_0 + \beta_1 * X_1 + \beta_2 * X_2 + \ldots + \beta_k * X_k)))$$

Where β_0 is a constant and β_i are coefficients of the predictor variables. p is a probability in the range 0 to 1. Using a link function $\text{logit}(p) = \ln(p/(1-p))$, the above formula can be given in a linear format:

$$\text{Logit}(p) = \beta_0 + \beta_1 * X_1 + \beta_2 * X_2 + \ldots + \beta_k * X_k$$

Logistic regression finds the best explanation for a response variable from a linear combination of explanatory variables (or their higher power form X_i^n, n=2, 3, 4…). Stepwise Generalized Linear Models (GLM) (Barry & Welsh, 2002) were implemented to select the best model using Akaike's Information Criterion (AIC) and adjusted coefficients of determination (R^2_{adjust}). All regressions were performed with the R statistical software (R Development Core Team, 2009).

Numerical zonation of the diatom percentage diagram, based on optimal sum-of-squares partitioning, was implemented using ZONE version 1.2 (Lotter & Juggins, 1991). Detrended correspondence analysis (DCA) (Hill & Gauch, 1980) was applied to diatom percentage data to explore temporal patterns of species change. The program CANOCO version 4.5 (ter Braak & Smilauer, 2002) was used with detrending by segments and downweighting of rare taxa.

Rates of diatom stratigraphic change were calculated for consecutive core samples along the profile using the program RATEPOL (J.M. Line and H.J.B. Birks, unpublished software). This technique calculates the dissimilarity between successive samples divided by the estimated period of deposition, in order to produce measures of any assemblage changes per unit time. The standard Euclidean distance was used as a distance coefficient (Overpeck, Webb & Prentice, 1985) and data were standardized to 20 years intervals.

Diatom-inferred total phosphorus concentrations (DI-TP) were reconstructed for the core using a diatom-TP transfer function. More details regarding this reconstruction can be found in chapter 3. All the proxies were plotted against the final depth-age model proposed in chapter 4.

6.4 Results

6.4.1 Chronology and sediment accumulation rates

Details of the chronology can be found in chapter 4. Given the inherent error of the age-depth model based on ^{210}Pb, ^{137}Cs and ^{14}C, all ages used in this chapter are approximate. The time-scale discussed here extends back to ~780 AD. Sediment accumulation rates (SARs) for the new combined core ESTH0 are shown in Fig. 6.3. Prior to the 1600s, SARs are low at ~0.01 cm^{-2} year^{-1}, followed by a continuous slight increase until 1885 AD. Since the 1900s, two sharp rises occur, one of which started in the 1900s and the other started in the 1960s. Between 1940-1960 SAR exhibited a large decrease. In the last four decades, SAR has been constantly high (average 0.06 g cm^{-2} year^{-1}).

6.4.2 Taxonomic description of *Stephanodiscus binatus*

Stephanodiscus binatus was found with relatively high abundances in the upper parts of the sediment cores from Esthwaite Water. Its diameter is 7-11 μm with spines present at the end of every interfascicle (Fig. 6.4). The central area is moderately raised and has a single, off centre valve face fultoportula (with two satellite pores) internally. Marginal fultoportula, also with two satellite pores, open through short tubes beneath every fourth to fifth spine. Radial uniseriate striae but with somewhat irregularly arranged areolae in the central region of the valve face become multiseriate, with 2-5 rows of areolae towards the valve face/valve mantle junction. This species is morphologically similar to other *Stephanodiscus* species, such as *Stephanodicus parvus* and *Stephanodicus hantzschii*. A comparison of key features which are visible with the light microscope for these species is given in Table 6.1.

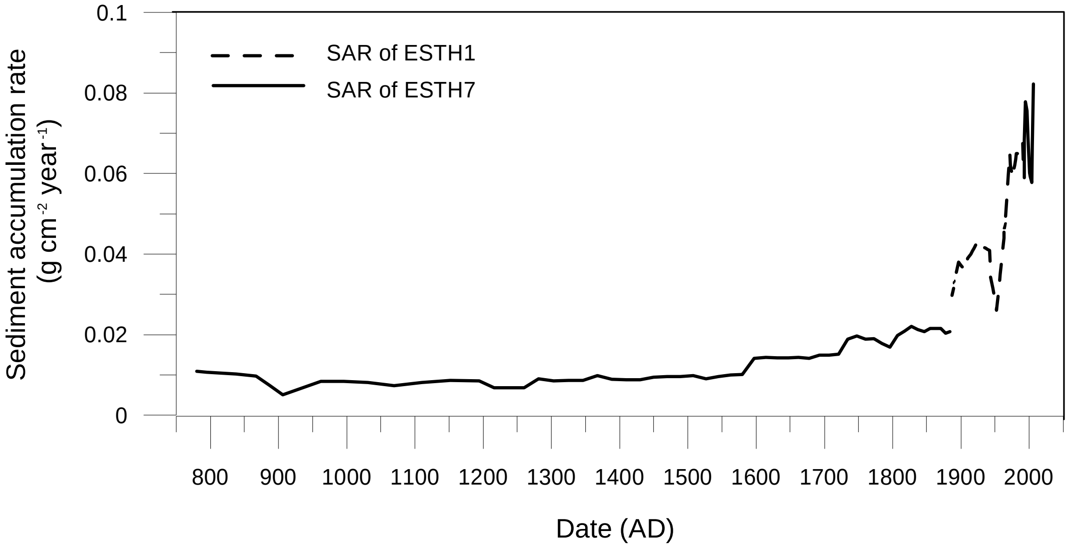

Fig. 6.3 Sediment accumulation rates of core ESTH0 from Esthwaite Water over the past 1200 years

6.4.3 Ecological preferences of the modern diatom flora

Planktonic diatoms in Esthwaite Water show a strong seasonal pattern (Fig. 6.5). *A. formosa* forms a bloom in spring (during the 9-21st week). Its abundances, most of which are >1,000 cell ml^{-1} and peak at over 4,000 cell ml^{-1}, are overwhelming higher than any other species. *A. subarctica,* as the second most abundant species, starts to grow in late autumn and continues until the following spring, exhibiting two maxima each year. The initial peak (~200 cell ml^{-1}), occurs in early winter (~ the 50th week). While the second one, with much higher concentrations (>800 cell ml^{-1}), starts in the late winter and lasts to the middle of the following spring. *A. granulata* var *angustissima* is most abundant in autumn, having first appeared in the lake in 1998 (see chapter 4, 5). *F. crotonensis* and *C. comensis* both peak in summer at concentrations of <150 cell ml^{-1}.

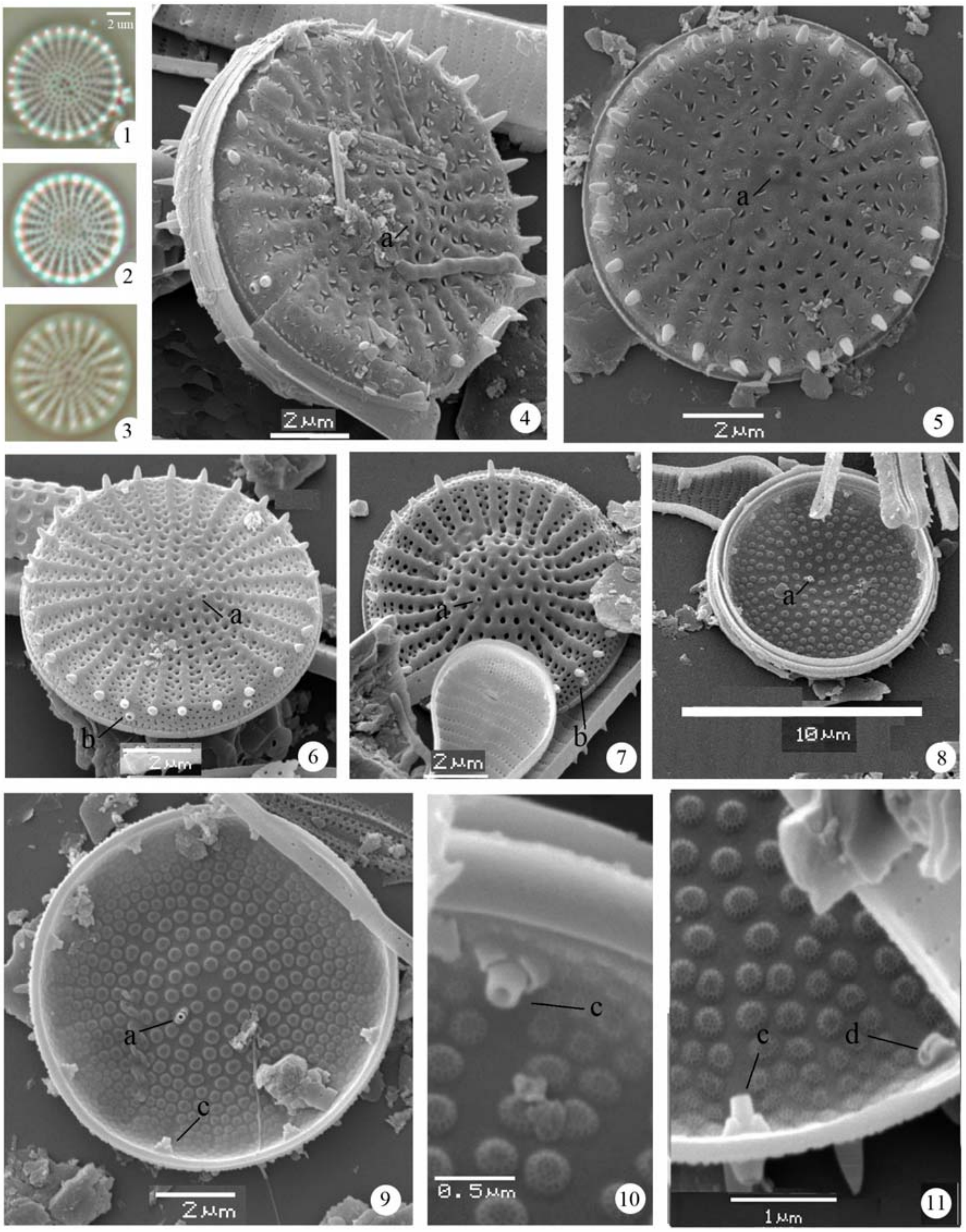

Fig. 6.4 Morphology of diatom *Stephanodicus binatus.* ①-③ view under light microscope (with the same scale in ①). ④-⑦ external valve view, with valve face fultoportula (arrow a) and marginal fultoportula (arrow b). ⑧-⑨ internal valve view, showing eccentric valve face fultoportula (arrow a with two satellite pores). ⑩-⑪ internal valve view, with eccentric valve marginal fultoportulae (arrow c, with two satellite pores) and rimportula (arrow d). Scales are shown in each panel.

Table 6.2 Comparison of morphological features of three small *Stephanodiscus* species: *S. parvus, S. minutulus* and *S. binatus*.

Species	*Stephanodicus parvus* [a]	*Stephanodicus hantzschii* [b]	*Stephanodicus binatus* [c]	*Stephanodicus binatus* [d]
Diameter range (m)	5-11	9-12	5-9	7-11
Valve topography	flat- fairly undulate	flat	undulate	undulate
Interfascicle arrangement	slightly raised	difficult to discern in central part of valve, but apparent as slightly raised ridges in outer part	slightly raised, occasionally branching at valve face/ mantle junction	moderately raised
Fascicles	1-2 seriate and occasionally 3 seriate at the margin	1-2 seriate and occasionally 3 seriate at the margin	1->3 seriate at the margin	1-3 seriate and occasionally 4 seriate at the margin
Occurrence of marginal fultoportulae	every 3-6 spines 3 satellite pores internally	every 2-5 spines 3 satellite pores internally	every 4-5 spines 2 satellite pores internally	every 4-5 spines 2 satellite pores internally
Valve face fultoportula	1 with 2 satellite pores	no	1 with 2 satellite pores	1 with 2 satellite pores
Rimoportula morphology	single tubule which occurs at the end of an interfascicle	single tubule in a marginal position	single conspicuous external tubule emerging close to a spine	single conspicuous external tubule emerging close to a spine

Note: a, described by Stoermer & Håkansson (1984) and Yang & Duthie (1993); b, described by Håkansson & Stoermer (1984) and Håkansson (2002); c, described by Håkansson & Kling (1990) and Sayer (unpublished data); d, in this study.

