Heterogeneity in Esthwaite Water, a Small, Temperate Lake: Consequences for Phosphorus Budgets

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Declaration

I declare that this thesis is entirely my own work and has not been submitted for a higher degree at another institution or university.

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Abstract

Eutrophication through phosphorus enrichment of lakes is potentially damaging to lake ecosystems, water quality and the ecosystem services which they provide. Traditional approaches to managing eutrophication involve quantifying phosphorus budgets. An important shortcoming of these approaches is that they take little account of the inherent heterogeneity of lakes. Furthermore, most studies of lake heterogeneity have been carried out in large lakes, a situation which reflects neither small lakes' importance in biogeochemical cycling nor their significant contribution to the global sum of lake environments.

This thesis reports investigations into heterogeneity in Esthwaite Water, UK, a small, temperate, eutrophic lake. The overarching aim of the work was to improve understanding of phosphorus fluxes and budgets in this type of environment. Heterogeneity, and its governing physical mechanisms were elucidated in the lake's surface waters and bed sediments. In addition, the effects that this heterogeneity had on phosphorus supply to phytoplankton from the main stream inflow and internal sediment sources were examined.

The research is presented as four studies, which address surface water heterogeneity, bed sediment heterogeneity, and phosphorus supply via inflowing streams and from internal sediment storage. Significant heterogeneity was found in the surface water, despite the lake being small and the physical forcing, relatively weak. Assumptions about the physical processes contributing to sediment heterogeneity based on models of large or shallow lakes were found not to be applicable. Taking account of bed sediment heterogeneity was found to be important for the accurate calculation of burial rates of both total phosphorus and organic carbon, as ignoring it led to discrepancies up to 110%. Soluble reactive phosphorus (SRP) dispersal in the shallow transition zone at the mouth of the main inflowing stream, and was found to be the result of not only hydrological dilution but also biological uptake. Ignoring SRP heterogeneity in this zone led to up to an 18% underestimate of lake-wide averaged concentration during the growing season. SRP pathways in the lake were both spatially and temporally heterogeneous, resulting in large seasonal and inter-annual variations in phosphorus supply. Internal and external supplies were of similar magnitude during the summer but internal anoxic sources dominated in the late summer and autumn. Inter-annual variation in the hypolimnetic build-up of phosphorus associated with differences in lake stability and mixing strongly affected the internal phosphorus supply.

Overall, the thesis concludes that spatial and temporal heterogeneity is a characteristic of this lake at many scales, despite the relative weakness of the governing physical forcing, and that it affects significantly not only the nature of the lake at specific locations, but also lake-wide averaged parameter values. Specifically, different phosphorus sources have distinctly different patterns of variability, which need to be taken into account when calculating phosphorus budgets. Finally, the importance of particular physical processes for phosphorus budgets is likely to differ between large and small lakes owing to the influence of basin morphometry and therefore understanding derived about these budgets in large lakes cannot simply be assumed when considering small lakes.

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List of Papers

This thesis is based upon the research reported in the following papers:

Mackay, E.B., Jones, I.D., Thackeray, S.J., and Folkard, A.M. (2011) Spatial heterogeneity in a small, temperate lake during archetypal weak forcing conditions. *Fundamental and Applied Limnology*. 179 (1), 27-40.

Mackay, E.B. Jones, I.D. Folkard, A.M. and Barker, P. (2011) Heterogeneity of surface sediment in small lakes: quantifying focusing effects on organic carbon and phosphorus burial. *Freshwater Biology*. doi:10.1111/j.1365-2427.2011.02616.x.

Mackay, E.B., Jones, I.D., Folkard, A.M. and Thackeray, S.J. (2011) Transition zones in small lakes: the importance of dilution and biological uptake on lake-wide heterogeneity. *Hydrobiologia*. doi: 10.1007/s10750-011-0825-y.

Mackay, E.B., Jones, I.D. and Folkard, A.M. Variability in phosphorus supplies during the growing season in a small eutrophic lake. To be submitted to Water Research.

Chapter 1 Introduction

1.1 Overview

The environmental consequences of increased phosphorus use in our industrialised global society eloquently illustrate the dual problems of growing resource scarcity on the one hand and worsening negative environmental impact on the other. It is widely recognised that the non-renewable reserves of phosphate rock used in fertilizer are reducing in quality and increasing in cost as their scarcity grows, with some projections suggesting that sources of phosphorus will be exhausted in less than 100 years (Cordell et al. 2009). Because of the growing use of phosphorus in human society, global levels of phosphorus supply to freshwaters are estimated to exceed the level viewed as acceptable by humanity, the so-called 'planetary boundary' level (Carpenter and Bennett 2011). Unsurprisingly, therefore, the negative consequences of phosphorus-induced eutrophication are becoming widespread in freshwaters (Schindler 2006, Smith et al. 2006).

Eutrophication and the impacts of excessive phosphorus loading to freshwater are not a new problem (e.g. Rawson 1939, Likens 1972, OECD 1982). However, increasing recognition of the role of freshwaters in the supply of ecosystem services has begun to highlight the wider consequences of eutrophication, which can impair or in some cases lead to the total loss of services (Millenium Ecosystem Assessment 2005, UK National Ecosystem Assessment 2011). Therefore, efforts to restore or improve the water quality of freshwater environments such as lakes frequently require a reduction in nutrient loading.

However, lake environments are complex systems, which are heterogeneous across different spatial and temporal scales, and these complexities inevitably influence the response of the lake to remediation efforts. Improving our understanding of this heterogeneity and the processes which lead to it is important not only for current lake managers but also for our ability to predict what might occur in the future as the use of land in catchments alters or the climate changes. In addition, relatively little consideration has been given to understanding how heterogeneity influences phosphorus sources and sinks in lakes and how this variability might affect lake management tools such as the development of phosphorus budgets.

The importance of the disproportionate role that small lakes ($\leq 1\text{km}^2$) play in global biogeochemical cycles has been highlighted recently (e.g. Downing et al. 2008, Downing 2010, Staehr et al. 2011). In addition, there is a new recognition of the global importance of small lakes because of their numerical dominance over larger lakes (Downing et al. 2006). However, relatively few studies have considered the influence of physical forcing on small lake heterogeneity and the consequences for phosphorus fluxes and budgets.

This thesis focuses on investigating some of the implications of both the effect that small lakes have on their physical forcing (the influence of lake morphometry) and the effect that physical forcing has on small lakes (the development of heterogeneity) in the context of phosphorus fluxes and budgets. Heterogeneity is considered in both the surface waters and the bed sediments. Through the examination of the physical processes occurring in the lake, the research presented seeks to improve our understanding of the development of heterogeneity. In addition, the variability of the various external (lake catchment) and internal (bed sediment) sources of phosphorus is considered, with the intention of improving estimates of phosphorus fluxes for small lakes and improving understanding of phosphorus pathways from these sources to the surface waters, where it is taken up by phytoplankton. By examining fluxes from a number of different phosphorus sources over the growing season, the thesis also provides insights into the variation of their relative importance over time. The example lake used in the study is Esthwaite Water, UK, a small, eutrophic, temperate zone lake. The field data collection for the study was largely carried out over the growing season in the lake (May – October) in 2008 and 2009.

1.2 Aim and objectives

The overall aim of the studies presented in this thesis is to investigate the contribution of heterogeneity within surface waters and bed sediments to phosphorus fluxes and budgets in the context of a small lake. The thesis has the following objectives:

1. To quantify spatial heterogeneity in the surface waters of the study lake due to typical, weak forcing conditions;
2. To relate the observed surface water heterogeneity to the physical forcing conditions and the morphometry of the lake;
3. To examine the extent to which estimates of different sediment distribution processes account for the heterogeneity observed within the bed sediments of the study lake by testing the adequacy of sediment focusing models derived from the study of large lakes;
4. To quantify and compare burial rate and whole lake flux-to-bed rates of organic carbon and total phosphorus using predictions from these sediment focusing models, measurements from a single site (i.e. assuming process

homogeneity across the lake), and a method which integrates over measurements taken at sites representing different water depths (i.e. taking into account process heterogeneity across the lake);

5. To compare the relative importance of hydrological dilution and biological (phytoplankton) uptake on phosphorus concentrations in the shallow transition zone where the main stream inflow enters the study lake;
6. To examine the influence of the stream-lake transition zone on the horizontal spatial heterogeneity of the lake, and on estimates of mean lake-wide nutrient concentrations;
7. To quantify the inter-annual variability in phosphorus loading pathways to the study lake over the summer stratified period; and
8. To examine the seasonal variation in the importance of different phosphorus sources and the influence of physical processes on this variability.

1.3 Structure of thesis

The structure of this thesis firstly provides a context for the work in the literature review (Chapter two) and then sets out to address the objectives outlined above in the following chapters (three to six) which take the form of four journal articles: Chapter three addresses Objectives one and two (spatial heterogeneity of surface waters); Chapter four addresses Objective three and four (spatial heterogeneity of bed sediment), Chapter five addresses Objectives five and six (spatial heterogeneity of inflow transition zones and dispersal of the inflowing phosphorus load) and Chapter six addresses Objectives seven and eight (variability in internal phosphorus fluxes from the lake bed to the epilimnion). Chapter seven presents a discussion and synthesis of the work and Chapter eight presents the main conclusions and identifies avenues for further work.

Chapter 2 Literature Review

2.1 Importance of lakes and freshwaters

Lakes as a resource provide a variety of services to humans and the environment. The Millenium Ecosystem Assessment states that ecosystem services from wetland ecosystems include water supply and purification, fisheries, climate and flood regulation and recreation including tourism (Millenium Ecosystem Assessment 2005). They also provide habitats for a number of animal and plant species (Hughes et al. 2004, Moss 2007). However, relatively little is known about the benefits of these services or their value to society (Wilson and Carpenter 1999, UK National Ecosystem Assessment 2011). An assessment by Costanza et al. (1997) estimated that, globally, the services provided by rivers and lakes were worth US$1.7 trillion per year (in 1994 US$), but noted that this value was subject to large uncertainties and was likely to represent a minimum estimate. Human pressures on lakes can result in negative consequences for their provision of ecosystem services as habitats become degraded. In the recent UK National Ecosystem Assessment (2011), nutrient enrichment was identified as one of a number of pressures on lakes and their provision of ecosystem services. For example, one of the consequences of nutrient enrichment, declining water clarity, has been found to reduce the value of lakeshore properties (Boyle and Bouchard 2003). Therefore, addressing nutrient enrichment in lake systems will have benefits for the provision of ecosystem services.

The role of lakes in maintaining global nutrient cycles (a regulating service), has been recognised as increasingly important (e.g. Cole et al. 2007, Williamson et al. 2008, Battin et al. 2009, Harrison et al. 2009, Carpenter and Bennett 2011). A recent estimate suggests that twice as much carbon is imported to inland waters as is exported (Cole et al. 2007), while current levels of global phosphorus supply to freshwaters are estimated to exceed the level viewed as acceptable by humanity, the so-called 'planetary boundary' (Carpenter and Bennett 2011), with the result that the negative consequences of eutrophication are widespread in freshwaters (Schindler 2006, Smith et al. 2006). Increasingly, the role of small lakes in these cycles is being highlighted as more important than their size might otherwise suggest (e.g. Downing et al. 2008, Downing 2010, Staehr et al. 2011).

2.1.1 Small lakes

Small lakes (<1 km^2) are important as a global freshwater resource, being thought to represent 99.8% of lakes worldwide (Downing et al. 2006). A recent survey of standing waters in Great Britain found that there were over 40,000 lakes with an area greater than 0.01 km^2; equating to 1% of the total land area of the country (Hughes et al. 2004). These recent assessments emphasise the need to improve our understanding of the processes within these systems, which have traditionally been understated (Downing et al. 2006, Downing 2010).

Implicit assumptions about the scalability of some physical processes observed in large lakes have resulted in a relative paucity of studies which explicitly consider small lakes. This seems to be particularly true of studies considering spatial heterogeneity and the physical processes which lead to its development, where large scales (e.g. Håkanson 1977, Carmack et al. 1979, Rowan et al. 1992, Pinel-Alloul et al. 1999, Thackeray et al. 2004, Laborde et al. 2010) or strong forcing conditions (e.g. Blukacz et al. 2009, Rinke et al. 2009) not typical of smaller lakes, have been the focus of much of the previous research. Physical forcing processes acting on lakes often result in complex responses both dependent and independent of lake size. Lake thermal structure has been found to differ between small and large boreal lakes in terms of mixed layer depth, the formation of secondary thermoclines and thermal stability (Fee et al. 1996, Xenopoulos and Schindler 2001). However, climatic changes over time such as the timing of ice-out or modelled increases in surface water temperatures have been found to be largely independent of lake size (Hondzo and Stefan 1993, Weyhenmeyer 2008). These physical processes exert a strong influence on both chemical and biological processes in lakes (Kalff 2002) and therefore improving our understanding of physical processes in small lakes will enable us to better characterise nutrient cycles and their influence on lake biota.

2.2 Water quality policy and eutrophication

2.2.1 Water quality policy

Adoption of the Water Framework Directive (WFD) 2000/60/EC by the EU in 2000 represented a significant shift in the perspective of, and approach to, water resources management, resulting in environmental objectives playing a much more significant role, and the explicit requirements for consideration of water in terms of 'ecology' and 'heritage' (Council of the European Communities 2000). The on-going process of implementing the WFD is driving a change to more integrated management based on river basins. The overall objective is an achievement of 'good status' and at a minimum the 'non-deterioration' in status of water quality measured both ecologically and chemically by 2015, or at the latest 2027 (Council of the European Communities 2000). The compatibility of these objectives with traditional sampling methodologies is likely to pose problems for this process (Laszlo et al. 2007), particularly where water bodies may change their defined typology due to the impact of climate change (Wilby et al. 2006, Nõges et al. 2007). The appropriate characterization of spatial and temporal variability within water bodies is essential for the correct determination of their status and for the formulation of plans for remediation. The move towards a catchment based approach to water management represents a significant development in water legislation, and its practical implementation is likely to be a key test of the new system (Kallis and Butler 2001). The implication for water quality is that a greater linkage will be made between the catchment (source) and receiving waters (impact). In the UK, this in turn has highlighted the importance of tackling both point and diffuse source pollution, particularly in terms of excess nutrient concentrations (Defra 2002, Environment Agency 2007).

In 2005, the Environment Agency for England and Wales reported that 84% of lakes under its jurisdiction were at risk of not achieving the WFD's objectives (Environment Agency 2005). Over half of these lakes are at risk from diffuse pollution, while point discharges affect just over a third. Among the most significant contributors to lake pollution are the nutrients nitrogen and phosphorus. Excessive levels of phosphorus are likely to be responsible for a quarter of lakes in England and Wales not meeting their WFD objectives (Environment Agency 2005). While these catchment sources for nutrients are strongly emphasized in policy literature (e.g. Defra 2002), relatively little attention has been given to lakes themselves as sinks and sources for nutrients, and the role of internal supply mechanisms.

2.2.2 Eutrophication

Nutrients are essential for the growth and reproduction of lake biota. Where the supply of nutrients or organic matter increases, the aquatic system becomes enriched, leading to higher biological productivity and lower diversity (Likens 1972). This change in state is termed eutrophication. While the process of eutrophication represents a natural change in the lake environment, human pressures on water resources can result in it becoming a cause of concern (e.g. Chorus and Bartram 1999, United Nations Environment Programme 2006). 'Cultural eutrophication' is a term used to describe the human-induced acceleration of the natural process (Likens 1972).

The potential negative impacts resulting from increased productivity (Fig. 2.1) relate to increases in algal biomass during the summer months, often dominated by blooms of blue-green algae or cyanobacteria, some of which contain toxins that may be harmful to human health through ingestion or contact (Chorus and Bartram 1999). From the ecological perspective, algal blooms, particularly of cyanobacteria, can be toxic both directly and indirectly (through consumption of dissolved oxygen leading to anoxia of lake waters) to other lake biota and their ability to outcompete other species may result in a reduction in overall lake biodiversity (Pitois et al. 2001). In terms of water resources, algal scums also affect water supplies through blocking filters and reducing potability (Pitois et al. 2001). A recent estimate suggests that the cost of addressing the negative effects of freshwater eutrophication in England and Wales is between £75 million and £114.3 million per year (Pretty et al. 2003).

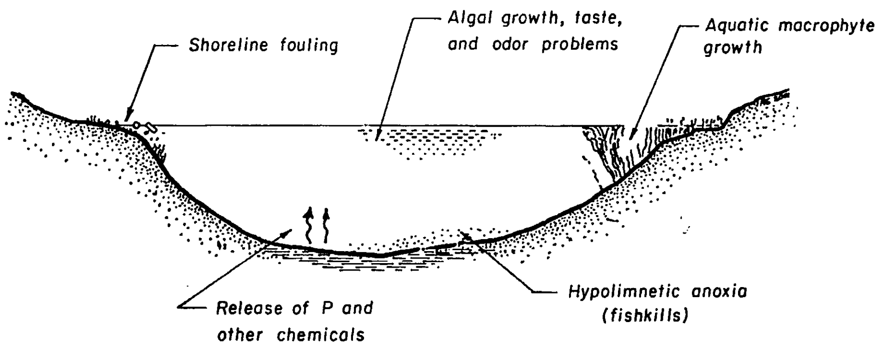

Figure 2.1 Diagram showing some of the negative consequences of eutrophication
Source: Smol (2008)

2.3 Phosphorus

2.3.1 Phosphorus utilization in lakes

The availability of nutrients, particularly phosphorus and nitrogen, has long been identified as a 'limiting' factor in aquatic biological production (Hecky and Kilham 1988, Schindler 2006). Where concentrations of these nutrients are at or below the levels required by the primary producers, they place a limit on the levels of growth and reproduction (Hecky and Kilham 1988). This is Liebig's Law of the Minimum, in which plant yield or organism health is determined by the nutrient present in the lowest quantity relative to the amount required (Rast and Thornton 2005). However, while this concept is useful in the study of eutrophication, the complexity of the multiple responses of organisms means that the simultaneous limitation of a number of elements is possible (Goldman 1972). Hecky and Kilham (1988) suggests that the composition of phytoplankton is also likely to be based on the relative loading of a range of nutrients combined with the effects of co-limitation with physical factors such as availability of light. The importance of phosphorus, within these multiple growth limiting factors, is that it is often present in low concentrations within a lake and is frequently in a form that cannot be used by the biota (Horne and Goldman

1994). Phosphorus is therefore widely regarded as the key nutrient leading to the development of eutrophication for a number of lakes (Schindler 2006).

The concentration of phosphorus required by algae in relation to other nutrients is low, the Redfield C:N:P ratio, the average molar ratio of particulate organic matter being 106:16:1 (Redfield 1934). Levels of phosphate (bioavailable inorganic phosphorus) turnover have been measured at the picomolar level within microbes (Hudson et al. 2000), which suggests that even small increases in lake concentrations can result in growth of algae (McDowell et al. 2004). This has implications both in terms of immediate onset of eutrophication within systems that experience anthropogenic enrichment and also on the long term recovery in lake condition after external loading ceases, particularly where internal loading from the bed sediments may prolong the eutrophic state (e.g. Søndergaard et al. 1993, Jeppesen et al. 2005).

2.3.2 Phosphorus budgets

Reducing lake nutrient concentrations has been the goal of lake managers for decades (Likens 1972, Vollenweider and Kerekes 1980, Conley et al. 2009). In order to assess the status of lakes in terms of phosphorus concentration, and thereby provide the potential for predicting the impact of changing this concentration, annual lake phosphorus budgets have been developed as a management tool. They provide a mechanism for conceptualizing the main factors controlling the concentration of phosphorus within a lake. Extensive work for the OECD during the 1960s and 70s led to the development of an annual index of phosphorus availability (mg m^{-3}) defined as (Vollenweider and Kerekes 1980):

$(P_y) = [LP/ q_s]/[1+(z/q_s)^{0.5}]$,

where LP is the areal rate of phosphorus loading across a lake's surface area (mg m^{-2}), z is mean depth (m) and q_s is the hydraulic loading rate (m a^{-1}) which is equal to $1/t_w$ where t_w is the hydraulic retention time.