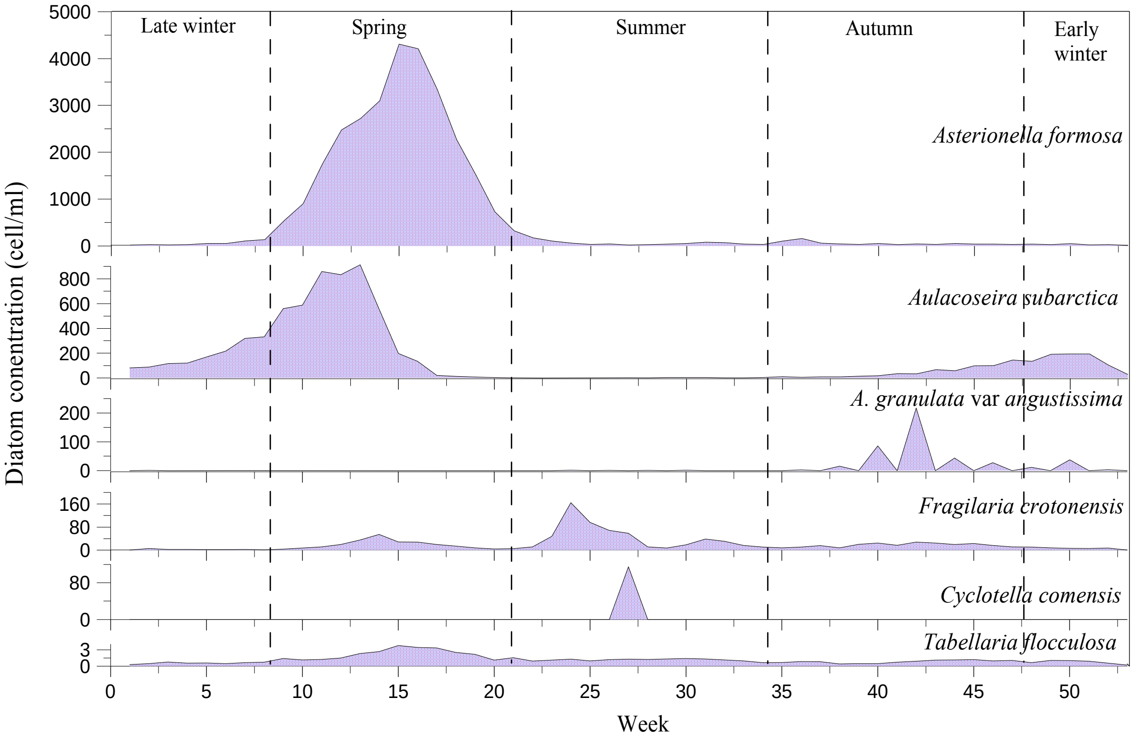

Fig. 6.5 Seasonality of the main diatom species over the 59-year long monitoring period in Esthwaite Water (Data were provided by CEH)

In Derwent Water, *C. comensis* is present over a wide spectrum of surface water temperatures but with all concentrations >20 cells ml^{-1} at temperatures between 4.8 and 22.6 °C (Fig. 6.6a). In contrast, it exhibits a decreasing sigmoidal response to SRP. Only 6 out of its 210 occurrences appear with SRP concentrations higher than 2 µg L^{-1} (Fig. 6.6b). This species mostly occurred in the summer (June average of 142 cell ml^{-1} over the period 1993 to 2008), but was also present in considerable amounts in spring and autumn (Fig. 6.6c). The logistic modelling revealed that the predicted occurrences of *C. comensis* respond in a non-linearly way to both temperature and SRP (Fig. 6.6d, e). *C. comensis* displayed a weak unimodal-like pattern along the temperature gradient: the likelihood of occurrence increased slightly with temperatures above 5 °C but decreased above ~12 °C. In contrast, the occurrences of this species decreased sharply when SRP reaching 2 µg L^{-1} and there were no further predicted occurrences when SRP exceeded 6 µg L^{-1}.

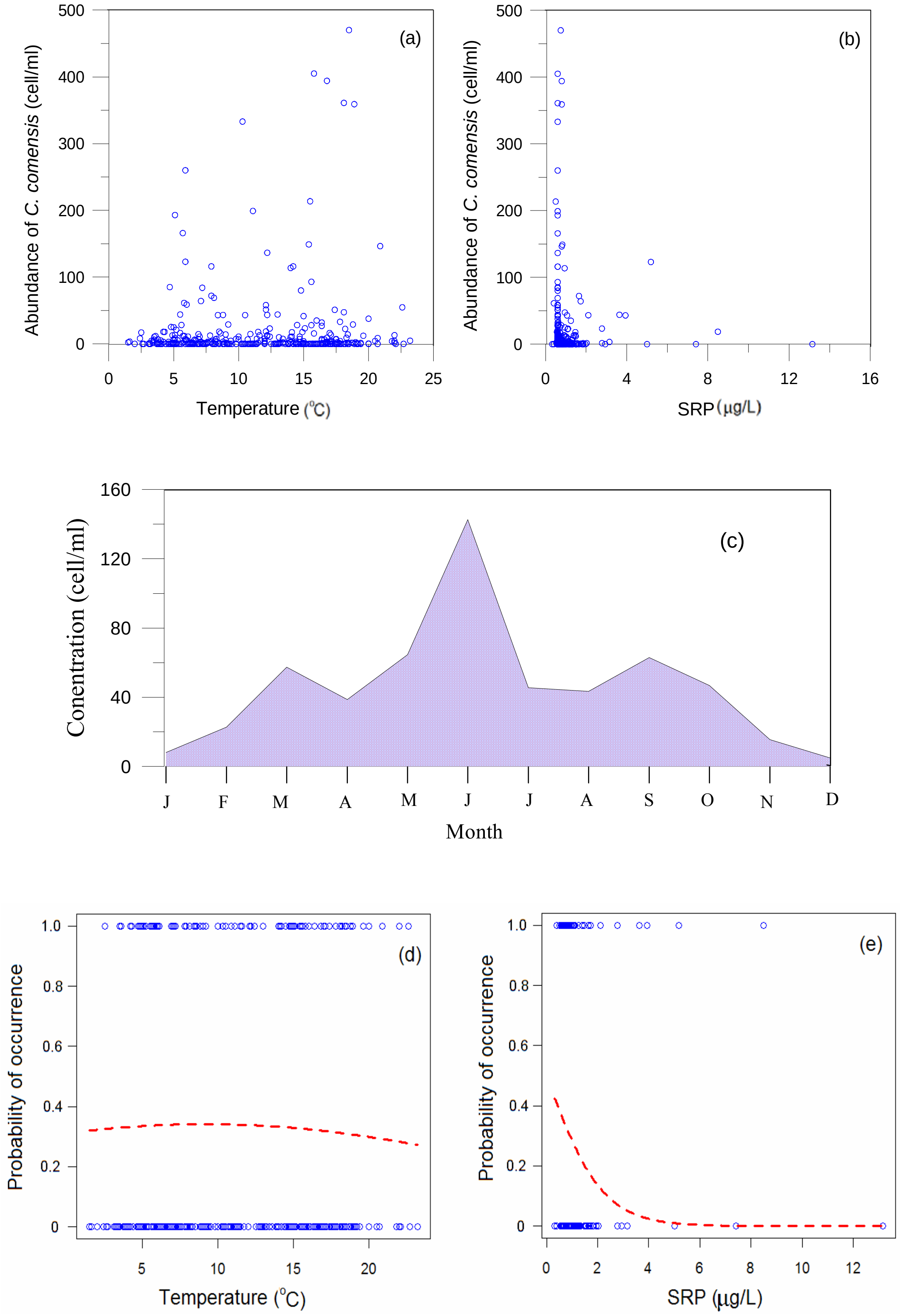

Fig. 6.6 Abundances of *C. comensis* in relation to key environmental factors (a) temperature, (b) SRP, (c) Seasonality of this species in Derwent Water, (d) and (e) show the result of logistic regression modeling of its occurrence probabilities predicted by Temperature and SRP, respectively. (Monitoring data were provided by CEH).

6.4.4 Diatom stratigraphy

In total, 121 diatom species were identified in core ESTH0. Planktonic species (29 of the total 121) dominated throughout the sequence, with percentages of between 51-94% (average 77%) (Fig. 6.7). The relative abundances of the most common species are presented in Fig. 6.7. The stratigraphy is divided into four zones.

Zone I (~770-880 AD) is characterized by *A. subarctica* and *C. comensis* with considerable amounts of *Achnanthidium minutissimum*, and *A. formosa*. Diatom concentrations are relatively stable with values ~5.8x10^{10} cells gdm^{-1} (an exception occurred ~850 AD with a high value of 8.3x10^{10} cells gdm^{-1}).

Zone II (~880-1350 AD) is dominated by *C. comensis*, which rises sharply to 52% at the beginning of this zone. Subsequently this species gradually decreases to a minimum of 35% at ~1100 AD before rising again. *A. subarctica* is sparse in this zone (at an average of 3%). In contrast, *A. minutissimum* and *Cyclotella radiosa* both increase, although the latter species remained at relatively low concentrations (<10%) throughout this zone. Diatom concentrations exhibited a decreasing trend, from 6.4x10^{10} cells gdm^{-1} in 880 AD to 3.6 x10^{10} cells gdm^{-1} in 1350 AD.

Zone III (~1350-1880 AD) sees a significant decline in *C. comensis* (average concentration 32%) and a steady rise in *A. subarctica* from <3% to ~20% (Fig. 6.7). This zone is divided into two sub-zones. In zone III-a (1350-1750 AD), *C. comensis* exhibits a steady increase from 29% to 42%, with a synchronous decline in *A. minutissimum*. Both *C. radiosa* and *A. subarctica* are of moderate abundances (~10%) in this zone. Diatom concentrations exhibit low values prior to 1480 AD but these increase (~5.0 x10^{10} cells gdm^{-1}) after this date. In zone III-b (1750-1880 AD), *C. comensis* declines to a minimum of 21% and then increases to ~30% at the zone III and zone IV boundary (~1880 AD). All other sub-dominant species such as *A. formosa, A. subarctica* and *C. radiosa* exhibit a slight increase in this subzone. Diatom concentrations fluctuated greatly between 2.6-7.8x10^{10} cells gdm^{-1} in this subzone.

Zone IV (post-1880 AD) sees the arrival of several new species such as *S. binatus, A. granulata* var *angustissima*, and *Fragilaria capucina* var *rumpens*. In zone IV-a (1880-

1975 AD), *A. formosa* and *A. subarctica* are dominant and both exhibit an increasing pattern. In contrast, *A. minutissimum, C. comensis* and *C. radiosa* all decline from 1880 AD to less than 10%, 4% and 2% from the mid 1930s, respectively. Another distinct characteristic of this subzone is the first appearance of *F. crotonensis*, which occurred sporadically at the beginning of the zone but constantly increased from 1910 AD. In subzone IV-b (1975-present), *A. formosa* and *A. subarctica* remain dominant. *F. crotonensis* and the new species *S. binatus* and *F. capucina* var *rumpens* all exhibit a sharp increase, with abundances of up to 29%, 15% and 5%, respectively. *A. granulata* var *angustissima* obtained a maximum abundance (24%) at around 1999 AD, although it remained at low abundances (~4%) in the other samples in this zone. Diatom concentrations were low in subzone IV-a (~3.0×10^{10} cells gdm^{-1}), with a maximum of 7.5×10^{10} cells gdm^{-1} at ~1910 AD. In subzone IV-b, diatom concentrations increase markedly with an average value of 7.3×10^{10} cells gdm^{-1}.

The diatom changes in core ESTH0 are summarized by DCA (Fig. 6.7). The first axis, explained 40% of the total diatom variance. The second, third and fourth axes explain only 4%, 3% and 1% of total variance, respectively. Scores of DCA axis 1 (SDCA1) exhibit a significant shift from low values (<1.4) prior to 880 AD to higher values (>1.7) afterwards. A stable period is observed between 880-1870 AD with small changes in SDCA1, although a slight decreasing trend occurred during 1780-1880 AD. After 1880 AD, SDCA1 declines rapidly.