This index was used to derive a regression model to allow for the prediction of annual mean lake chlorophyll concentrations thereby predicting the impact on phytoplankton of varying phosphorus loading and allowing the definition of the standard criteria used for categorising the boundaries between oligotrophic, mesotrophic and eutrophic lakes (OECD 1982). More recently it has been used for the prediction of compliance to phosphorus standards developed for the WFD (e.g. Duethmann et al. 2009). While the index provides a good basis for understanding some of the factors that influence phosphorus concentrations within a lake at a general level, it is a steady-state model and the complexity of the natural system means that other factors such as the role of lake sediment as a source or sink of phosphorus (Sas 1989, Søndergaard et al. 2003), the structure and response of the biota (e.g. Scheffer et al. 1993, Carpenter et al. 1995, Elser et al. 2000) and the influence of physical lake processes (e.g. James and Barko 1991a, Brooks and Edgington 1994) are likely to be important in the response of a lake's phytoplankton. These processes are by their nature dynamic and vary both temporally and spatially within a lake. Many previous studies have tended to consider only single factors, or to have been restricted to studies of single years, thus not resolving inter-annual variation. There is a clear need to improve our understanding of phosphorus dynamics by taking account of these factors in the construction of lake phosphorus budgets.

2.3.3 Phosphorus forms

The composition of phosphorus in the aquatic environment is the result of a complex and dynamic interplay of physical, chemical and biological processes. As a result, it must be considered not only in terms of physical form (particle, solute or colloid) but also its chemical composition (organic or inorganic) and biological status (bioavailable or inert). It is also conventionally defined by the operational fractionation of phosphorus (Fig. 2.2).

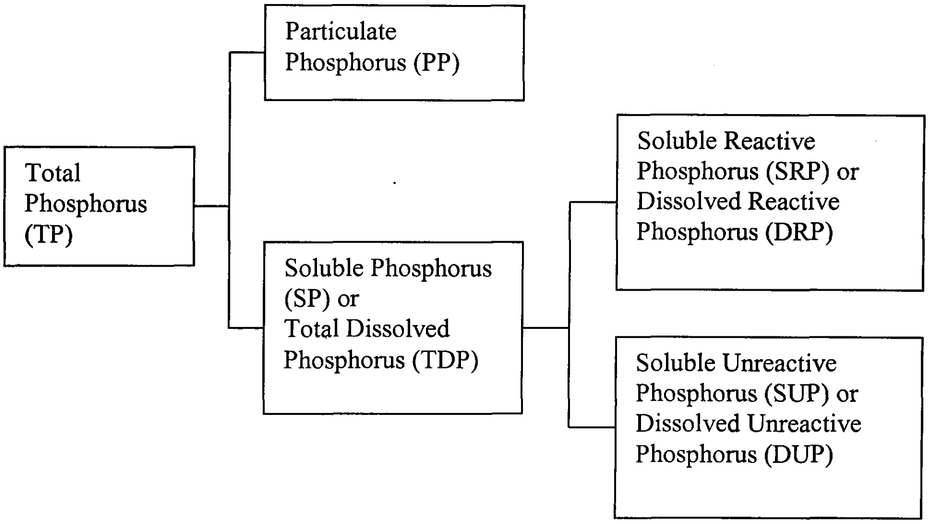

Figure 2.2 Physical fractions of phosphorus
Source: Adapted from (Holtan et al. 1988)

The division between PP and SP is made on the basis of established filtration methodology, which uses a standard filter pore size of approximately 0.45µm. The filtrate is then considered to be the soluble fraction, whilst the retained material is the particulate fraction. Particulate phosphorus (PP) represents the bulk of phosphorus present within natural waters. It originates from a variety of sources, largely organic but also of inorganic origin: biologically-produced cells, mineral weathering products, direct precipitation of inorganic phosphorus or sorption of phosphorus to other precipitates, degradation and fragmentation of cells, flocculation of organic macro-particles and the formation of organic/inorganic co-precipitates or inclusion of phosphorus by metal-phosphorus binding into organic aggregates (Broberg and Persson 1988).

Soluble phosphorus (SP) typically comprises less than 10% of total phosphorus within a system (Horne and Goldman 1994). Soluble organic phosphorus (SOP) represents the main form of soluble phosphorus and derives from the active cell metabolism and cell death (Broberg and Persson 1988). The main soluble inorganic phosphorus (SIP) compounds are the orthophosphates ($H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-}) (Holtan et al. 1988), originating from anthropogenic sources, rock weathering products, bio-metabolism or degradation and the poly- and metaphosphates which are produced by biological and human activity (Broberg and Persson 1988). The relative proportions of these anions is pH dependant, with dihydrogen phosphate ($H_2PO_4^-$) and hydrogen phosphate (HPO_4^{2-}) being the main species in natural waters. These forms are soluble in water, and their hydrogen ions can be readily replaced by the alkaline earth and transition metals (especially iron, aluminium and calcium) which are insoluble and form PP (Reynolds and Davies 2001). Studies on soluble phosphorus tend to consider soluble reactive phosphorus (SRP) which is the fraction containing orthophosphate and colloid bound phosphorus and represents the fraction that is fully utilised by algae (Reynolds and Davies 2001).

Phosphorus bioavailability

Bioavailable phosphorus is phosphorus that can be readily taken up and used by biota and which is either immediately available or potentially available i.e. it must be transformed (e.g. desorbed, dissolved, degraded by enzymes) prior to biological utilisation (Boström et al. 1988). Algal uptake of phosphorus is characterised by three processes (Horne and Goldman 1994): The first is 'luxury consumption', whereby more phosphorus than required is assimilated, the excess being stored in cells as polyphosphate granules. The second is the uptake of phosphate at low concentrations, the phosphate growth constant, the level at which phosphorus is required for growth, is very low for phytoplankton reflecting their adaption to phosphorus' normal scarcity in the environment. The third is the production of the alkaline phosphatase enzyme, which cleaves the bond between the phosphate and organic molecules by hydrolysis, freeing the phosphate ion. Alkaline phosphatase activity on the algal cell surface is induced by phosphorus deficiency in the water, enabling the algae to utilise organic forms of phosphorus (Healey 1973). When considering bioavailability, it is also useful to consider the operationally-defined phosphorus fractions of the standard extraction methods. A summary of these is provided by Reynolds and Davies (2001), adapted in Table 2.1 below.

Table 2.1 Phosphorus fractions and their bioavailability

Phase: reactivity	**Phosphorus species**	**Bioavailability**	**Other comment**
Dissolved phosphorus (DP)	Orthophosphate in solution	Readily	
- soluble reactive phosphorus (SRP)	DP plus colloid bound P		
- molybdate-reactive phosphorus (MRP)	DP plus colloid bound P		
Particulate phosphorus (PP)		Conditionally	
- H_2O-extractable P (IMRP)	Interstitial MRP		
- NH_4Cl-extractable P	Exchangeable P		Also known as labile P
- citrate-dithionite-extractable P ($Na_2S_2O_4$-P)	Ferric-bound P		Normally analysed together
- NaOH-reactve P	Al-bound P		
non-NaOH-reactive Particulate phosphorus		Scarcely	
- HCl-reactive P	Apatite; P co-precipitated with $CaCO_3$		
- Residual P			Also known as refactory P
$HClO_4$-digestible P (Total Phosphorus TP)		Various	

Source: Adapted from Reynolds and Davies (2001)

Orthophosphate in solution is the main immediately bioavailable source of phosphorus. While the size of this inorganic pool is generally low, it is rapidly cycled during the periods of highest biomass production (Rigler 1964, Lean 1973). Some organic phosphates may also be directly used by the biota through the production of alkaline phosphatase. These phosphates tend to have a low molecular weight and include polyphosphates and phosphomonoesters (Franko and Heath 1979). In addition, the reduction of some soluble phosphorus compounds of a high molecular weight on exposure to ultraviolet light can release free orthophosphate for use by the biota (Franko and Heath 1979). This fraction may be related to the reduction of iron complexes under exposure to sunlight. Thus SRP, as defined in Table 2.1, covers a wide range of components and extent of bioavailabilty. This can lead to SRP delaying algal growth, if there is a large proportion of SRP in the high molecular weight fraction (Boström et al. 1988).

Particulate phosphorus (PP) compounds are only conditionally bioavailable, in that they must be transformed chemically to a soluble form to enable their uptake by the biota, therefore they are considered in terms of their 'potential bioavailability', the upper limit of the phosphate content of the particle. The examination of PP bioavailability requires a longer time horizon than that of dissolved phosphorus, because the time for the transformation of the particles requires an understanding of the residence time of particles within the water column and mechanisms of re-suspension or dissolution of phosphorus from the sediment (Boström et al. 1988). There is evidence that the mobility and potential bioavailability of particulate phosphorus can be significant. A study of algal availability of particulate phosphorus from different origins found over 40% of particulate phosphorus was bioavailable when it originated from rural population wastewaters, urban secondary treated wastewaters and dairy industry outflow (Ekholm and Krogerus 2003).

The spatial and temporal availability of both particulate and soluble phosphorus is therefore likely to depend on its origin and the processes that it undergoes once in the lake water (e.g. Franko and Heath 1979, Peters 1981). The consideration of a 'biological control' on availability is likely to form an important component of the processes that affect availability in the lake. A number of organisms other than algae utilise phosphorus within the water column and therefore have an influence on the success and species composition of algal colonies. Orthophosphate uptake rates in bacteria have been found to be higher than those of algae, even when the higher excretion rates of bacteria are accounted for (Currie and Kalff 1984). Currie and Kalff (1984) suggest that bacteria effectively determine the phosphorus available to the algae, as a result of their superior competitiveness for phosphorus uptake.

2.3.4 Phosphorus sources

A number of different phosphorus sources have been identified for lakes and other waters (Fig. 2.3). The most significant natural source of phosphorus is from the weathering of rocks containing the compound apatite ($3Ca_3(PO_4)_2 \cdot Ca(OH)_2$) (Harper 1992). Catchment geology is a key factor in determining the background level of phosphorus export: sedimentary catchments in general, have higher background phosphorus levels than those on igneous bed rock (Dillon and Kirchner 1975). Anthropogenic loading has been found to significantly increase phosphorus export above these background levels where land use has been changed to pasture, intensive agriculture and urbanization (Dillon and Kirchner 1975).

Point source emissions of phosphorus relate largely to sewage treatment works (STWs) and some industrial outfalls which input directly into water bodies. Discharge concentrations from point sources have an inverse relationship to flow and are of most importance during lower flow periods (Neal and Jarvie 2005). As these may be anticipated to occur during the growing season in a lake, point sources are likely to be an important source for summer phytoplankton growth, particularly under future climate scenarios of lower summer river discharges (e.g. Jones et al. 2011).

Diffuse sources from agricultural land are associated with application of artificial fertilisers and manures directly onto the land surface. The mobilisation of phosphorus fractions has been related to erosion of particulate phosphorus bound to soil particles and the dissolution of soluble phosphorus carried in solution by runoff (Heathwaite et al. 2003, McDowell et al. 2004, Haygarth et al. 2005). Poor land management practices can exacerbate the problem (Cooke and Williams 1973). In addition, point sources which discharge into the vadose zone (thereby being mobilised and dispersed as diffuse pollution) such as septic tanks in rural areas and intensive animal units also have the potential to add significantly to the diffuse load (Neal et al. 2005). Atmospheric deposition may also be a diffuse source of particulate phosphorus as wet or dry deposits onto a lake's surface. Although generally considered a low proportion of the total contribution, it is highly spatially variable, being lowest in unpolluted areas and highest in the urban periphery (Pitois et al. 2001).

The final potential phosphorus source is that of lake sediments, where a proportion of the catchment phosphorus will be retained in the lake through sedimentation of organic and inorganic particles. Sediment phosphorus can form a significant source for internal loading within a lake, to the extent that even after reducing external sources, the lake may remain hypertrophic or eutrophic for a number of years (e.g

Søndergaard et al. 1993, Jeppesen et al. 2005, Kneis et al. 2006). A sediment's net retention relates to the difference in fluxes of sedimenting particles and the release of phosphorus from the sediment (Søndergaard et al. 2003). Release or internal loading occurs where the bio-chemical sorption capacity of the sediment is exceeded (Gachter and Mares 1985). The proportion of clay in lake sediment is the most important determinant of its phosphorus holding capacity (Horne and Goldman 1994), and these small size fractions of particles consequently have higher phosphorus contents (Broberg and Persson 1988).The sediment-water interface represents an important location for the chemical transformations between particulate and soluble phosphorus, and therefore an important source for internal loading within the lake.

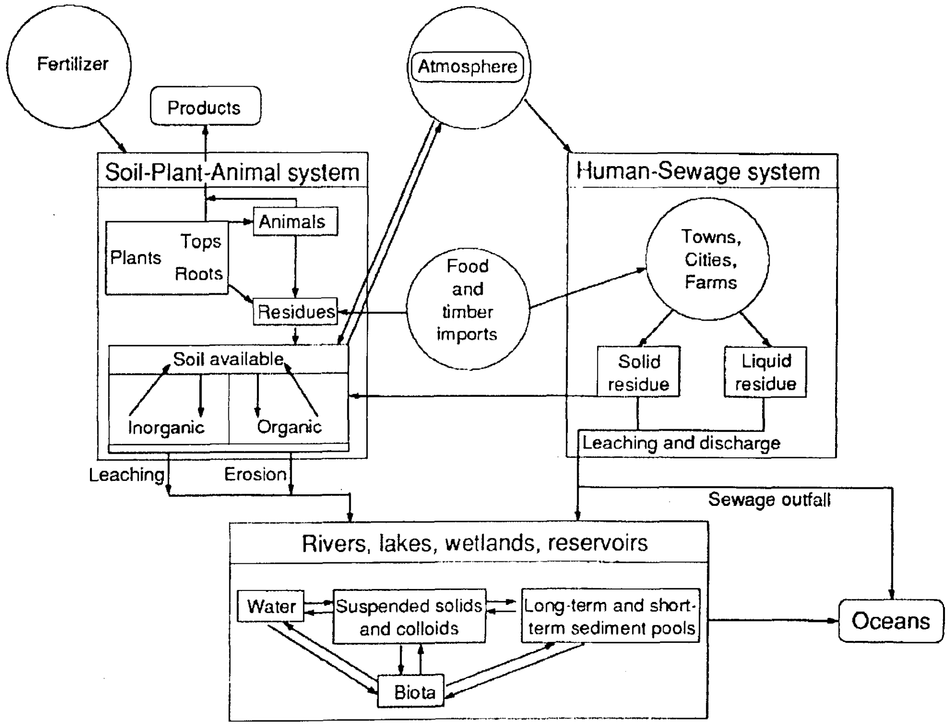

Figure 2.3 Conceptual diagram of phosphorus sources for lakes and other waters
Source: Donelly et al. (1998)

Understanding the chemical reactions resulting in phosphorus release from sediments has been the subject of much research. The original work of Einsele (1938) and Mortimer (1941) proposed that under anoxic conditions, sediment phosphorus sorbed to ferric iron oxyhydroxides ($FeOOHPO_4$) are reduced, producing phosphate (PO_4^{3-}) and ferrous iron compounds (Fe^{2+}), which are released into the hypolimnion. The reaction is reversible, as under oxic conditions, phosphate naturally sorbs to the insoluble iron oxyhydroxides or is precipitated as $FePO_4$ and becomes sedimented. In addition to the reaction with metal oxides, an association has also been found between phosphorus binding to iron and aluminium complexes and humic matter in water and sediment (Jackson and Schindler 1975).

Later research suggests a more complex picture, in which sulphide (S^{2-}) (reduced from sulphate (SO_4)) reacts with iron to form the insoluble iron sulphide and disulphide (FeS and FeS_2, respectively). This reaction is thought to free phosphate from the iron oxyhydroxide adsorption by removing reduced iron from solution (Kalff 2002). A number of other metal and nonmetal ions and silicate are also implicated in the control of phosphate within sediments (Kawai et al. 1985). The presence of dissolved silica has been found to enhance phosphate sorption and retention onto the iron oxyhydroxides (Mayer and Jarrell 2000). In hard water lakes, the calcium cation Ca^{2+} creates an additional control on phosphorus through the precipitation of phosphate as apatite as a coprecipitate of calcium carbonate (Golterman 1998). Where pH falls under anoxia this reaction may reverse to some extent, dissolving apatite and freeing phosphorus, thereby also highlighting the role of acidification in phosphate release (Golterman 1998). The relative proportions of the different ions and compounds are critical within this process, as dissolved orthophosphate and the iron- and calcium-bound phosphates reach a chemical equilibrium dependant on water depth, pH, Ca2+, Fe(OOH) and sediment binding capacity (Golterman 1998). Calcium co-precipitation with phosphate has been found to be linearly related where temperature, pH and the concentrations of the two reactants remain stable (House 1990). Where calcite concentrations are higher, precipitation is enhanced (Zicker et al. 1956, Dittrich and Koschel 2002) and the amount released is reduced under lower pH conditions (Golterman 1998).

Another proposed release mechanism for phosphorus is the mineralisation of organic phosphorus to inorganic phosphate within the sediment, released under anoxic conditions (Prairie et al. 2001). It is suggested that phytase produced by bacteria may produce or mineralise phytate phosphate which is released under anoxic conditions (Golterman et al. 1998). Work by Gächter et al. (1988) also found evidence of a regulatory role in phosphorus uptake and release in sedimentary bacteria. Through these processes, bacteria appear to have a role in the flux of phosphate across the sediment-water interface; fluxes were found to be higher for low bacterial activity, whilst phosphorus accumulated within the sediments where bacterial activity was present (Clavero et al. 1999). Increases in pore water SRP and ferrous iron (Fe^{2+}) have also been related to bacterial activity (Eckerrot and Pettersson 1993).

Phosphorus release from sediments also occurs under oxic conditions in the epilimnion. The mechanism in this case appears to relate most strongly to pH levels within the water (Rippey 1977, Drake and Heaney 1987). Desorption of inorganic loosely bound iron- and manganese- phosphorus and adsorbed aluminium-, clay mineral- and humic- bound phosphorus occurs rapidly when pH rises towards 10

(Drake and Heaney 1987). Although desorption and phosphorus release is more rapid under anoxic conditions, a laboratory study found that total oxic phosphorus release over time was similar to that of the anoxic release (Lee et al. 1977). Similarly, a comparison of littoral and pelagic phosphorus release from sediment found that under both oxic and anoxic conditions, the littoral sediment was responsible for a higher phosphorus release (Andersen and Ring 1999). Where littoral areas form a significant part of the lake area, phosphorus release from this shallow zone may exceed hypolimnetic and external loading (Drake and Heaney 1987).

2.4 Consideration of heterogeneity

Quantifying the potential sources of phosphorus for a lake provides only a partial understanding of the processes which result in the eutrophication of the system. There is a recognition that the management of freshwater resources has in the past, largely ignored spatial heterogeneity present in the structure and function of ecosystems (Steinman and Denning 2005). In order to address effectively the negative consequences of eutrophication and nutrient enrichment set out by the WFD, we need a better understanding of both the heterogeneity in the physical phosphorus supply mechanisms and the underlying heterogeneity in the natural lake environment where the response to enrichment occurs.

2.4.1 Heterogeneity in the environment

Both temporal and spatial heterogeneity are regarded as important components of natural systems (Legendre and Fortin 1989, Shaver 2005). This heterogeneity is argued to be a fundamental part of many ecological theories relating to populations and communities (Legendre and Fortin 1989). Distributions of organisms have been found to form patchy or gradient-like spatial patterns in response to heterogeneous physical and chemical forcing or biological processes, which are also dynamic over time (Legendre and Fortin 1989, Legendre 1993).

Spatial heterogeneity is an important feature of lakes ranging across spatial scales from the level of lakes within landscapes, to whole lake-, basin- and sub-basin scale features, which can also be heterogeneous in time (George 1993, Kratz et al. 2005). Within-lake heterogeneity is structured by both biotic and abiotic forcing factors such as wind stress or predator-prey interaction (e.g. George and Edwards 1976, Folt and Burns 1999, Castro et al. 2007). Understanding these drivers can be important for the interpretation of patterns in lake function, for example, gradients in lake productivity and the spatial distribution of organisms or nutrient loading (George and Jones 1987, Pinel-Alloul et al. 1999, Kratz et al. 2005). Many of the studies which have attempted to quantify spatial heterogeneity have been carried out on large lakes or under atypical forcing conditions such as storm events or exceptionally calm weather conditions (George and Heaney 1978, Thackeray et al. 2004, Blukacz et al. 2009, Rinke et al. 2009). Less well conceptualized is the importance of spatial heterogeneity under forcing conditions in lakes which are more typical or 'archetypal'. Typical conditions can provide important information on underlying or systematic spatial heterogeneity in a lake, useful as a guide to the level of natural variability that might be anticipated when characterising a lake system. This systematic heterogeneity is controlled by lake characteristics (e.g. geography, wind exposure, morphology, water chemistry, biological community composition). These characteristics are likely to differ between large and small lakes, as forcing conditions and their effects can be scale dependent. For example, due to the lower frictional drag of water compared to land surfaces, wind speeds are higher over lakes with a large surface area as the fetch is longer (e.g. Jones and Maberly 2008). It may be anticipated that horizontal accumulation of phytoplankton and zooplankton associated with temperature gradients seen in large lakes (e.g. Jones et al. 1995, George and Winfield 2000, Thackeray et al. 2004, Blukacz et al. 2009) do not occur to the same extent in small lakes where physical forcing is lower. The relationship between the physical forcing found in large lakes and the resulting spatial heterogeneity also needs to be examined under these weaker conditions.