Rates of diatom change exhibit similar turnover points of change as the DCA scores and are inversely related (Fig. 6.7). Overall, rates of diatom change remained low prior to 1880 with slightly higher values from 1750 to 1880 AD. A peak of 4.3 at ~1880 AD occurred after which rates of change continuously increased most notably in the last few decades, indicating major species turnover and a period of marked environmental change.

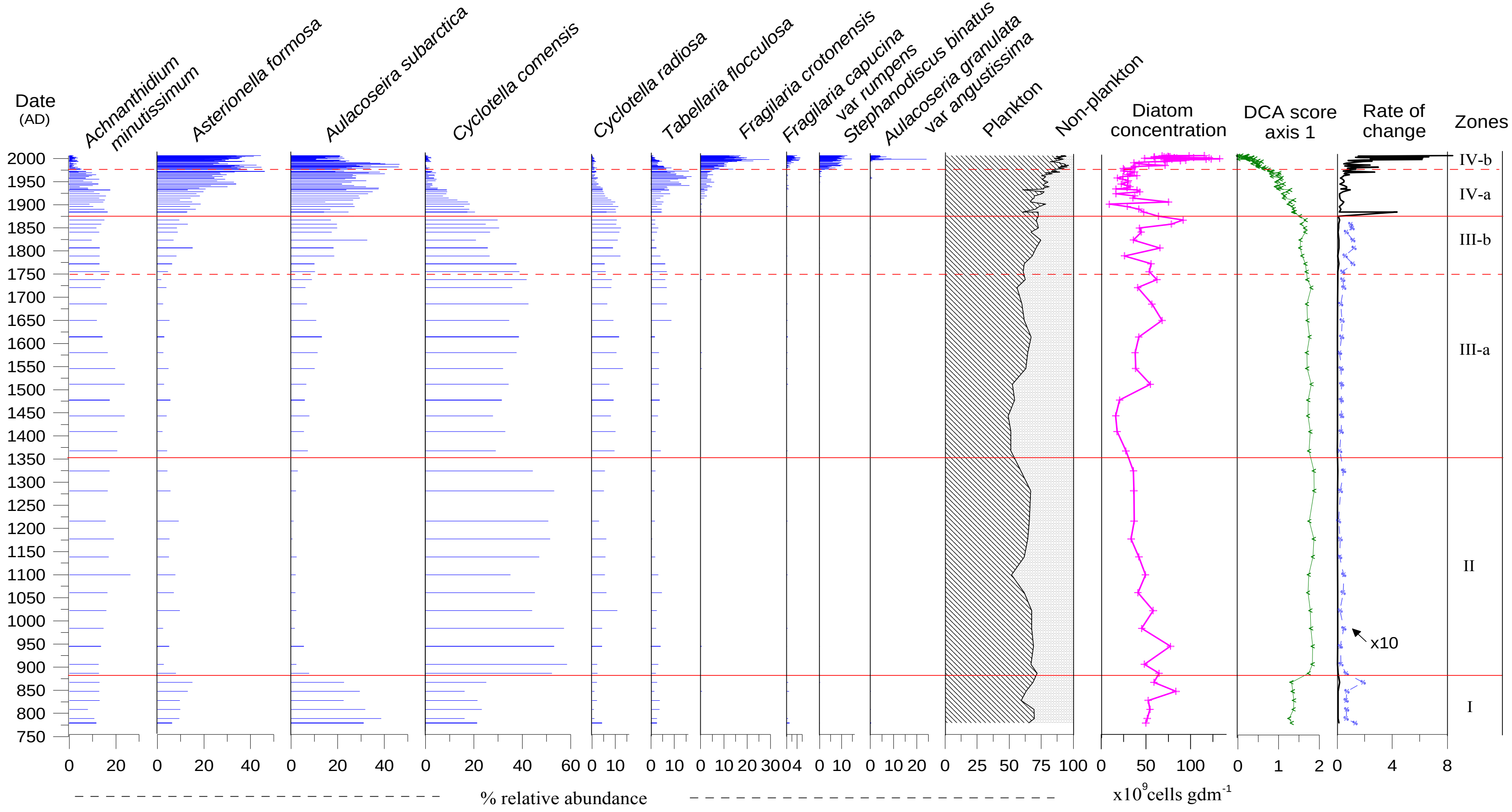

Fig. 6.7 Percentage abundances of the major taxa, sum of planktonic and non-planktonic taxa, total diatom concentrations, DCA scores of first axis and diatom rates of change in Esthwaite Water core ESTH0. Given the wide range of diatom change rates, lower values in zones I, II and III are plotted with x10 magnification (as shown). The main zones of compositional change are indicated by solid horizontal lines with dash lines for the subzones).

6.4.5 Diatom accumulation rates and DI-TP

Diatom accumulation rates (DAR) display high variability over the past millennium (Fig. 6.8). Total DAR ranged from $0.9\text{x}10^{7}$ to $9.5\ \text{x}10^{8}$ cells cm^{-2} year^{-1}. *C. comensis*, *A. formosa*, *A. subarctica* had relatively high DAR over the period 750-880 AD, but rates declined markedly for the latter two taxa in zones II and III, while *C. comensis* rates remarked relatively stable. From the late 1800s (zone IV), DAR of *A. formosa* and *A. subarctica* increased steadily, with the exception of a period of lower values in the 1950s. In contrast, *C. comensis* rates declined in Zone IV. *F. crotonensis* occurred in zone IV only and increased rapidly to ~$1.0\ \text{x}10^{8}$ cells cm^{-2} year^{-1} in the past decade.

DI-TP reconstructions are illustrated in Fig. 6.8. A short period of relatively high TP values (~14 µg L^{-1}) was inferred for the period prior to 880AD. Subsequently the DI-TP values remained low at 7-10 µg L^{-1} for a long period of time until 1750 AD. DI-TP concentrations started to increase gradually from 1750 AD reaching ~14 µg L^{-1} by ~1880 AD, indicating slight nutrient enrichment. After 1880 AD, DI-TP further increased to 30 µg L^{-1} by 1976 AD and still further to 64 µg L^{-1} by 2003. This was followed by a slight decline to ~60 µg L^{-1} at present.

6.4.6 Loss on ignition and grain size

Physical features including LOI and medium grain size (MD) of the ESTH0 sediment profile were divided in to four zones (Fig. 6.9), which correspond with the zonation of the diatom stratigraphy. Zone I (prior to 880 AD) had a relatively low MD and high LOI, with average values of 7.7 µm and 28%, respectively. In zone II (880-1350 AD), LOI remained relatively stable with a range of 28-30%; however, MD fluctuated widely, with an average of 7.3 µm. During 1350-1870 AD (zone III), LOI exhibited a steady decline, with values falling from 30% to 20%. In contrast, MD increased with a peak of 8.8 µm at ~1605 AD. Zone IV (post-1880 AD) was characterized by increasing LOI values to the present day, reaching a peak of ~28% in 2006. MD increased steadily from 1870 AD to the mid-1970s and declined thereafter to ~9 µm.

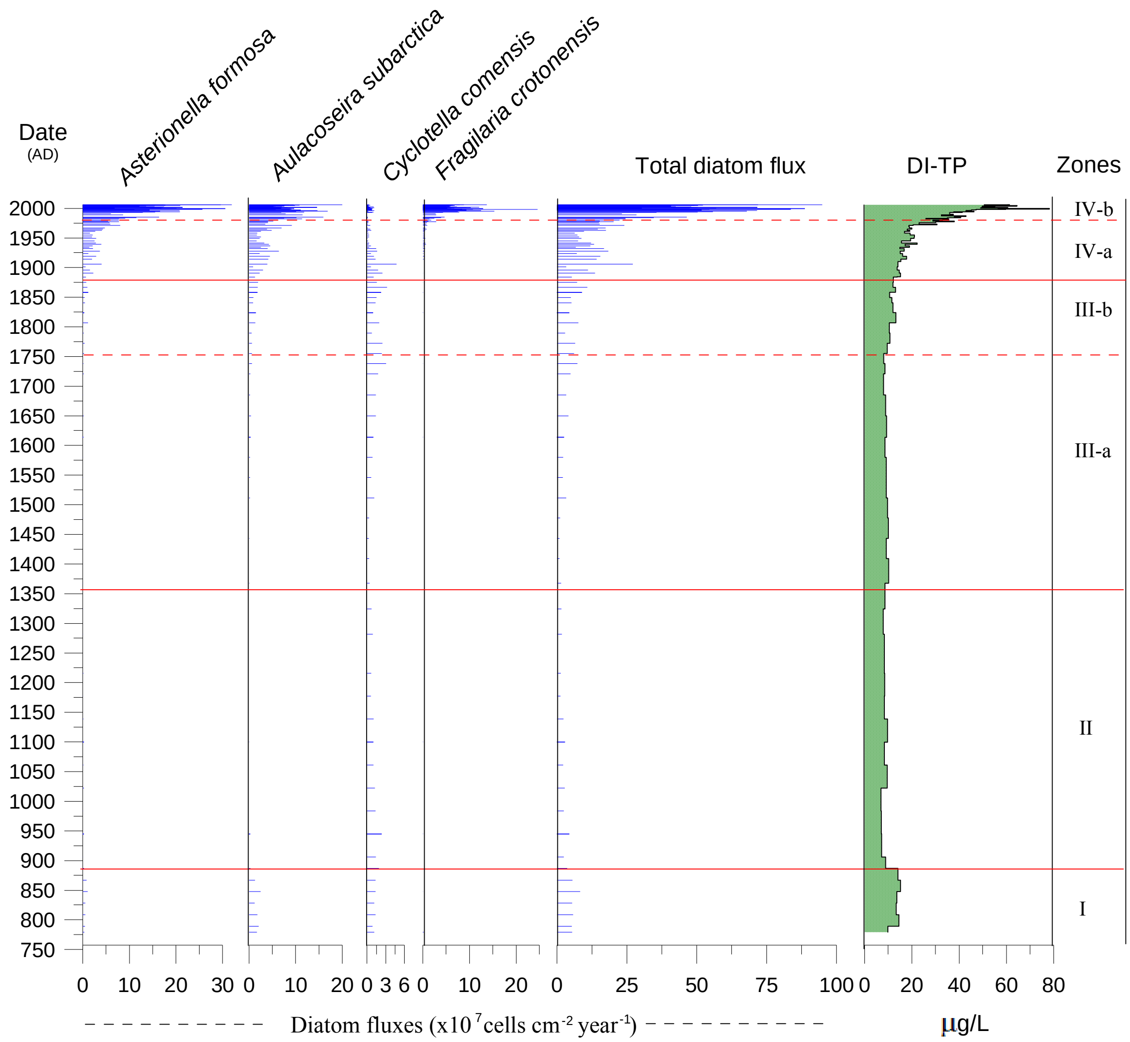

Fig. 6.8 Diatom accumulation rates of the major taxa and diatom-inferred TP of core ESTH0 in Esthwaite Water. Zones are indicated as in Fig. 6.7.

6.4.7 Geochemical records

Both concentrations and sediment fluxes of geochemical elements exhibit distinct patterns in core ESTH0 (Fig. 6.9, 6.10), which match well with the diatom stratigraphy (Fig. 6.7).

Ti, Al, K and Na all vary in the same way throughout the core. Prior to 1350 AD, these elements exhibited a gradual increase from low concentrations to peak values of 3500, 59, 18 and 5 g kg^{-1} at ~1870 AD, respectively (Fig. 6.9). After 1870 AD, these elements declined dramatically to very low values of around 2600, 45, 11 and 4 g kg^{-1} respectively, in recent years.

P was low and relatively stable prior to 1880 AD (average of 2,085 g kg^{-1}), but after this time, it underwent a rapid increase to a peak in ~1998 AD followed by a slight decline to the present day.

Mn and Fe exhibited similar changing patterns, although the latter was much more variable (40-65 g kg^{-1}). With the exception of a peak around 1400 AD, Mn and Fe concentrations declined prior to the 1870s. After 1870 AD, both elements increased and became more variable.

Pb, Zn and Ni exhibited similar patterns of change over the whole core profile. Characterized by low and relatively stable concentrations until 1750 AD, all of these elements increased to peak values in the mid-1990s. Thereafter, all three metals declined to the present day.

Ratios of Na/K and Na/Al exhibited similar trends prior to 1350 AD, with a decrease in zone I (750-880 AD) and an increase in zone II (880-1350 AD) (Fig. 6.9). Na/Al ratios rose during 1350-1880 AD; however, Na/K ratios experienced a continuous decline from 1600 to the mid-1850s. From 1890 to ~1940 AD, both Na/K and Na/Al increased, after which both ratios declined.

Fe/Mn followed the same trend as that for Fe prior to 1350 AD (Fig. 6.9). However, this ratio increased slightly over the period 1350 to 1880 AD. A slight decrease was observed from 1880 to 1970 AD, after which values increased to the core surface.

Fluxes of all elements exhibited similar patterns (Fig. 6.10), which are significantly affected by sediment accumulation rates in this lake (Fig. 6.3). Prior to 880 AD, all element fluxes had relatively high values. These started to decline from ~880 AD to low values at ~900 AD, followed by a long period of stable but low values until ~1600 AD. From 1600 AD onwards, all element fluxes increased, with two sharp increases occurring at ~1750 AD and ~1880 AD. Further increases of element fluxes occurred up until the 1940s, after which there was a decline in the period from 1940 to 1960. From the 1970s, all element fluxes exhibited high variability but with a general increasing trend, except for Pb which declined.

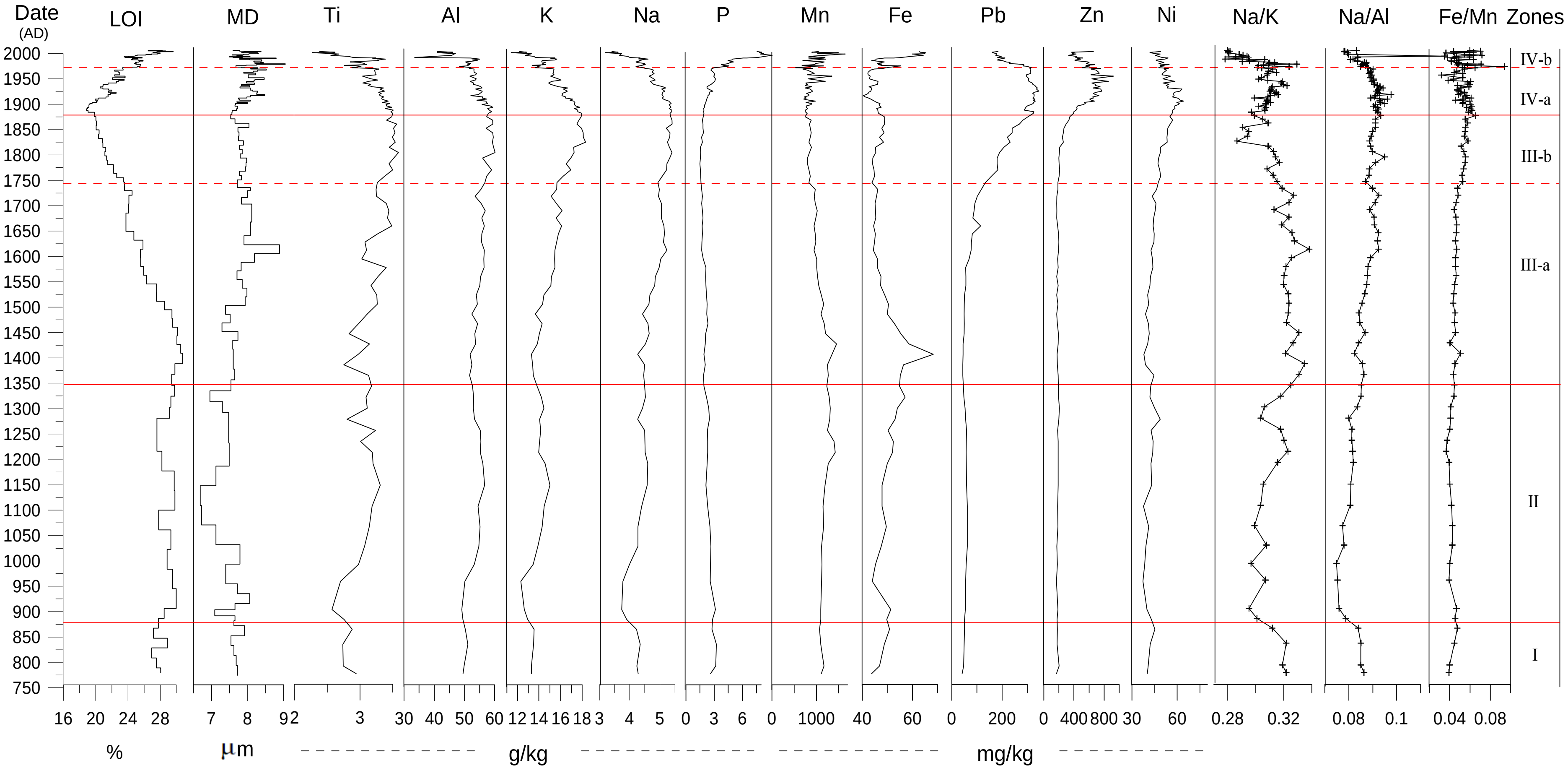

Fig. 6.9 Loss on ignition (LOI), median grain size (MD), concentration profiles of selected geochemical elements in core ESTH0. Zones are indicated as in Fig. 6.7.

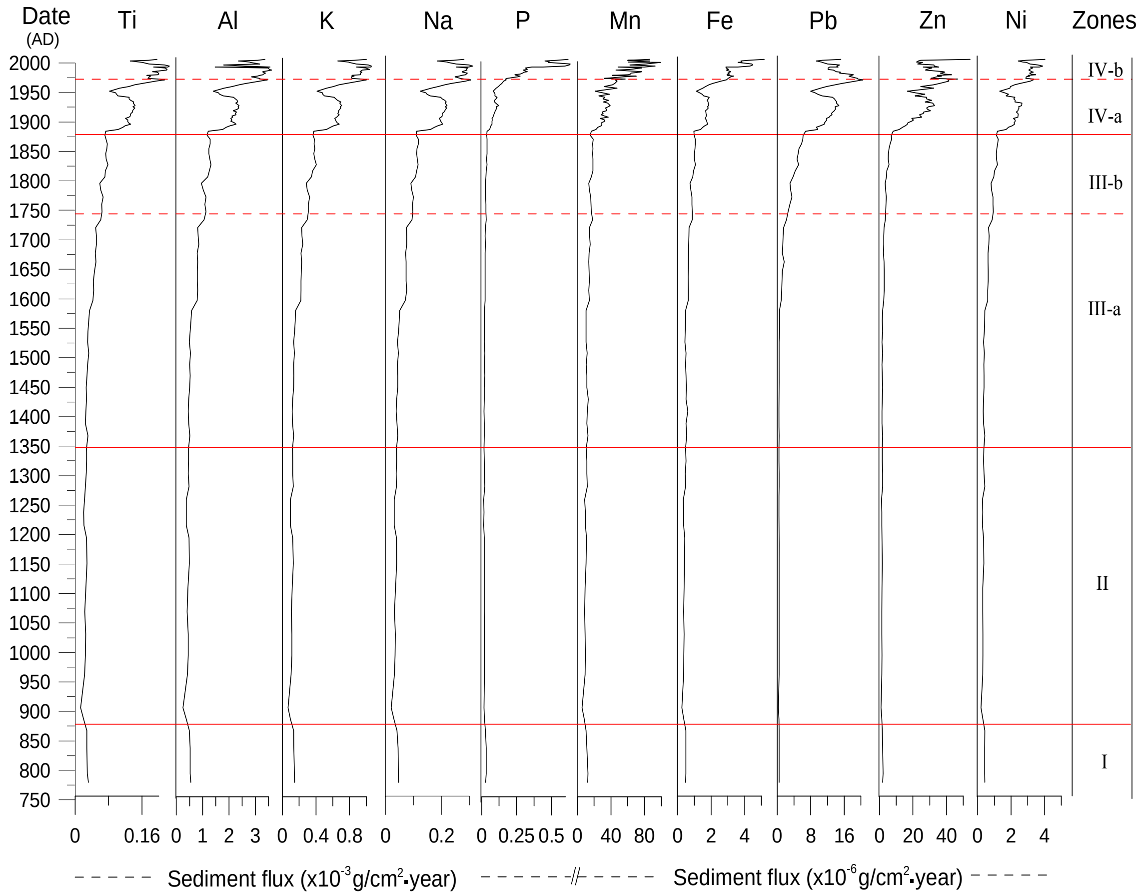

Fig. 6.10 Accumulation rates of selected geochemical elements and element ratios in core ESTH0 from Esthwaite Water. Zones are indicated as in Fig. 6.7.

6. 5 Discussion

Given the importance of contemporary diatom ecology to the interpretation of palaeo-environmental reconstructions, the ecological preferences of planktonic diatom assemblages in Esthwaite Water are discussed in section 6.5.1. Similarly, to facilitate the geochemical interpretation, background information is presented in section 6.5.2.

6.5.1 Diatom autecology

The long-term monitoring dataset is of great value in terms of defining the preferences of the dominant diatoms encountered in the core and thus for interpreting the diatom stratigraphy in core ESTH0. Seasonal and inter-annual patterns of diatom communities and their relationship with environmental variables (in term of climate and nutrients) were discussed in chapters 2 and 5. Combined with published literature, Table 6.3 gives detailed information regarding the autecology of each planktonic diatom encountered in the sediment record. Given the overwhelmingly high abundances of *C.*

comensis prior to 1900 AD in the core, autecological information on this species is vital for the palaeo-environmental interpretation of changes in Esthwaite Water.

The logistic models demonstrate that *C. comensis* can thrive over a wide temperature range. Its temperature optimum is around 10 °C (Fig. 6.6d). Furthermore, monitoring records from both Esthwaite Water and Derwent Water shows that this species reaches its maximum abundance in summer, indicating its preference for higher temperatures. This taxon has been reported in many Arctic and temperate lakes around the world (e.g. Fritz, Kingston & Engstrom, 1993; Ohlendorf *et al.*, 2000; Hausmann & Lotter, 2001; Werner & Smol, 2006). For example, in alpine lake Hagelseewli, Switzerland (with surface SRP mostly <4.0 µg L^{-1}), *C. comensis* is the dominant planktonic diatom and blooms during the entire summer season (Ohlendorf *et al.*, 2000). A similar seasonal distribution has been described for *C. comensis* in other alpine and arctic lakes (Rautio, Sorvari & Korhola, 2000; Koinig *et al.*, 2002). Hausmann & Lotter (2001) reported a temperature optimum for this species of 13 °C in Swiss Alpine lakes, which is close to the local average summer temperature. Similarly, Wunsam, Schmidt & Klee (1995) concluded that *C. comensis* had a high temperature optimum >18.8 °C.

A low SRP optimum is expected for *C. comensis*, since the monitoring record from Derwent Water reveals higher occurrence probabilities at lower SRP concentrations. Several diatom-environment training sets have also assigned low P optimum concentrations for this species: 5.6 µg L^{-1} SRP in Fritz, Kingston & Engstrom (1993), 5.6 µg L^{-1} SRP in Reavie & Smol (2001) and 5.6 µg L^{-1} SRP in the European Diatom Database (EDDI, http://craticula.ncl.ac.uk/Eddi/jsp/help.jsp). Nevertheless, phosphorus seems not to be the only determinant of *C. comensis* occurrence. The experiments of Pappas & Stoermer (1995) indicate that increasing nitrogen levels and increasing N:P ratios had a positive influence on the abundance of *C. comensis*. Further, Werner & Smol (2006) found a positive correlation between the abundance of *C. comensis* and TN:TP. This may suggest that increases in *C. comensis* may be related to increased nitrogen levels. Other studies have suggested that changes in epilimnetic Si:P ratios may also influence the abundance of *C. comensis* (Wolin & Stoermer, 2005).