Spatial heterogeneity in lakes occurs not only in the water column but also in the sediments, an important source and sink for phosphorus (Kalff 2002, Nürnberg 2009). Accurately quantifying this pool of phosphorus requires an understanding of how sediments in lakes are reworked and 'focused' into deeper water (Håkanson and Jansson 1983), thereby developing heterogeneity in their distribution. Distribution patterns of different components of the sediment are determined both by the size and density of the individual particles, and the processes acting on them (Miller et al. 1977, Håkanson and Jansson 1983). A number of studies have developed generalised focusing models to explain the distribution pattern of sediment variables in all lakes based on wave mixing or bed slope processes (Håkanson 1977, Rowan et al. 1992, Blais and Kalff 1995). These models have largely been applied to large or shallow lake systems and few studies have considered the applicability of these models in small lakes where physical forcing conditions are likely to be different. In addition, these models make an implicit assumption that all sediment components will have the same heterogeneity in their distribution. However, this is not intuitive, as particle sizes and densities vary between different sediment components, phosphorus being associated with small particles and organic material having a lower density than inorganic material (Miller et al. 1977, Gloor et al. 1994), for example. An improved understanding of the physical processes and the heterogeneity associated with the burial of organic carbon and phosphorus is important in the context of quantifying lake budgets and the role of sediment as a store of material within global biogeochemical cycles (Downing et al. 2008, Buffam et al. 2011).

Temporal variability in the functioning of lakes is well understood, as variations in the physical controls on the system result in seasonal cycles of, for example, stratification and mixing (Fischer et al. 1979, Kalff 2002), changes in water and sediment chemistry (Davison et al. 1980, Sutcliffe et al. 1982) and phyto- and zooplankton succession (Pettersson et al. 2003, Talling 2003). The negative impacts of eutrophication tend to be largely manifest during the summer growing season, where the combination of stratification, algal blooms and dissolved oxygen consumption in the hypolimnion through decompositional processes can result in reduced water quality, loss of amenity and loss of habitat quality for fish (Jones et al. 2008, Jacobson et al. 2010). Nutrient inputs from the different sources to a lake during this period are likely to sustain or enhance algal growth, particularly as dilution effects from high flows tend to be lower in summer than at other times (Jones et al. 2011). Internal sediment sources of phosphorus are also most significant during the summer, when the conditions for chemical sediment release are optimised (Penn et al. 2000). Improving our understanding of phosphorus supply processes during the summer growing season in lakes is therefore important from the perspective of linking the source to the impact in managing lake recovery.

2.4.2 Heterogeneity in the supply of phosphorus

Inflow supply

River and stream inflows form part of a hydrological continuum between catchments and lakes; this linkage provides the pathway for the introduction and concentration of catchment derived nutrients and the heterogeneity of biological productivity (George 1993). Spatial gradients in the productivity of phytoplankton and macrophytes have been found to occur at a lake-basin scale in relation to inflows (George and Jones 1987, Auer and Bub 2004, Feldmann and Nõges 2007). These areas of enhanced productivity have been found to be a source of phytoplankton for the lake (Pickrill and Irwin 1982, Izydorczyk et al. 2008). This has been related to the enhanced nutrient supply in their vicinity compared to the rest of the lake. Negative nutrient gradients have been described where streams or rivers join lakes and reservoirs (Twinch 1984, García-Ferrer et al. 2003). In addition, temporal variability of gradients in sedimented particulate phosphorus have also been reported where gradients changed over time from positive to negative (Kufel 1993). While the existence of gradients in nutrient concentrations around stream inflows is well described, few studies have considered the extent to which these gradients and the spatial heterogeneity they generate might influence estimates of lake-wide concentrations of phosphorus based on sampling at a single site in the pelagic zone of the lake.

Hydrological processes around inflows are well resolved for large river-lake systems with large depth changes at the river mouth and are associated with differences in the density of the inflowing and resident lake water. This has been found to affect mixing in this region as the density differences between water masses results in the vertical segregation of the influent water (Carmack et al. 1979, Fischer et al. 1979, Pickrill and Irwin 1982, Fischer and Smith 1983, Stevens et al. 1995, Vidal 2006, Botelho and

Imberger 2007), which have been found to determine the fate of inflowing nutrients and other contaminants (Nepf and Oldman 1997, Vidal 2006). Less attention in the literature has been given to entrance mixing and initial dilution processes which occur prior to flow separation due to channel expansion and the entrainment of inflow water (Spigel et al. 2005). These shallow water processes have been found to be important mixing processes in shallow artificial cooling ponds (Jirka and Watanabe 1980). It follows that dilution processes in shallow inflow transition zones in natural systems are likely to be equally important but have been largely unexplored by previous studies.

Nutrient concentrations in streams and lake are altered not only by physical processes of mixing and dilution, but also by other chemical and biological processes. Chemical and biological uptake by sediments (the latter through epiphytic algae) has been suggested as the phosphorus removal process in both streams and lakes and across the transition zone between them (McColl 1974, Twinch 1984, Björk-Ramberg 1985, García-Ferrer et al. 2003, Vandenberg et al. 2005, Aldridge et al. 2010). High levels of nutrient uptake have also been associated with bacterial abundances in the proximity of inflows (Rigler 1956, Moll and Brahce 1986, Kapustina 1996). However, few studies have considered the relative importance of physical, chemical and biological processes in influencing the dispersal of phosphorus as it enters a lake.

Horizontal mixing and supply

A major component of heterogeneity imposed by physical variables is their potential to spatially and temporally vary the distribution of phosphorus within the lake through its transport and mixing. Differential heating and cooling of lake waters due to their different depths spatially affects the development of vertical stratification within the basin, resulting in the creation of horizontal density gradients and a 'thermal siphon' of water movement (Monismith et al. 1990). These horizontal flows of water also have the potential to transport nutrients from the shallow littoral zone to the deeper pelagic zone where they can be readily accessed by the lake's phytoplankton. Night time convective movement has been found to result in net fluxes of total phosphorus from the littoral to the pelagic zone, as the density current comes into contact with phosphorus in the sediment (James and Barko 1991b). Through this transport mechanism, littoral phosphorus loading can represent a significant share in a lake's phosphorus budget, for example forming ~22% of the summer internal total phosphorus load in Eau Galle Reservoir (James and Barko 1991a). Generation of secondary thermoclines and surface water convection during daytime heating has also been suggested as a transport mechanism for phosphorus from littoral areas on an episodic basis with potential for ≈1 kg day $^{-1}$ moved offshore (George 2000). Surface convection has also been demonstrated as a mechanism for contaminant transport in Upper Mystic Lake, Massachusetts (Nepf and Oldman 1997).

In addition to thermal convective transport, the development of wind-derived waves and currents also acts as a significant transport mechanism at a variety of scales within a lake. Sediment resuspension can be particularly significant in shallow lake areas where cycling of the available material is episodic and occurs rapidly (Evans 1994). The propagation of shear stress on a lake bottom is related to wind speed, depth and effective fetch with the associated resuspension resulting in increased concentrations of total phosphorus, total nitrogen and chlorophyll *a* (Hamilton and Mitchell 1988, 1997). The simulation of resuspension has been found to result in increased concentrations of phosphate 8 to 10 times that of undisturbed sediment (Fan et al. 2001). Sediment resuspension of phosphorus and the impact on lake phytoplankton is also highly temporally variable, being associated with storm events, diel cycles and seasonal wind patterns (Robarts et al. 1998, Havens et al. 2007, Zhu et al. 2007). The recovery in phosphorus concentrations of interstitial waters to perturbation by wind events has also been found to be temporally dynamic (Kawai et al. 1985).

Wind direction can be important where the topography of the surrounding land impacts on the effective fetch (Zhu et al. 2007). Wind sheltering has been found to cause lower on- to offshore diffusion and mixing of nutrients than expected (Alvarez-Cobelas et al. 2005). Circulation patterns associated with prevailing winds have been related to the focusing of sediment deposition and the concentration of algal blooms, and when oriented along a main lake axis have generated basin-wide circulation patterns, as opposed to perpendicular winds associated with multiple circulation cells (Schernewski et al. 2005, Qin et al. 2007).

Internal waves, or seiches, can be caused by wind stress thickening of the epilimnion at the upwind end of a lake, resulting in tilting of the thermocline, and its oscillation once the wind stress is relaxed (Kalff 2002). Seiches have been found to interact with the lake basin margins resulting in wave breaking and the potential for episodic vertical transport of nutrients from the hypolimnion and horizontal movement of littoral sediments (Shteinman et al. 1997, MacIntyre et al. 1999, MacIntyre and Jellison 2001, Lorke et al. 2006). Internal seiches have also been found to have a significant influence on sediment resuspension from the benthic boundary layer

(Gloor et al. 1994). Thermocline-tilting can also result in the upwelling of metalimnetic or hypolimnetic water at the upwind end of the lake. This has been found to result in vertical and horizontal transport of nutrients and lake biota, resulting in the spatial heterogeneity discussed earlier (George and Edwards 1976, Okely and Imberger 2007).

Vertical mixing and supply

In the hypolimnion of lakes subject to high internal loading, a seasonal pattern in phosphorus release occurs, largely during the summer months (Gachter and Mares 1985). This release results in a gradual build up of phosphorus in the deep water of the lake (Larsen et al. 1981). Once phosphorus is released from hypolimnetic sediments it has to be physically transported if it is to reach the epilimnion. A number of transport processes have been identified as potentially contributing to the vertical supply including bioturbation and gas ebullition in shallow lakes, vertical diffusion and the entrainment of hypolimnetic waters through mixed-layer deepening (Wodka et al. 1983, Effler et al. 1986, Sondergaard et al. 1993, Soranno et al. 1997). The build-up of hypolimnetic phosphorus concentrations in the water and the action of these processes, is very temporally variable and yet few studies have considered the relative importance of individual processes or how they vary over the course of the summer or on inter-annual scales. Understanding these internal supply dynamics is important since projected future changes to the climate would enhance sediment release processes, thus increasing vulnerability to eutrophication, particularly for lakes with long residence times (Pettersson et al. 2003, Malmaeus et al. 2006). In addition, the recovery of lakes from eutrophication has been found to be prolonged where internal phosphorus supply forms an important element of the total load (Jeppesen et al. 2005).

2.5 Summary

This review has highlighted both the importance of, and gaps in knowledge associated with, our understanding of phosphorus cycling within lakes and the heterogeneity inherent in small lake systems. Traditionally, policy and management of the impact of phosphorus on lakes has not readily taken account of either the temporal or spatial heterogeneity present. Few studies have considered the development of this heterogeneity in both the surface waters and sediments of small lakes, which are typically subject to much weaker physical forcing conditions than the larger lakes on which studies have tended to focus. There is a need for a better understanding of the processes of external phosphorus dispersal, internal phosphorus supply and its distribution in these small systems. This would lead to improvements in our predictions of phosphorus burial in the sediment and understanding of the relative importance of different supply pathways and dispersal processes over time.

2.6 Study Site

The study site chosen for the fieldwork that provided the basis for the research presented in this thesis is Esthwaite Water in Cumbria (54°21'N, 3°0'W). Located in the English Lake District in north west England, Esthwaite Water is a glacial ribbon lake, orientated roughly north-south along a valley (Fig. 2.4). It has a total length of 2.5 km and is on average 0.5 km wide. As a result of this orientation and the prevailing south-westerly weather conditions, the lake is exposed to spatially variable wind forcing (Mackay et al. 2011a). The areal extent of the lake, as determined by a new survey which forms part of Chapter four is 0.96 km^2, the total volume is 6.7×10^6

m^3, it has a maximum depth of 16 m and an average depth of 6.9 m (Mackay et al. 2011a). Annual rainfall in the catchment is around 1750 mm (Reynolds and Irish 2000), there is one primary and five smaller streams which drain into the lake and the catchment has a surface area of approximately 17 km^2. The lake has an mean residence time of around 90 days and there is only one outflow, Cunsey Beck at the southern end of the lake (Reynolds and Irish 2000).

Esthwaite Water has a long history of limnological study and many of its physical, chemical and biological properties have been previously summarised (e.g. Mortimer 1941; Sutcliffe et al. 1982; Talling & Heaney 1988; George et al. 1990; George 2000). The lake forms part of a long-term lakes monitoring network run by the UK Centre for Ecology and Hydrology, who also operate an automatic monitoring buoy on the lake and a meteorological station on the shore. They provide high resolution meteorological and hydrographic data for a number of variables (see Rouen et al. 2001 for details, Madgwick et al. 2006). Data from these facilities have been used extensively throughout this thesis.

Frequently referred to as the most productive lake in the Lake District, based on the original classification carried out by Pearsall in the 1920s (Pearsall 1921). The recent Lakes Tour report (Maberly et al. 2011) found that the lake has the highest annual average concentration of soluble reactive phosphorus and the second highest annual average concentrations of total phosphorus of the 20 lakes studied. The lake was classified as eutrophic based on the annual mean Secchi depth and strong seasonal hypolimnetic anoxia (Maberly et al. 2011). The recent River Basin Plan by the Environment Agency (2009) for the north west district of England classifies the lake as being of moderate condition for the WFD categorization. Based on this initial assessment, it is not anticipated that the lake will obtain good ecological status until 2027.

The underlying catchment geology is made up of Lower Palaeozoic, Silurian rocks (formed 400 to 350 million years before present), known as the Bannisdale slates (Fryer 1991). Of sedimentary origin, these rocks are mainly composed of siltstones, mudstones and sandstones, which result in the relatively high alkalinity of the lake (Reynolds and Irish 2000). Overlying the solid geology, predominantly within the main valley floor is a layer of glacial till, while around Esthwaite Water itself, there are lacustrine and alluvial deposits (British Geological Survey 1998). The underlying geology gives rise to three different soils within the catchment, all are a form of loam (Jarvis et al. 1984). Historically, the natural climax vegetation within the catchment was Sessile Oak and Ash (*Quercus petraea*, *Fraxinus excelsior*) woodland with some Yew (*Taxus baccata*), although most of this has now been cleared for agriculture in the form of sheep farming and coniferous forestry (Reynolds and Irish 2000). Increasing stock densities and the improvement of grassland with organic and inorganic fertilizers over the last 40 years has coincided with the increasing enrichment of the lake reported in both water quality (Heaney et al. 1992) and fossil diatom records (Bennion et al. 2000). These increases can also be related to the development of the sewage treatment works serving Hawkshead's resident and tourist populations and rainbow trout fish farming activities on the lake (Hall et al. 2000).

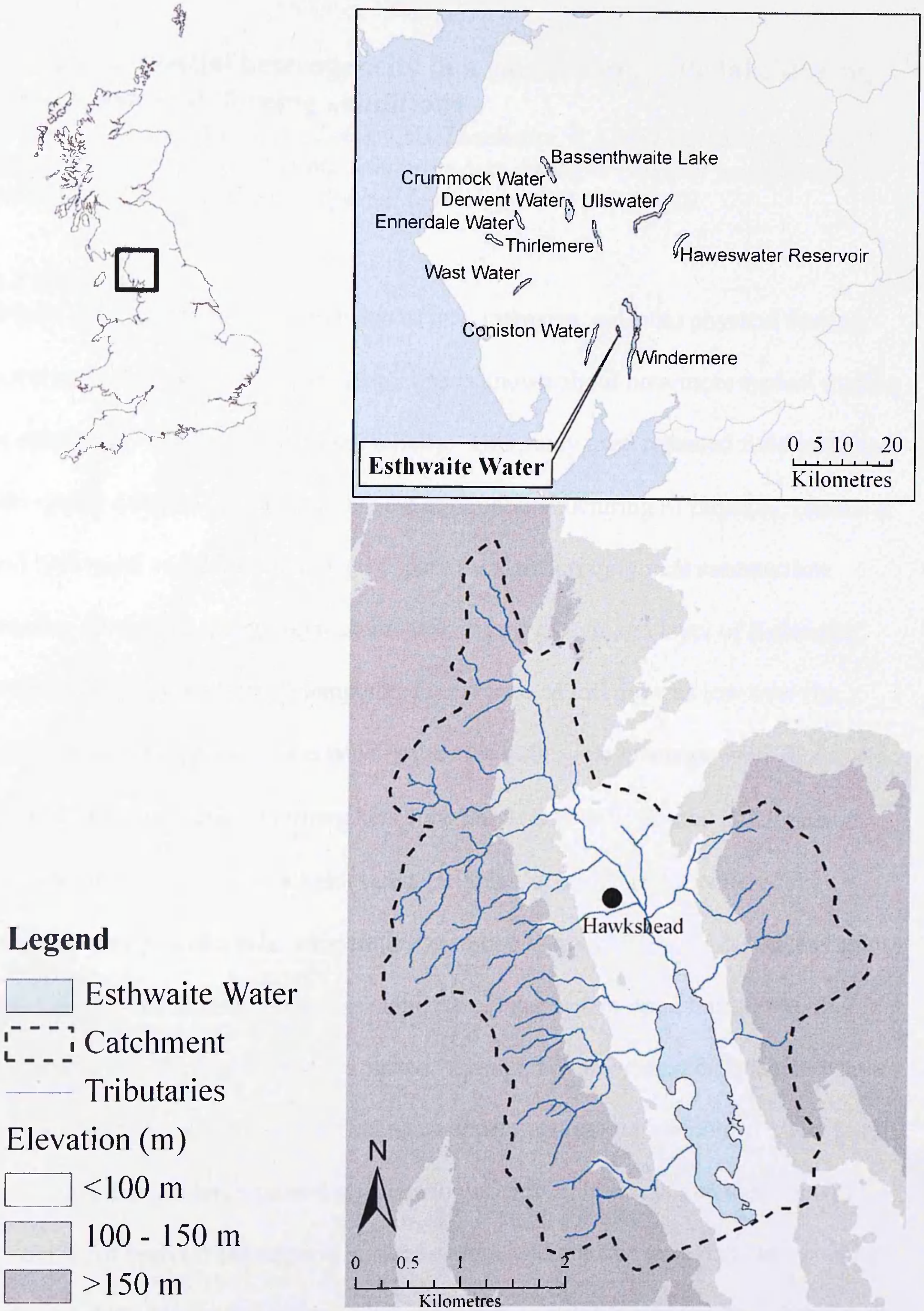

Figure 2.4 Location of Esthwaite Water, its catchment and tributaries in Great Britain

Chapter 3 Spatial heterogeneity in a small, temperate lake during archetypal weak forcing conditions

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3.1 Abstract

Whilst there is significant knowledge of how intensive, episodic physical forcing governs spatial patterns in large lakes, less is known about how more typical forcing in small lakes affects spatial heterogeneity. This study used repeated field sampling and spatial data analysis to examine the horizontal structuring of physical, chemical and biological variables at a range of spatial scales during typical summertime weather conditions. Sampling took place in the surface mixed layer of Esthwaite Water (UK), a typical, small temperate lake. Physical forcing was low over the morning sampling period, as is usually the case at this site: average wind speed was ≈ 2 m s^{-1} and the average morning heat flux was 110 W m^{-2}. Spatial patchiness at small scales was found for all measured variables, at larger scales, where lake morphometry played a role, temperature variation was significantly dependent upon water depth, and chlorophyll *a* was significantly dependent upon fetch. We infer that while shallower waters were, as expected, warmer, the associated differential heating in this temperate lake was not sufficient to impact upon other variables. These results also imply that the fetch-related organisation of chlorophyll was due to downwind advection of buoyant plankton in surface waters, and not due to vertical entrainment. Calculated Wedderburn numbers were indicative of a stable system, suggesting that the lack of a significant fetch related temperature structure was due to near-surface motions only and not to thermocline-tilting phenomena. Whilst previous studies have focused on intense and episodic physical events or large systems, we show that

physical mechanisms still have an identifiable effect upon horizontal spatial heterogeneity in a small lake during typical, relatively weak, forcing conditions.

3.2 Introduction

Patterns and drivers of spatial organisation within ecological systems have been the focus of much attention in marine and freshwater research over the last four decades (Pinel-Alloul and Ghadouani 2007). Spatial heterogeneity has been recognised as an important feature in a number of lake systems, for a wide range of environmental variables and organisms from temperature and nutrients to phytoplankton, zooplankton and fish (George and Edwards 1976, Pinel-Alloul et al. 1999, Thackeray et al. 2004, Rinke et al. 2009). Previous work has tended to focus on the patterns generated by intense, episodic forcing events i.e. storms, rather than the more usual quiescent weather conditions experienced by lakes. Similarly, less attention has been paid to the generation of patterns due to the physical processes of surface heat and momentum fluxes in small lakes, which form a large proportion of surface water bodies (Downing et al. 2006). We wished to address this gap in the literature and provide information on the degree of spatial organisation in a small lake, under typical, temperate, summertime weather conditions.