Table 6.3 Ecological preferences of the major planktonic species found in the Esthwaite Water diatom record, mainly derived from the two-year (chapter 2) and 59-year monitoring datasets (chapter 5), but also from other published literature (see text for more references)

Taxon name	**Seasonal occurrence**	**Phase of thermal regime and/or turbulence requirement**	**Temperature optima**	**Light environment**	**Nutrient requirements**
Asterionella formosa	Spring	Terminating spring circulation	Intermediate	High	Medium [P], high Si:P
Aulacoseira subarctica	Whole winter and early spring	Favours turbulence	Low	Low	High [Si], very high Si:P
Aulacoseira granulata	Autumn-winter	Favours turbulence	High	Low	High [Si], medium [P]
Aulacoseira granulata var *angustissima*	Summer	Favours turbulence	High	Low	Low [P]
Cyclotella comensis	Summer	Summer stratification	High	Low	Very low [P]
Cyclotella radiosa	Summer-autumn	Summer stratification	High	Medium	Medium [P]
Fragilaria crotonensis	Late spring, summer	Summer stratification	High	Low	High [P]
Fragilaria capucina var *rumpens*	Summer	Summer stratification	High	Low	High [P]
Stephanodiscus binatus	Winter	Winter isothermy	Low	High	High [P], low Si:P

6.5.2 Palaeolimnological interpretations of geochemical proxies

Mackereth (1966) considered Na and K to be preferentially supplied from the catchment by erosion, leading to enrichment of the sediments in these elements. He argued that during periods of high erosion, clastic sediment from catchment soils is supplied at a faster rate and therefore there is less time for leaching of Na and K from the soils, leading to higher sediment concentrations of Na and K. During periods of less intense erosion, soils develop deeper weathering profiles with greater leaching of Na and K, and hence lake sediments contain lower concentrations of Na and K. The difference between the behaviour of K and that of Na is due to the fact that K, derived mainly from decomposition of potash feldspars, is mostly retained in the weathering product (soil) as K-rich clays (e.g. illite), whereas most of the Na, derived mainly from plagioclase feldspar, is removed from the weathering product and transported away by runoff (Dean, Gorham & Swaine, 1988). Therefore, the Na/K ratio has little correlation with the sediment accumulation rate, and is a key proxy indicating the weathering degree of sediments before they are transported into a lake (Nesbitt & Young, 1982; Sawyer, 1986). Similar behaviour is observed for Al, which is widely considered to be immobile during weathering (Tardy, 1971; Gardner, 1980; Dean, 1997). Consequently, high Na/K and Na/Al ratios tend to suggest poor weathering of the sediment. Temperature and moisture are two important factors influencing the weathering of debris. Evaporation is lower than precipitation in the Esthwaite Water catchment, and therefore weathering is influenced mainly by temperature. Similarly to Al, Ti is also effectively conserved in soil that has undergone chemical weathering and that is essentially immobile after its deposition in a lake (Gardner, 1980). Thus it can be used to track changes in catchment sources of sediment and the intensity of erosion (Young & Nesbitt, 1998).

Sedimentary phosphorus (Geo-P) in Esthwaite Water reflects well the changes in DI-TP in terms of the timing and rates of change (Fig. 6.11). With the exception of a discrepancy exhibited by the five oldest samples covering the period of 800-900 AD, Geo-P corresponds well with DI-TP, the latter having been shown to provide reliable estimates of historical TP concentrations by close comparison with measured SRP data (see chapter 3). In general, P retention in lake sediments is controlled by many factors such as sediment redox potential, water temperature, NO_3-N, pH and bacterium activity, but in deep lakes most importantly by the reductive dissolution versus oxidative precipitation of Fe and associated P during the hypolimnetic anoxia period (Mortimer, 1941-1942; Davison, Woof & Rigg, 1982; Engstrom & Wright, 1984; Dean, Gorham & Swaine, 1988; Gächter, Meyer & Mares, 1988). Based on the seasonal dynamics of Fe and Mn in sediment traps in Esthwaite Water, Davison, Woof & Rigg (1982) found that most of the Fe that enters the lake is retained in the sediments, but that most of the Mn is washed out. Most of the Fe and Mn flows into the lake during the winter and is precipitated as Fe and Mn oxides and hydroxides. During the development of an anoxic hypolimnion in summer, only a small fraction of the annual Fe loading is dissolved, given that this process occurs in the driest time of year (Davison, Woof & Rigg, 1982). In contrast, most of the Mn (about 90%) is reduced and transported out of the lake. Therefore, for most periods of the year Fe in sediments retains most of the particulate P, which is comparable to the epilimnetic total P. This is the most likely reason for the close agreement between Geo-P and DI-TP in the Esthwaite Water sediment record.

Given the different behaviour of Fe and Mn in lakes, the oxygen balance in the water column is important in controlling the concentration and ratio of these elements (Davison, 1993). An unstable water column, which may result from strong wind, high precipitation or large fluctuations in temperatures, tends to provide more oxygen to deep waters. In addition, Davison, Woof & Rigg (1982) have found that most of the oxides of Fe and Mn that enter the lake in winter are reduced under anoxic conditions in summer. Assuming that Fe/Mn ratios are unchanged in the detritus prior to their flushing into a lake, the Fe/Mn ratio is a good proxy for water column stability, the latter being influenced by wind, precipitation and temperature in summer. Consequently, higher Fe/Mn ratios might indicate warmer, windier or wetter summers.

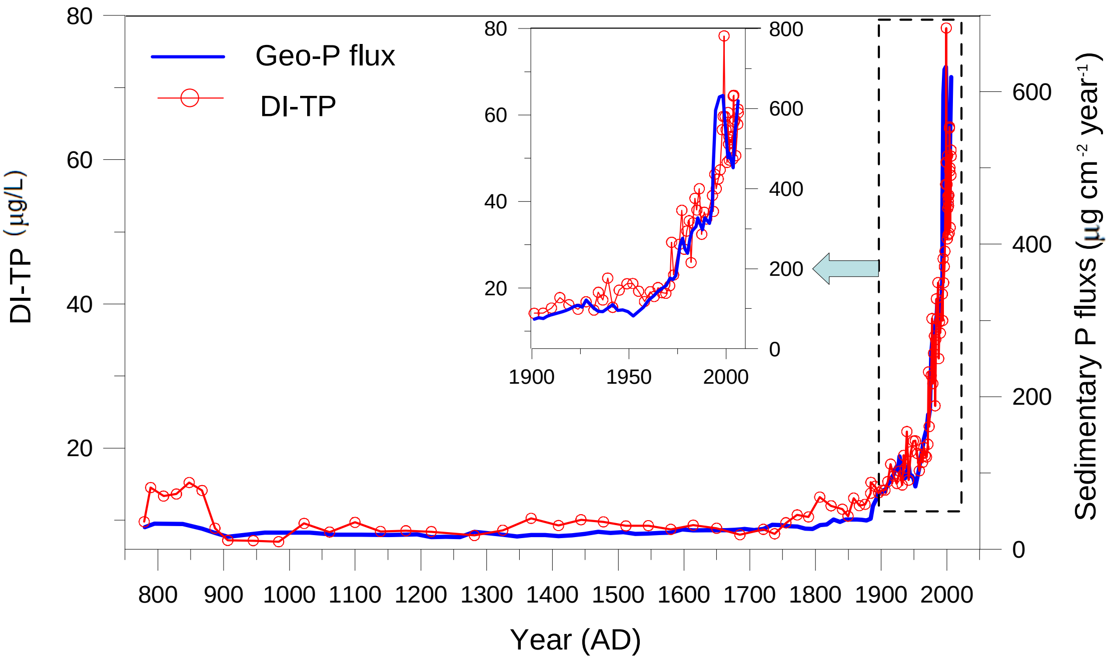

Fig. 6.11 A comparison of the geochemical P flux (Geo-P flux) and diatom-inferred TP (DI-TP) for Esthwaite Water.

However, it should be noted that for highly productive lakes abundant organic matter will also consume considerable oxygen during decomposition, thus higher Fe/Mn ratios can also be a good indicator of nutrient enrichment (Anderson, Rippey & Gibson, 1993).

The trace metals, Pb, Zn and Ni, can act as indicators of local human activity, particularly mining (Hilton, Davison & Ochsenbein, 1985; Boyle *et al.*, 2004). Given the historical records (Table 6.1), which show an expansion of local mining activities over the last century and elevated global flux patterns since 1850 AD (e.g. Smol, 2002), it might expected that concentrations of these elements increase over the last century. However, the element concentration data for Pb, Zn and Ni in Esthwaite Water core exhibit a decline in the past 100 years (Fig. 6.9). Compared with concentration data, element flux data can provide a more reliable estimate of inputs of geochemical mass into the lake. Concentrations are measured relative to the sample mass and are, therefore, not independent from each other. If the rate of supply of one component increases relative to the others, then its concentration increases, while the others decrease. Thus, an increase in the concentration of any particular element might be explained either by an increase in its supply rate or by a decrease in the supply rate of one or more of the other components (Boyle, 2001). Only accumulation rate data can unambiguously distinguish these cases.

6.5.3 Environmental history of Esthwaite Water: response to climate and nutrients

This section summarises the stratigraphical changes in physical sediment characteristics, diatoms and geochemistry to reconstruct the environmental history of Esthwaite Water and its catchment over the past 1200 years. The driving forces behind these changes involve complex interactions between climate and human activities and local and regional factors. The proxies employed all exhibit four major phases and therefore the following discussion will be divided into these four time periods.

6.5.3.1 Prelude to the Medieval Warm Period (~780-880 AD)

During this period, diatom communities are marked by high abundances of *A. subarctica* and *A. formosa* (Fig. 6.7, 6.8). Monitoring records of Esthwaite Water phytoplankton have revealed that these two species appear in winter and spring, when the lake has high nutrient concentrations. Therefore, their presence in the sediment record probably indicates relatively nutrient-rich conditions during that period. There is also evidence that *A. formosa* is an opportunistic taxon that responds rapidly to disturbance and nutrient enrichment. For example, it is often among the first diatoms to follow human settlement and agriculture in the catchments of European lakes (Renberg, Korsman & Anderson, 1993; Anderson, Renberg & Segerstrom, 1995). Thus the appearance of *A. formosa* is likely to be a response to local catchment disturbance during this period. DI-TP concentrations indicate mesotrophic conditions (average TP 14 $\mu g\ L^{-1}$), suggesting considerable nutrient inputs. Indeed, human activities expanded in the Esthwaite Water catchment during this period, since pollen records revealed a phase of forest clearance and mixed agriculture indicated by the increases in Poaceae, *Plantago* and cereal-type pollen and a decrease in woodland (Fig. 6.2), from the 7th century (Dickinson, 1975; Wimble, Wells & Hodgkinson, 2000; Chiverrell *et al.*, 2004; Coombes, Chiverrell & Barber, 2009). Increasing human activity would have led to more intensified soil erosion, thus introducing nutrients into the lake. This conclusion is further supported by the high SARs and element fluxes for this period (Fig. 6.3 and 6.10).

High abundances of *A. subarctica* during this period possibly indicate a colder and more turbulent water column. This species is typical of the late-winter and early-spring period of temperate lakes when the water is well mixed and cold (Stoermer & Ladewski, 1976; Gibson & Foy, 1988; Kilham, Theriot & Fritz, 1996; also see chapter 2). It has a high sinking rate and it is only present in the water column when there is sufficient turbulence (Lund, 1954). Further it is thought to be a good competitor under low light conditions (Kilham, Theriot & Fritz, 1996; Interlandi, Kilham & Theriot, 1999). It seems likely, therefore, that conditions were colder and windier during this period. Indeed, stronger winds and high precipitation could also account for the observed increase in sediment grain size. With strengthened wave action and intensified runoff, coarse material could transport further away from the shore to reach deeper areas of the lake. Further, ratios of Na/K and Na/Al were relatively low, suggesting reduced weathering at lower temperatures. Thus the palaeo data indicate a colder, windier period from 780 to 880 AD. This interpretation is supported by documentary evidence of a colder and more disturbed climate, accompanied by wet conditions in the last millennium (i.e. the Dark Age Cold Period), particularly between about 750 and 900 AD in northern, western and central Europe (Lamb, 1995). It is from the sixth and ninth centuries also that most of the storms and sea floods around the coasts of the North Sea are known to have occurred in this millennium (Lamb, 1995). Further indication of a cooler and more disturbed climate in Northern Europe around this time can be seen in the widespread abandonment of land and cultivation in the relatively low-lying Jaeren coastal region of southwest Norway (Salvesen, 1979).