Within freshwater systems, horizontal, surface layer spatial patterns have been categorised into four scales; large (>1 km), coarse (10 m – 1 km), fine (1 – 10 m) and micro (<1 m) (Pinel-Alloul 1995, Pinel-Alloul and Ghadouani 2007). At the large scale, these patterns vary both between lakes (George and Jones 1987) and within lakes (Betsill and van den Avyle 1994, Pinel-Alloul et al. 1999). Large scale patterns due to strong physical forcing processes have been reported in several studies. For example, accumulations of warmer water and phytoplankton at scales above 1 km have been detected in the South Arm of Lake Opeongo in Ontario (Blukacz et al. 2009), and significant autocorrelation statistics have been reported over distances of 0.5 – 3.8 km and 1.8 – 51.1 km for temperature and zooplankton in Windermere (Thackeray et al. 2004) and temperature and chlorophyll in Lake Constance (Rinke et al. 2009), respectively. Fewer studies have investigated these kinds of patterns at sub-kilometre scales or within smaller lake systems (Pinel-Alloul and Ghadouani 2007). Nevertheless, these small systems (<1 km^2 surface area) make a significant contribution to global freshwater resources, accounting for 99.8% of lakes and 43.3% of lake surface area, making an understanding of the processes at this scale important (Downing et al. 2006).

Factors contributing to the spatial heterogeneity of biotic and chemical variables in lake surface waters may be physical or biological (Folt and Burns 1999, Pinel-Alloul and Ghadouani 2007), and these factors are theorised by the 'multiple driving force hypothesis' to interact often over different spatial scales (Pinel-Alloul 1995). The expectation is that, at the largest scales, physical forcing phenomena such as wind-induced circulation, thermocline-tilting and associated upwelling and downwelling patterns, wind mixing processes and lake inflows will dominantly determine heterogeneity in chemical variables (e.g. specific conductivity, dissolved oxygen, nutrients) and distributions of biota (George and Jones 1987, Pinel-Alloul et al. 1999, George and Winfield 2000, Langenberg et al. 2008, Blukacz et al. 2009, Rinke et al. 2009). In contrast, at the fine and micro scales, biological controls are expected to dominate, with feeding, predator avoidance and mating (Folt and Burns 1999, Romare et al. 2003, Castro et al. 2007) as key drivers of biotic heterogeneity, and hot spots of chemical variables (e.g. dissolved oxygen) being associated with phytoplankton blooms (e.g. Arhonditsis et al. 2003).

The extent to which biological or physical factors dominate at each spatial scale will be dependent on the strength and consistency of the different forcing mechanisms acting. The strength and persistence of the wind field has been found to be important in relation to accumulations of phytoplankton on both small and large scales (Blukacz et al. 2009). A 'conveyer belt' circulation in the epilimnion has been conceptualised where, under consistent wind forcing of a lake, near surface concentrations of positively buoyant organisms are transported downwind and become concentrated in areas of downwelling while near surface concentrations of negatively buoyant organisms are transported upwind and become concentrated in areas of upwelling (George and Edwards 1976). This mechanism has been found to operate under circumstances where wind direction is consistent for a 24 hour period prior to sampling (George and Edwards 1976, Thackeray et al. 2004) and where the upwelling is strong (e.g. Rinke et al. 2009). Evidence for downwind accumulation of positively buoyant algal species such as *Microcystis* has also been found in tank experiments by Hutchinson & Webster (1994). A critical wind speed threshold of 2 – 3 m s^{-1} was suggested to separate surface accumulations of algae at low wind speeds from a regime of more turbulent mixing which overcomes the buoyant velocities of the algae, resulting their entrainment into deeper waters and no surface accumulation at higher wind speeds (Webster and Hutchinson 1994). Such a distinction is particularly relevant to studies of lakes of different size, as lower wind speeds are more commonly associated with smaller lakes because of their shorter fetches.

Relative exposure to wind forcing and consistency in wind direction also contribute to spatial heterogeneity in lake surface waters. When the wind direction is reversed, restructuring of biotic gradients to reflect the new wind pattern has been observed (Jones et al. 1995) while the development of gyres and algal patches have been found where lakeshore morphometry results in wind sheltering (Schernewski et al. 2005). Changes in the strength of wind forcing have also been found to produce different spatial patterns within the same lake; for example, George and Heaney (1978) found small distinct patches were characteristic of very low wind speeds while windward accumulations of phytoplankton occurred at higher wind speeds. This implies that the physical drivers responsible for the observed spatial heterogeneity have often been interpreted as short term physical events within the lake. In contrast, this study focuses on the effects of typical conditions of relatively low forcing which are characteristic of many small lakes.

Lake morphometry can also exert a strong influence on surface spatial heterogeneity, with pelagic and littoral areas distinguished by differences in heating (e.g. James and Barko 1991a, George and Winfield 2000, Finlay et al. 2001), wind exposure (e.g. Monismith et al. 1990) and biotic community structure, for example, littoral zone macrophytes result in refuge groupings or shore avoidance behaviour in zooplankton (Nurminen and Horppila 2002, Romare et al. 2003). Differential heating between shallow and deep water has been found to be important for the formation of convective motions and the exchange of nutrients from littoral to pelagic waters, where temperature gradients of 0.58°C have been found to produce offshore flows of 0.004 m s^{-1} (James and Barko 1991b). In small lakes, these shallow, shore areas constitute a significant proportion of the whole basin, particularly where shoreline complexity is high (Dodds 2002). While the focus of much previous work on spatial heterogeneity has been exclusively in the pelagic, here we examine spatial structures in a small lake, where there is a stronger interaction between the shore areas and pelagic zone.

Thus, the aim of this study was to examine and quantify surface horizontal spatial heterogeneity in a small lake, where wind speeds are typically smaller and frequently fall within the range of the critical threshold of Webster & Hutchinson (1994) and where lake morphometry is likely to interact with the spatial pattern. We also wanted to investigate the importance of mild, temperate summer heating conditions in the lake, which have received less attention than the stronger heating characteristic of more continental or tropical lakes. Moreover, we wanted to quantitatively examine heterogeneity under conditions 'typical' of the lake system in question by using repeat surveys, which differs from the more episodic approach of previous studies. We test two hypotheses: firstly, even weak physical forcing, defined here as surface heat fluxes and wind conditions, will have a statistically significant influence on the spatial organisation of the physical, chemical and biological variables measured and secondly, that the lake morphometry will affect significantly the spatial influence of the physical forcing; allowing that these influences may, themselves, be weak.

3.3 Methodology

3.3.1 Study site

Esthwaite Water (54°21'N, 3°0'W) is a lake of glacial origin, forming a part of the larger Windermere catchment within the south eastern area of the English Lake District. As is typical of glacial lakes, it has an elongated morphology aligned along the valley axis, with a total length of 2.5 km and an average width of 0.5 km (Fig. 3.1). Classified as a small lake by area (Kalff 2002), it has a surface area of 0.96 km^2, a total volume of 6.7 x 10^6 m^3, and an average depth of 6.9 m. More than 55% of the lake is less than 5 m deep (Mackay et al. 2011a). Esthwaite Water can be divided into three basins, which are separated by sills. The northernmost basin is the largest (0.54 km^2) and deepest (maximum depth 16 m) and is where the sampling for this study took place. The prevailing westerly weather patterns which characterise this part of the British Isles (Barker et al. 2004) and the orientation and morphology of the lake result in significant spatial variation in the exposure to wind across the lake surface.

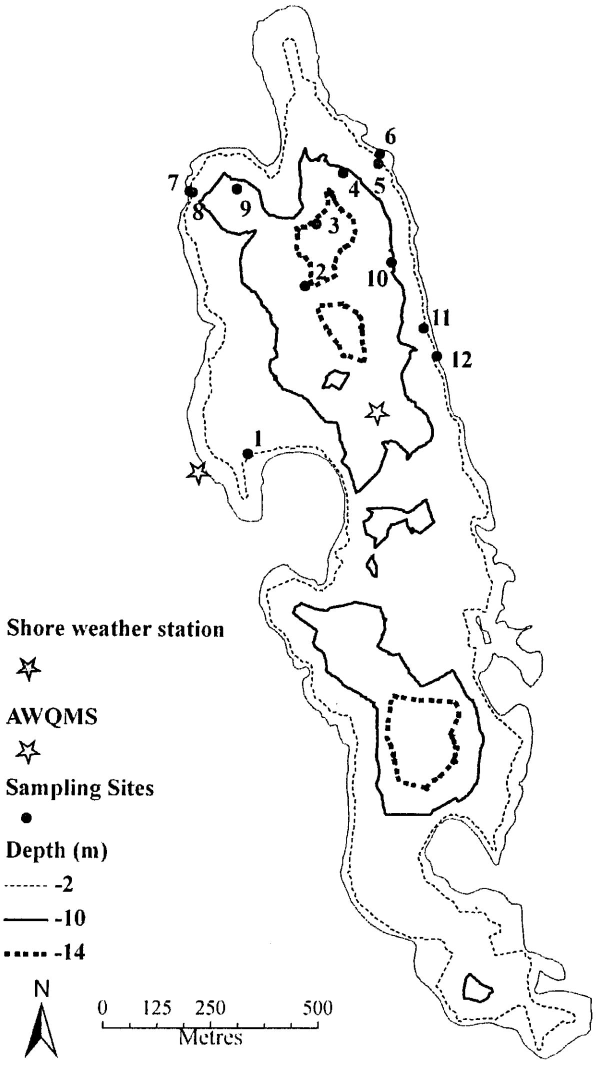

Figure 3.1 Map of Esthwaite Water showing the location of sampling sites, the shore weather station and AWQMS buoy and selected bathymetric contours.

Esthwaite Water has been one of the most intensively studied lakes in the world and as a consequence, a great deal is known about its biological, chemical and physical characteristics (Mortimer 1941, Sutcliffe et al. 1982, Talling and Heaney 1988, George et al. 1990, George 2000). As part of its national lakes monitoring network, the UK Centre for Ecology and Hydrology (CEH) operate an Automatic Water Quality Monitoring Station (AWQMS) in the north basin of the lake and a meteorological station on the shore, which provide high resolution meteorological and hydrographic data.