The discrepancy between Geo-P and DI-TP values (Fig. 6.11) during this period could also be affected by the unstable climate conditions. Mixing processes (principally induced by wind, temperature and high precipitation) could have increased P release from the sediments under both oxic and anoxic conditions (Søndergaard, Kristensen & Jeppesen, 1992; George, Hurley & Hewitt, 2007), and the consequent elevated nutrient concentration could have favoured the growth of diatoms in the water column. Furthermore, higher rainfall and runoff could have increased the flushing of nutrients from the catchment to the lake during this era. Indeed, Mortimer (1941-1942) reported large fluctuations in Fe and P concentrations during summer 1940 due to unstable conditions in the water column. The lower Fe/Mn ratio values, however, seem contradictory to the interpretation of a disturbed water column, which theoretically provides more oxygen for redox processes. The low Fe/Mn may be due to increased organic production in the lake and thus deceleration of Mn release. Furthermore, SARs may be higher than those estimated by the age-depth model which assumes smoothed SARs between certain known age points. Any error in these calculations will also result in errors in the accumulation rates of the geochemical elements.

6.5.3.2 Medieval Warm Period (~880-1350 AD)

The environmental conditions changed significantly at ~880 AD, as shown by increases in LOI (average 29%) and decreases in grain size (average 7.3 µm) (Fig. 6.9). Elevated organic matter inputs indicate increased biological accumulation which may be related to a warmer climate. All the element fluxes, as well as SAR, remained low, suggesting lower allochthonous inputs and possibly reduced rainfall and sediment delivery to Esthwaite Water. This weak hydrological condition, resulted from low precipitation, is also mirrored by high proportions of the finer components in the sediment. Ratios of Na/K and Na/Al were both low, indicating stronger weathering processes. Given the relatively weak hydrological condition, this enhanced weathering effect is most likely due to a warm climate.

Diatom concentrations and fluxes both declined during this period. Marked changes were seen in the DCA axis 1 (Fig. 6. 7), reflecting a shift in community composition as *C. comensis* began to dominate, concurrent with a dramatic decrease in the heavily silicified diatom *A. subarctica*. This particular species replacement of *Aulacoseira* taxa by *Cyclotella* taxa has been widely observed in Arctic and alpine environments (e.g. Sorvari, Korhola & Thompson, 2002; Ruhland, Paterson & Smol, 2008) and in lakes at temperate latitudes (e.g. Fritz, Kingston & Engstrom, 1993; Marchetto *et al.*, 2004; Harris, Cumming & Smol, 2006). Increasing evidence, both from palaeolimnology and modern monitoring records, shows that such diatom shifts are induced by a warm climate (Kilham, Theriot & Fritz, 1996; Lotter & Bigler, 2000; Rautio, Sorvari & Korhola, 2000; Chu *et al.*, 2005; Forsström *et al.*, 2005; Pannard, Bormans & Lagadeuc, 2008). Similarly in Esthwaite Water, a warmer climate offers a plausible explanation for the diatom shift from *A. subarctica* to *C. comensis*, which is also indicated by the changes in LOI and element ratios. Indeed, documentary evidence reveals that the climate was characterized by a prolonged interval of warmth from about 900 to 1300 AD, exceeding conditions which prevailed during the early part of the twentieth century, a period known as the "Medieval Warm Period" (Hughes & Diaz, 1994; Lamb, 1995; Broecker, 2001). The climate became warmer with drier summers and milder winters during this time (Lamb, 1965).

In this era the palaeorecord indicates that the lake was of low trophic status, as it is characterized by abundances of oligotrophic species *C. comensis* and *A. minutissimum* (Fig. 6.8). While there are records of Norse Irish settlement in the Lake District from the late 9th century (Table 6.1), pollen analysis of sediments from Hulleter Moss reveals that this was short-lived in the area as reflected by the expansion of *Quercus* and other woodland taxa from *ca.* AD 1000 to 1350 (see Fig. 6.2, and Coombes, Chiverrell & Barber 2009). Therefore, nutrient input to the lake would have been mainly from natural processes such as soil erosion. The reduced nutrient levels would slow down diatom growth and this may explain the low diatom concentrations and fluxes observed during this period.

6.5.3.3 Little Ice Age (~1350-1880)

During this period, there were two major changes in the diatom profile. Firstly, at ~1350 AD, *C. comensis* decreased significantly, accompanied by increases of *A. subarctica* and *C. radiosa* (Fig. 6.7). This diatom community composition lasted until ~1750 AD, when a second increase occurred in *A. subarctica* along with *A. formosa*. Both the DCA axis 1 scores and the rate of change exhibited a significant shift at ~1750 AD. Similarly to *C. comensis, C. radiosa* is also a summer species but it is typically associated with mesotrophic waters (Håkansson & Regnéll, 1993; Lotter *et al.*, 1998). Its increase from 1350 AD suggests that the nutrient supply was slightly enhanced but nevertheless was not sufficient to support *A. formosa* until 1750 AD. With the continuous increase in nutrients after 1750 AD, the relative abundance of oligotrophic *C. comensis* further decreased. Both diatom concentrations and fluxes increased over this period, reflecting the higher productivity of the lake. This pattern is corroborated by DI-TP, which exhibited an increase to >10 $\mu g\ L^{-1}$ from 1350 AD with an average of 12 $\mu g\ L^{-1}$ from 1750-1880 AD. This slight increase in lake productivity is likely due to deforestation activity in the catchment (see discussion below), although such disturbance is still rather weak prior to 1600 AD.

One of the most distinct features during this period is the continuous decrease in LOI (Fig. 6.9). LOI may vary because of temporal changes in sediment composition (controlled by factors such as productivity, inorganic inputs, and decomposition) and the patterns of sediment accumulation (controlled by factors such as basin morphology and water level (Shuman, 2003). Because of the many possible controls, changes in the LOI of a single core are often hard to interpret. Given high precipitation in the Esthwaite Water catchment and relatively low trophic status prior to the 1970s, organic matter should mainly originate from the catchment. The catchment soil erosion signal, SAR and grain size, also have an apparent correlation with LOI (see Fig. 6.9), supporting this hypothesis (Dalton *et al.*, 2005). When higher SAR occurred (e.g. in the periods of 780-880 and 1350-1880 AD), sediments are of higher medium grain size and lower LOI. This suggests that higher SARs are associated with greater transport of terrestrial material (mineral, soil or clastic) to the lake. Generally, warm and humid climate conditions favour growth of terrestrial vegetation and thus more organic matter accumulation in the soil. Thus high LOI likely represents phases of higher vegetation production in the catchment and thus warmer climatic conditions, while troughs may correspond to cooler phases (Dalton *et al.*, 2005). Consequently, in Esthwaite Water, low LOI accompanied by an increase in lake productivity likely indicates cooler conditions. Moreover, both Na/K and Na/Al ratios remained high indicating weak weathering processes and low erosion rates, which is also in line with the suggestion that the climate was colder and drier at this time. Different trajectories of Na/K and Na/Al ratios during 1750-1870 AD, indicating slight acidification after 1750 with the development of local industry, since orthoclase ($K[AlSi_3O_8]$) is more easier hydrolyzed to kaolinite ($AI[Si_4O_{10}][OH]_8$) and which cause further losses of K under an acid environment (Hellmann *et al.*, 2003). However, this acidification was possibly rather weak and caused limited effect on the lake, given there is no evidence of acidity from the diatom communities.

Deforestation in the catchment may explain the observed increase in SAR, since SAR exhibits a clear inverse trend with tree pollen over the whole period (see Fig. 6.2 and 6.3). Pollen data demonstrate woodland clearance after 1700 AD associated with decreases in *Betula, Alnus* and especially *Corylus avellana* type. The sum of tree pollen gradually decreased from 1350 AD to 1750 AD and recovered thereafter (Fig. 6.2). These inferred changes in catchment vegetation match well with documentary evidence of local human activity (Table 6.1). In particular, three significant increases in SARs clearly relate to events in the region: i) in 1600 AD, ii) in 1750 AD and iii) in 1800 AD. Firstly, historical records show that England's population declined from a peak of 6 million (in 1300 AD) to no more than 2.3 million (in 1526 AD), and remained stagnant for the next two centuries due to the outbreak of Black Death in 1348 AD (Mayhew, 1995). This was likely to have affected the population of Cumbria until numbers recovered in the early 17th century (Winchester, 1987). With this population recovery and a massive expansion in sheep rearing after ~1600 AD, slopes in the catchment would have been intensively destabilised, leading to increases in SAR. The second coincidence between SAR and tree pollen records occurred at ~1750 AD, when the Lake District experienced a large-scale amenity planting and woodland conservation programme (Pearsall & Pennington, 1947). These activities increased woodland cover but also destabilised upland soils under the concurrent expansion of agriculture (Chiverrell, Harvey & Foster, 2007). This consequently led to another period of high SAR. However, with the woodland conservation programme gradually coming into effect, soil erosion rates were likely reduced which may account for the slight decrease in SAR during 1750-1800 AD. The third increase in SAR at ~1800 AD probably resulted from a rapid increase in the local population. For example, there was a 36% increase in the population of nearby Furness and Cartmel between 1800 and 1831 AD (Bouch & Jones, 1961). As a result of the increasing SARs, all the element fluxes exhibited increases in these three time periods (Fig. 6.10).

In summary, during this period Esthwaite Water was mainly affected by natural processes. Climate forces appear to be the main driver prior to 1600 AD but after this time anthropogenic pressures became more pronounced. The period 1350 to 1880 AD covers the climate episode known as the “Little Ice Age”, which is characterized by cool, wet summers and cold, dry winters (Grove, 1988). The significant decrease in *C. comensis* at ~1350 AD is almost certainly a response to a decline in summer temperatures. However, the further decrease of *C. comensis* at ~1750 AD may result from the enhanced nutrient inputs arising from growing human pressures in the catchment. Hence from this time onward it becomes difficult to disentangle the effects of climate and nutrients on the ecosystem and thereby discern climatic signals from the lake sediment record.

6.5.3.4 Modern land use and recent climatic warming: ~1880-present

The post-1850 AD period was characterized by unprecedented human disturbance in the Esthwaite Water catchment as seen elsewhere in Europe. Increasing agriculture (e.g. sheep farming, ditching, ploughing), changes in forestry practice (e.g. the establishment of the National Park) and expansion of mining-related industries (gun-powder plants, lead mining and development of the transportation system) in the Esthwaite Water catchment changed the landscape significantly (Rollinson, 1967). Unsurprisingly, SAR increased from ~0.02 g cm^{-2} year^{-1} in 1870s to 0.08 g cm^{-2} year^{-1} in recent decades, although a period of lower values occurred from 1940 to 1960. Climate records of precipitation and temperature do not display significant abnormalies during this 20 years (see Fig. 5.1 in chapter 5) and given the background of increasing catchment disturbance, the marked decrease in SAR is likely due to human activity, such as modification to the drainage system or shorelines which in turn may have affected the local hydrology.

Consistent with the increasing SARs, accumulation of heavy metals in the lake sediments also increased from ~1880 AD (Fig. 6.9). This is coincident with the documented development of industry and the increased combustion of fossil fuels, although domestic and agricultural sources within the lake catchment may also have contribution. The increasing fall-out of airborne pollutants, due to the progressive industrialization of Europe (Renberg, 1986; Rippey & Douglas, 2004), may be another important source. An analysis of spheroidal carbonaceous particles (SCP) in core ESTH1 from Esthwaite Water revealed that increased deposition started from the mid-19th century (Rose, unpublished data).

The diatom assemblages of ESTH0 exhibited the greatest variation during the period from 1870 AD to present (Fig. 6.7). The proportions of planktonic species increased continuously and the rates of change were approximately ten times higher than in the earlier part of the sediment record. The environmental changes can be divided into two phases. Prior to 1976 AD, increases in eutrophic species *F. crotonensis* (albeit in low concentrations) and *A. formosa* suggest an increase in nutrient input. After 1976 AD, a second eutrophication phase occurred, probably due to the establishment of a sewage treatment works in the nearby village of Hawkshead in the early 1970s (Table 6.1). From 1970 AD the diatom communities were characterized by further increases of *A. formosa* and *F. crotonensis*, as well as the arrival of *S. binatus*. *S. binatus* has a preference for high nutrients, high conductivity and low light, an environment associated with eutrophication (Håkansson & Kling, 1990; Sayer, 1997; Findlay *et al.*, 1998). Furthermore two new species, *A. granulata* var *angustissima* and *F. capucina* var *rumpens*, arrived after 1998 AD. Conversely *T. flocculosa* declined after ~1970 AD. It is a summer species and appears in the early phase of enrichment but tends to decrease with progressive phosphorus enrichment (Talling & Heaney, 1988; Anderson, Renberg & Segerstrom, 1995). Consequently, *T. flocculosa* initially increased from the late 19th century but decreased after the 1970s when the lake became eutrophic. Both the reconstructed DI-TP and sediment P flux clearly demonstrate that the lake experienced a moderate increase in nutrients prior to 1976 AD but a more pronounced increase after 1976 AD. The arrival of *A. granulata* var *angustissima* and *F. capucina* var *rumpens* was probably co-driven by nutrients (e.g. silica and nitrate) and climatic factors (e.g. summer temperature, wind), since annual values of these variables exhibited high variability over the period of *Aulacoseira* abundance (see further discussion in chapter 5).

6.5.4 Climate change and its interaction with nutrient evolution

The 1200 year palaeolimnological record in Esthwaite Water tracks the response of the lake to changes in climate and land use in the catchment. Human activities affect lake conditions indirectly by changing hydrological conditions, vegetation structure and catchment landscape. One of the most significant consequences of anthropogenic activity is an increase in nutrient inputs to lake systems, often via soil erosion following vegetation clearance. For example, during period of low woodland cover from 750-880 AD and 1750-1880 AD, sediment accumulation rates were relatively high and DI-TP values indicate nutrient-rich conditions. Inversely, low DI-TP and sediment P flux values prevailed during the period 1150-1600 AD when the catchment was highly forested. These observations suggest a close linkage between catchment vegetation, human activity and in-lake P concentrations. Consequently, the millennium timescale offers an ideal timeframe within which to explore the interactions between climate and nutrients.

Numerous studies have provided strong evidence for the occurrence of the MWP and LIA over the last millennium, at approximately 1000-1300 AD and 1550-1850 AD, respectively (Bradley & Jones, 1992; Crowley & Lowery, 2000; Grove, 2001). However, it is difficult to define a universal set of dates for the "onset" and "end" of the two periods due to regional variations (e.g. Luckman, 1996; Grove, 2001; Nesje & Dahl, 2003). To our knowledge, there are limited records for the start and termination of the two climate episodes for the Esthwaite Water catchment. Diatoms in Esthwaite Water exhibit distinct seasonality and temperature has been shown to be one of the most important factors in controlling community dynamics (see chapter 2 and chapter 5). The sensitivity of diatoms to temperature changes has been demonstrated by numerous other studies (e.g. Lotter *et al.*, 1997; Rosen *et al.*, 2000; Bigler & Hall, 2002; Bloom *et al.*, 2003). Given the relatively low intensity of human activity prior to 1880 AD (particularly pre-1600 with the exception of 750-1000 AD), it is expected that the diatom assemblages should be mainly controlled by climate (temperature) during the early period in the lake history. The diatom shift from *A. subarctica* and *A. formosa* to *C. comensis* at ~880 AD is coincident with the timing of the MWP. Nevertheless, considerable human disturbance, as indicated by pollen data and historical catchment record, also occurred at ~ 880 AD, and therefore a combination of climate and nutrients is likely to be controlling the diatom communities at this time. Under relatively stable nutrient conditions from 900 to 1750 AD, the significant change in the diatom assemblages at 1350 AD, characterized by an increase in the cold species *A. subarctica* and a decrease of in the thermophilic species *C. comensis*, indicates the start of the LIA period. After ~1750 AD, the sediment record suggests that nutrients played a more important role in regulating diatom communities, and hence the termination of the LIA is difficult to define although it is estimated to occur after 1750 AD.

In addition to the diatom evidence, other proxies such as LOI and ratios of Na/K and Na/Al support the definition of the climate episodes described above. The qualitative inference of past climate conditions from the palaeo studies is generally consistent with available records (Fig. 6.12). Given the high spatial variability of precipitation and the limited ability to infer rainfall from the Esthwaite Water sediment record, the following discussion focuses on temperature. Inferred temperatures for both central England and the northern hemisphere indicate higher temperatures from 1000 to 1350 AD and lower temperatures from 1350 to 1880 AD. These changes correspond with the temperature shifts inferred from the fossil diatom record. Nevertheless, it should be recognised that diatom response to changing temperature is usually indirect as a result of temperature effects on water-column stratification, nutrient cycling and alkalinity generation, and thus interpretation of the fossil record requires an understanding of the processes that are operating in the water column (Battarbee, 2000). For example, changes in temperature and the length of the warm summer period have a significant bearing on water-column properties, exerting a strong influence on competitive abilities of diatoms (Panizzo *et al.*, 2008). The stability of the water column may also directly control buoyancy of diatoms or indirectly control release of nutrients (Battarbee, 2000).

Over the last millennium changes in both climate and nutrients (closely linked to human disturbance in the catchment) have imposed significant effects on the diatom flora of Esthwaite Water, although each driver has exerted different degrees of control at various times in the lake's history. In summary, nutrients outperformed climate from ~750 to 880 AD and post-1880 AD, leading to higher diatom concentrations, higher rates of change and most recently the presence of new diatom species under more productive conditions. In contrast, from ~880-1750 AD diatom assemblages

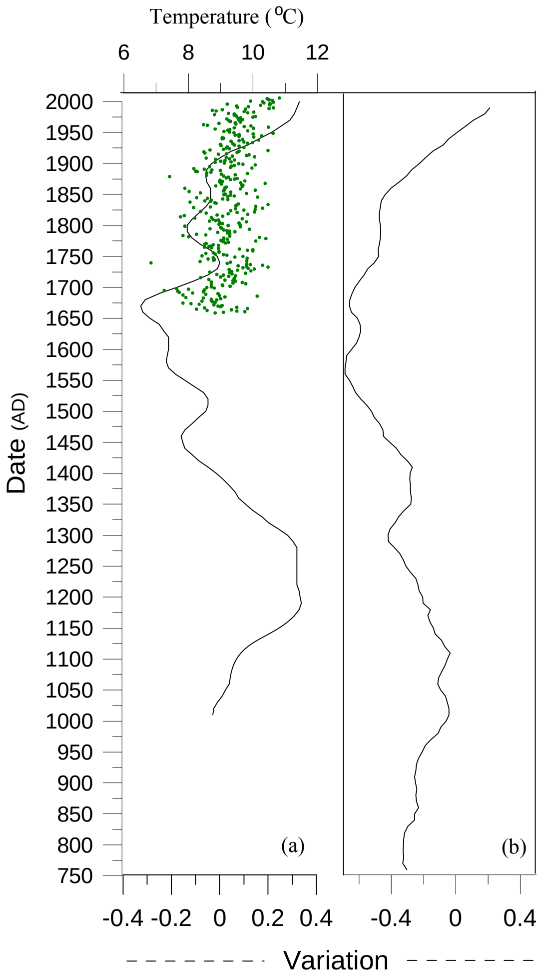

Fig. 6.12 Estimated relative temperature variations for (a) Central England Temperature variation based on a combination of thermometer, historical and proxy data records (data from Mann (2001)). Points in (a) are measured annual CET also shown in Fig. 6.1b; (b) reconstructed Northern Hemisphere Temperature (data from Mann & Jones, 2003). The records have been smoothed to illustrate long-term variations.

exhibited relatively subtle changes and concentrations remained low during a period when nutrient levels appear to be low and climate influences dominated. However, it is difficult to discern the individual effect of the two main drivers, principally because they are highly related. A two-year monitoring study in Esthwaite Water from July 2007 to June 2009 demonstrated that seasonal climatic factors (air temperature) are significantly related to nutrient variables (SRP, NO_3-N and SiO_2) (see chapter 2). Furthermore, the response pattern of the biota to these parameters varies according to the timescales of interest. At seasonal scales, both temperature and SRP exhibit long gradients and thus are of almost equivalent importance in explaining diatom variance (see chapter 2). At the inter-annual scale, as illustrated by the 60-year monitoring record, SRP is more important than annual air temperature in explaining the diatom distribution since shorter gradients of the latter exist compared to SRP (see chapter 5). Consequently, over long timescales such as the last 1200 year record discussed here, it is plausible that both climate and nutrients have played a role in controlling diatom dynamics.

6.6 Conclusions

The multi-proxy palaeolimnological study, in combination with historical documentary record, indicates that Esthwaite Water has experienced several distinct stages of environmental change in terms of climate and nutrients over the past 1200 years. High sediment P accumulation rates and high inferred DI-TP concentrations suggest relatively high nutrient status of the lake between 750 and 880 AD most likely from local human disturbance, as indicated by a decline in tree pollen. A cold and unstable climate was inferred at this time based on the high abundance of *A. subarctica* and high Na/K and Na/Al values. In the following 1000 years (~880-1880 AD) diatom assemblages were dominated by *C. comensis, C. radiosa* and *A. minutissimum*, suggesting a long period of relatively low productivity and, by implication, that climate was the main control on the community during this period. Two climatic phases, namely the MWP and the LIA, were apparent. Shifts in the diatom assemblages and other proxies including LOI, grain size and ratios of Na/K and Na/Al were evident in the periods 880-1350 AD and 1350-1880 AD. It is, therefore, proposed that the MWP was initiated from ~880 AD and was terminated by the LIA at ~1350 AD. After 1750 AD, nutrients appear to play a more important role in regulating diatom communities as shown by eutrophic diatom assemblages and increasing LOI and sedimentary P fluxes. Hence the termination date of the LIA is difficult to define but is likely to be after 1750 AD. After 1880 AD the palaeoecological data indicate a period of stronger human impact in the catchment resulting in intensified soil erosion and the introduction of more nutrients to the lake, and hence higher productivity as shown by eutrophic diatom assemblages and increasing LOI and sedimentary P fluxes.

The multi-proxy palaeolimnological records of Esthwaite Water have demonstrated that both climate and nutrients have impacted the lake system over the last 1200 years. Generally, climate impacts were more pronounced when nutrient concentrations were relatively stable. However, during phases of enrichment and particularly in recent decades, the nutrient signal outweighs that of climate. This study highlights the difficulty in discerning the individual effect of the two main drivers due to their interaction and the fact that each exerts a different control on the diatom communities depending on the timescale of interest.

Chapter 7 Summary and future directions

7.1 Summary

In this thesis, both contemporary and palaeolimnological records were used to understand how climate and nutrients have impacted the lake ecosystem of Esthwaite Water, UK, over a range of timescales from months to several centuries. Diatoms were used as the key indicator because of their sensitivity to water quality change. The following four key questions guided this research: 1) How faithfully do the sedimentary diatom remains record changes in the planktonic diatom populations in the water column?; 2) How do diatom assemblages respond to changes in climate and nutrients over a range of timescales (seasonal, decadal to centurial scale)?; 3) Can we quantitatively disentangle their sole contributions?; and 4) How does the combination of contemporary limnology and palaeolimnology improve our understanding of environmental change in Esthwaite Water? The extent to which this thesis has answered these questions is discussed in the following sections.

Question 1 The study demonstrated that the sedimentary diatom remains do faithfully record changes in the planktonic diatom populations in the water column. The comparison of the diatom composition from the water column, sediment traps and surface sediments over a two-year monitoring period, showed a close agreement between the three records (chapter 3). Additionally, the comparison between the fossil diatoms from a ^{210}Pb dated sediment core and the diatoms in a 59-year monitoring record revealed similar community structures in each set of paired samples (chapter 3). The dominant species in the phytoplankton records were also found in the sediments with comparable abundances, although some species (e.g. *A. formosa*) were under- and others (e.g. *A. subarctica*) over-represented in the sediment record compared with the phytoplankton data.

Questions 2 and 3 The influence of climate and nutrients on the diatom flora of Esthwaite Water was explored over seasonal, annual, decadal and centennial timescales. Statistical analyses (correlation analysis, redundancy analysis, and generalized additive modelling) of the two-year and 60-year monitoring series of physico-chemical lake characteristics and diatom assemblages revealed that nutrients played a more important role in regulating diatom growth than climatic factors at these timescales. For example, for the two-year monitoring dataset, variance partitioning analysis indicated that SRP was the most important factor in explaining the diatom data, accounting independently for 8.3% of variance in the species data, followed by SiO_2 (6.5%), ST (5.5%) and alkalinity (4.7%). An additive mixed model further illustrated that SRP was the most important factor controlling the diatom assemblages for the 60-year monitoring period but AirT imposed limited effect, particularly when nutrients were inadequate for diatom growth.

The response of the diatom assemblages to changes in climate and nutrients over a 1200 year timescale was investigated by means of a multi-proxy study involving diatoms, grain size, LOI, pollen, and geochemical analysis (chapter 6). Four stages of environmental change were defined, each being consistent with changes in documented human activity and known climate patterns. From 750 to 880 AD relatively high nutrient status and a cold, unstable climate was inferred. In the following 1000 years (880-1880 AD) diatom assemblages were dominated by *C. comensis, C. radiosa* and *A. minutissimum*, suggesting a long period of relatively low productivity and, by implication, that climate was the main control on the community during this period. Two climatic phases, namely the MWP and the LIA, were apparent. Shifts in the diatom assemblages and other proxies including LOI, grain size and ratios of Na/K and Na/Al were evident in the periods 880-1350 AD and 1350-1880 AD. It is, therefore, proposed that the MWP was initiated from ~880 AD and was terminated by the LIA at ~1350 AD. Nutrients appeared to play a more important role in regulating diatom communities from the mid-eighteenth century and, therefore, the termination date of the LIA was difficult to define but is likely to be after 1750 AD. After 1880

AD the palaeoecological data revealed a period of strong human impact in the catchment and hence higher productivity, as shown by eutrophic diatom assemblages and increasing LOI and sedimentary P fluxes.

Overall, climate impacts were more pronounced when nutrient concentrations were relatively stable. In contrast, during phases of enrichment and particularly in recent decades, the nutrient signal outweighs that of climate. This study highlights the difficulty in discerning the individual effect of the two main drivers due to their interaction and the fact that each exerts a different control on the diatom communities depending on the timescale of interest.

Question 4 The thesis has highlighted the importance of integrating contemporary limnology and palaeolimnology to improve our understanding of environmental change. This has been shown in several ways. Firstly, the ecological information derived from the contemporary limnological datasets proved to be highly valuable for refining the inferences of changes in nutrients and climate from the sedimentary diatom record. Given the importance of contemporary diatom ecology to the interpretation of palaeo-environmental reconstructions, the seasonal and inter-annual variability of planktonic diatom assemblages in Esthwaite Water were examined based on monitoring datasets for a two-year (chapter 2) and a 59-year record (chapter 6). Both records revealed three principle shifts in the diatom assemblages each year, from dominance of i) *A. formosa* in spring to *F. crotonensis* in summer; ii) *F. crotonensis* to *Aulacoseira* species in autumn and winter; iii) *Aulacoseira* species to *A. formosa* in the spring. The exact timing and abundance of the crop varied with changing environmental conditions. In addition to this ecological information, further diatom autecological information was collected from published literature, particularly for those species whose information could not be obtained from the monitoring records. Given the particularly high occurrence of *Cyclotella comensis* in the sediment core but its limited occurrence in the modern phytoplankton of Esthwaite Water, another long-term monitoring record collected from a nearby lake (Derwent Water) was used to reveal the seasonality and environmental preferences of this taxon (chapter 6).

Secondly, the diatom representativity study involving a comparison of the fossil diatoms in the sediment record and the diatoms in a 59-year monitoring record revealed similar community structures in the two datasets and therefore confirmed that the sediments faithfully represent the contemporary communities. This provided a firm foundation for the palaeolimnological study. Thirdly, the contemporary data were instrumental in refining the chronology of the sediment record. The age-depth model was established for a disturbed sediment core, ESTH7, by the combination of radiometric dating techniques and core correlations using monitoring and palaeolimnological records (chapter 4). Both the reasonable diatom representativity and reliable chronology ensured that the core was suitable for inferring environmental change in this lake. However, the study also demonstrated that great care is needed when selecting coring sites for palaeolimnological studies even in relatively small lakes.

7.2 Management implications

The insight into the interaction between climate and nutrients over a variety of timescales provides useful information for lake restoration. The European Water Framework Directive requires that all water bodies in Europe must be in ‘good’ ecological status by 2015 (European Union, 2000). This is a major challenge given that most systems are subject to multiple stressors, such as climate change and nutrient enrichment at Esthwaite Water, and since the response of lake ecosystems to these multiple pressures is not easily predicted. The latter was confirmed by the analyses in this thesis which revealed the complexity of climate-nutrient interactions and the different roles of the two drivers dependant on timescale (chapter 2, chapter 5 and chapter 6). Nonetheless, statistical analyses of the 60-year dataset highlighted that changes in nutrients are likely to have a more significant influence on the lake ecosystem, at least in terms of the diatom assemblages, than climate factors. This suggests that reduction of nutrient concentrations in the lake should remain the principal goal of lake management as it is likely to be the most effective way to restore Esthwaite Water. Fortunately, the Environment Agency has recently taken actions to limit nutrient inputs to the lake, by removal of the fish farm in 2009, and monitoring is ongoing to track the degree of recovery. The palaeoecological data provided by this study will prove valuable for determining the extent to which the diatom assemblages return to those present in the lake prior to enrichment.

7.3 Research constraints and future directions

It is recognised that this thesis focused on only limited nutrient and climate variables and their role in explaining the diatom community of Esthwaite Water. However, diatom dynamics are controlled by many other factors such as pH, organic pollution, competition for nutrients with other biological groups, and with invasive species (Reynolds, 1980). From a nutrient perspective, the focus of this study was on phosphorus as the key limiting nutrient, but there is now considerable evidence that nitrogen may also be an important driver of diatom dynamics in some lakes (Wolfe, Baron & Cornett, 2001; Wolfe, Van Gorp & Baron, 2003; Saros *et al.*, 2003; Saros *et al.*, 2005). The role of these other potential drivers of change was not explored in this thesis but may be an interesting avenue for future research.

The long-term monitoring records for Esthwaite Water, spanning 60 years, provided a unique opportunity for comparison with the sedimentary diatom record. However, there are no measured data for the lake extending back beyond this period to help inform the interpretation of the historical nutrient and climate changes. The CET series and rainfall records track back several centuries but long-term nutrient data are lacking. In this thesis, therefore, proxies such as sediment P flux and DI-TP were employed to describe past nutrient status. It is recognized that the latter is not an independent proxy as it is derived directly from the diatom data. Therefore, evidence of environmental change from additional proxies would benefit the study and may improve the ability to disentangle the role of nutrients and climate over centuries to millennium timescales. For example, numerous studies have revealed that temperature is the most important factor controlling chironomid distribution and abundance on regional scales (e.g., Walker *et al.*, 1991; Lotter *et al.*, 1997; Larocque, Hall & Grahn, 2001; Porinchu & Cwynar, 2000). Consequently, chironomids may provide a valuable proxy for historical temperature changes, which in turn could be validated with the CET series. Pigment analyses could also be conducted to provide historical information on the structure of biological communities, in addition to diatoms, and to act as a proxy for aquatic productivity (Leavitt & Hodgson, 2002; McGowan, 2007). Indeed analysis of the pigment composition of the short core ESTH8 (results not shown in this thesis) and it did exhibit clear signals reflecting nutrient dynamics. Hence further pigment analysis is planned for the longer core (ESTH7). In addition, organic isotope analysis might to be conducted since it is a good indicator of past productivity (and source) in the lake (Schelske & Hodell, 1995; Brenner *et al.*, 1999).

This thesis examined the diatom populations of Esthwaite Water on a seasonal and annual basis in order to establish information on the ecological preferences of the dominant taxa. Nevertheless, the study was able to focus on only a small number of species. Hence, further studies to increase our knowledge on the seasonality of a broader range of diatom species, particularly in relation to climate and nutrient variables, would be of value for inferring shifts in ecological function, such as the length of the growing season (e.g. Sayer *et al.*, 2010).

Finally, the issues surrounding the reliability of the sediment chronology must not be overlooked. Potential errors resulting from non-uniform sediment accumulation rates, associated with sediment mixing through physical and biological processes, clearly limit high-resolution interpretations of palaeolimnological records. In this study, dating issues arose owing to a slumping event and an hiatus in the Esthwaite Water sediment record, although the work undertaken went some way to resolve the chronology. In the absence of an accurate chronology it is accepted that there may be a mis-match between dates when comparing the palaeoecological and contemporary records. This may be particularly problematic when attempting to quantitatively separate the effects of nutrients and climate. One way to overcome such difficulties would be to conduct similar studies on sites with annually laminated sediments, although such highly resolved sequences are only found in a limited range of lake types.

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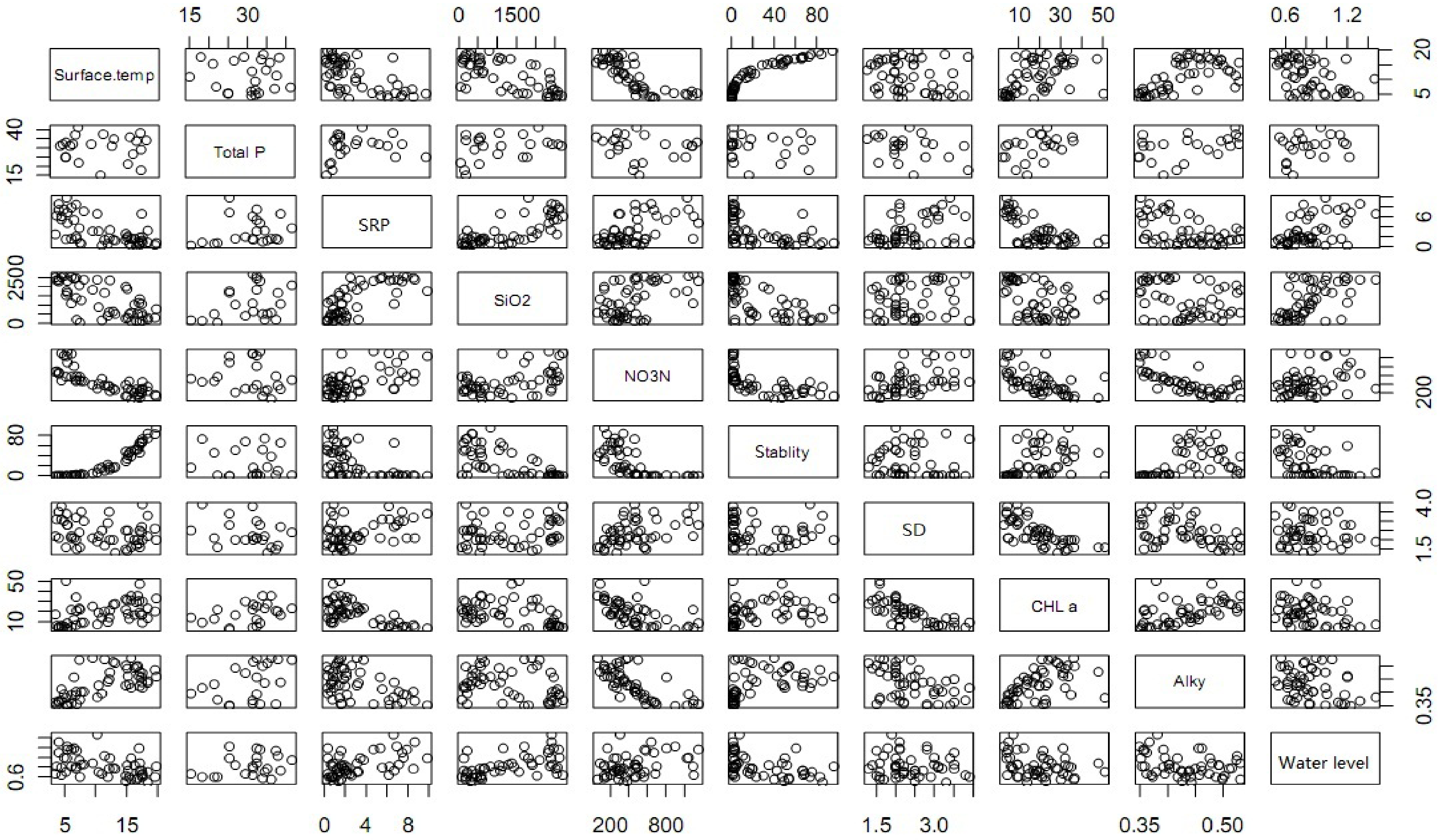
Appendix I: Scatterplot matrix illustrating the relationships between paired environmental vairables



Appendix II: Diatom assemblage changes (with all speices whose percentages are >2% at least in one sample) over the past 60 years in core ESTH0 from Esthwaite Water