3.3.2 Field and laboratory methods

Intensive field sampling was undertaken on seven occasions over a 12-day period in early August 2009. Two transects were selected which crossed the northern basin and intersected at the deepest point in the lake. A hierarchical sampling design was used: three samples were taken along the length of the boat (approximately one metre apart) at twelve sites located at specific depths on each transect (Fig. 3.1). The distance to the next nearest site varied between 7 – 408 m reflecting the differing basin morphometry and the transect orientation. This allowed examination of spatial patterns at both the fine and coarse scales defined by Pinel-Alloul (1995). Shallow water sites were largely unvegetated (five of seven), with one in reeds and one shaded by trees. At each sample location, surface dip samples for zooplankton abundance, total phosphorus and chlorophyll analysis were taken and water temperature and dissolved oxygen, were recorded at 0.2 m depth using a Hydrolab Quanta® Water Quality Measurement System (Loveland, Colorado, USA). Approximate water depths were recorded with a Plastimo Echotest II (Southampton, Hampshire, UK) echosounder in deeper water and a weighted graduated line in shallow water.

Zooplankton counts were made on Whatmann GF/C filter papers following filtration of 1 litre of water for each site and converted to a number per litre (L^{-1}). This method has been shown to provide an acceptable measure of crustacean zooplankton abundance (Talling 2003). Chlorophyll *a* samples were filtered using Whatmann GF/C filters and frozen on the day of sampling for later analysis. Samples were extracted in hot methanol following the method of Talling (1974). An estimation of the dominant phytoplankton species within the lake at the time of sampling was made through the calculation of biovolumes for each species, derived from the fortnightly phytoplankton count data collected as part of the ongoing CEH long term lake monitoring programme (CEH, unpubl. data). Count values were converted to biovolumes through the use of standard values for single cells, lengths or filaments obtained from published literature (Wetzel 1983, Reynolds 1984a, Hillebrand et al. 1999, Internationale Kommission zum Schutz des Rheins 2002, John et al. 2002, United States Geological Survey 2005, Madgwick et al. 2006, Olenina et al. 2006, Brierley et al. 2007) supplemented by personal communication (Carvalho, L., Maberley, S. C., Parker, J. and Reynolds, C. R.). Total phosphorus samples were refrigerated following the sampling until analysis, which took place no more than five days later. Total phosphorus concentrations were determined using the molybdenum blue reaction on a SEAL AQ2 auto analyser (Seal Analytical Ltd., Fareham, Hampshire, UK) following an autoclave digestion in potassium persulphate and sulphuric acid.

Wind speed was measured with a Vector A100L2-WR cup anemometer with optical rotation sensing (Vector Instruments, Rhyl, Wales) and solar radiation was measured using a Kipp & Zonen CNR1 Net Radiometer (Kipp & Zonen B.V, Delft, Holland), both obtained as hourly averages from the AWQMS in the north basin of the lake. As the buoy is a rotating platform, wind direction data were obtained as hourly averages from a Vector W200P-WR wind vane (Vector Instruments, Rhyl, Wales) in an unsheltered location on the shore of the north basin of the lake. Additional data on the thermal structure of the lake were obtained as two minute averages from a thermistor chain attached to the buoy, consisting of 12 Platinum resistance thermometers (PRTs)

(Labfacility Ltd, Bognor Regis, UK) spaced at one meter intervals to a depth of 11.5 meters.

3.3.3 Data analysis and statistical methods

All sampling took place between 0900 and 1300 hrs each day. As temperatures could alter over this timescale, temperature measurements at each site were corrected to the 1100 hrs temperature (approximately the mid-point of each sampling period) to account for short-term temporal changes and ensure comparability among sites. A correction factor was generated from the high resolution thermistor chain by subtracting the 12-minute moving average of the top PRT temperature around 1100 hrs from the 12-minute moving average of the top PRT temperature around the time that each sample was taken. The moving averages were centred around 1100 hrs and the sample times, respectively. For each sampling site, the (positive or negative) correction factor was added to the temperature recorded at that sampling site. This correction factor allowed us to partition out purely temporal temperature variation, which might potentially be confounded with the spatial temperature variations among sites. Average temperature corrections each day ranged from 0.03 - 0.46 °C. The same temperature data were used to correct for the effect of temperature changes on the saturation level of oxygen in the water based on saturation levels calculated by Benson & Krause (1980). Mixed layer depth was defined as the near surface region where the water temperature differed by < 1°C from the surface water temperature.

The effect of meteorological conditions as drivers for the horizontal heterogeneity were considered in terms of the surface fluxes of heat and momentum. Sensible and latent heat fluxes were calculated using standard bulk formulae (see Jones et al.

2005); net long-wave radiation was calculated following the method of Gill (1982), incoming solar radiation was obtained from the AWQMS on the lake and the reflected component estimated as 7% following Nunez et al. (1972). The total heat flux was then calculated as the sum of these fluxes following Gill (1982). The expected change in temperature associated with this heat flux, *T*, for site 'i', was calculated as:

$$\Delta T_i = \frac{Q\,\Delta t}{\rho\, Cp\, D_i}, \qquad (1)$$

where Q is the average heat flux over a given time period, Δt (in seconds) and ρ (1000 kg m^{-3}) and C_p (4200 J kg^{-1} K^{-1}) are the density and specific heat capacity of water, respectively. D_i (m) is the depth over which the temperature change is taking place, specifically the water depth in the shallow water sites and the mixed layer depth in the deep water sites.

In order to assess their wind exposure quantitatively, a measure of effective fetch for each site was calculated (Beach Erosion Board 1972, Håkanson and Jansson 1983) in ESRI ArcMap using the USGS Wind Fetch Model (Finlayson 2005, Rohweder et al. 2008). An effective fetch for a given wind direction is the weighted average fetch along several radials centred on the particular wind direction, taking account of small variability in wind direction (Håkanson 1977). Wind directions were grouped into 16 classes (N, NNE, NE, ENE, E etc.), and for each site the effective fetch was computed for each class. The total effective fetch for each site was then calculated as the average of these fetches, based on the 72 hour wind history prior to each sampling day. As wind direction was generally consistent over the sampling period, lake morphometry controlled systematic differences in effective fetch between sites.

Among site differences in effective fetch were insensitive to changes in the length of the wind history used in the calculations (over a range from 12 to 96 hours prior to sampling).

In order to assess the level of tilting occurring along the thermocline during the sample period and to indicate whether upwelling was likely to be occurring, the Wedderburn number (W) was calculated (Imberger and Patterson 1990);

$$W=\frac{g'h^2}{u_*^2 L'}, \tag{2}$$

where g' is reduced gravity ($= g\,\Delta\rho/\rho_0$), g is gravitational acceleration (9.8 m s^{-2}), $\Delta\rho$ is the density jump across the thermocline and ρ_0 is the density of the hypolimnion, h is the depth of the surface mixed layer, u_* is the water friction velocity and L' the maximum fetch length at the depth of the thermocline. When values of W are <1 strong up- and downwelling is likely to be occurring, values between 1 – 5 suggest tilting of the thermocline, while values >5 are indicative of a stable system (MacIntyre et al. 1999).

The overall spatial structure in the data for each day was analysed using the Spatial Analysis in Macroecology (SAM) programme (Rangel et al. 2006). Spatial autocorrelation was tested by calculating Moran's I statistics (Moran 1948, 1950) for a number of distance (between-sample-site) classes to produce a spatial correlogram for each day. Equal numbers of paired observations were calculated for each distance class to provide the same confidence in each statistic, removing any bias from the location of sampling points (Pinel-Alloul et al. 1999, Thackeray et al. 2004). Positive values of the Moran's Index represent positive autocorrelation i.e. sites close together in space are more similar than would be expected if the variable of interest varied randomly in space (clustering), while negative values indicate negative autocorrelation i.e. sites close together are more different than expected (dispersed) (Fortin and Dale 2005). Moran's I values were normalised by their corresponding daily maximum value to enable valid comparison between days (Rangel et al. 2006). An adjusted Bonferroni p value was calculated following Legendre and Legendre (1998) to assess the significance of statistics within each distance class.

An average of each measured variable over the seven sampling days was taken for each sampling point. These were used to investigate the influence of lake morphometry on their spatial structure, using a Generalised Least Squares (GLS) approach which can be used to address violations of statistical assumptions of independence within spatial data (Zuur et al. 2009). In these analyses water depth and fetch were included as main effects only, since the interaction between them was found to be non-significant. GLS was used to fit linear models with a range of random variance structures to the data using the restricted maximum likelihood estimation method. The spatial autocorrelation of the residuals was then modelled by a variogram. When a model with a particular variance structure provided a more parsimonious fit to the data than the original model and accounted for the observed autocorrelation, it was retained. Candidate models were compared using AIC values. An ANOVA F statistic and p value for each explanatory variable was then calculated using maximum likelihood estimation. All ANOVA and GLS analyses were carried out using the base and nlme packages in the R environment (Ihaka and Gentleman 1996, Pinheiro and Bates 2000).

3.4 Results

3.4.1 Temporal patterns in meteorological and lake variables

Wind speed was low (average value ≈2 m s^{-1}) while the direction remained predominantly from the SW quadrant, the prevailing wind direction for this area, throughout (Fig. 3.2a). The Wedderburn number reflected this, remaining high during the sampling period, while both the daily heat flux and the average heat flux between 0600 and 1100 were typical for summer time in this maritime, temperate region (Fig. 3.2b, Table 3.1). Mixed layer depth shoaled slightly over the sampling period, and averaged approximately 3.9 m (Fig. 3.3a). The variables measured did not vary greatly over the sampling period (Figs. 3.3a and 3.3b). Daily mean (± range) water temperatures were around 18±2 °C, chlorophyll *a* concentrations averaged 22±8 mg m^{-3} and total phosphorus averaged 34±10 mg m^{-3}. These results were very similar to the summer (May to September) mean values for 2009, based upon the fortnightly CEH monitoring programme (Table 3.1). Zooplankton abundances (data not shown) were very low for the entire sampling period, averaging 0.8 per L^{-1}. Correlations between the measured variables were not significant ($r =< 0.31$ $p > 0.05$), except for a weak but significant correlation between chlorophyll *a* and dissolved oxygen ($r = 0.38$, $p = <0.05$) and dissolved oxygen and total phosphorus ($r = -0.40$, $p = <0.05$). Biovolume calculations using the count data from the CEH fortnightly monitoring programme revealed that *Aphanizomenon flos-aquae* (Linnaeus) was the dominant species during the sampling period, accounting for over half of the total biovolume.

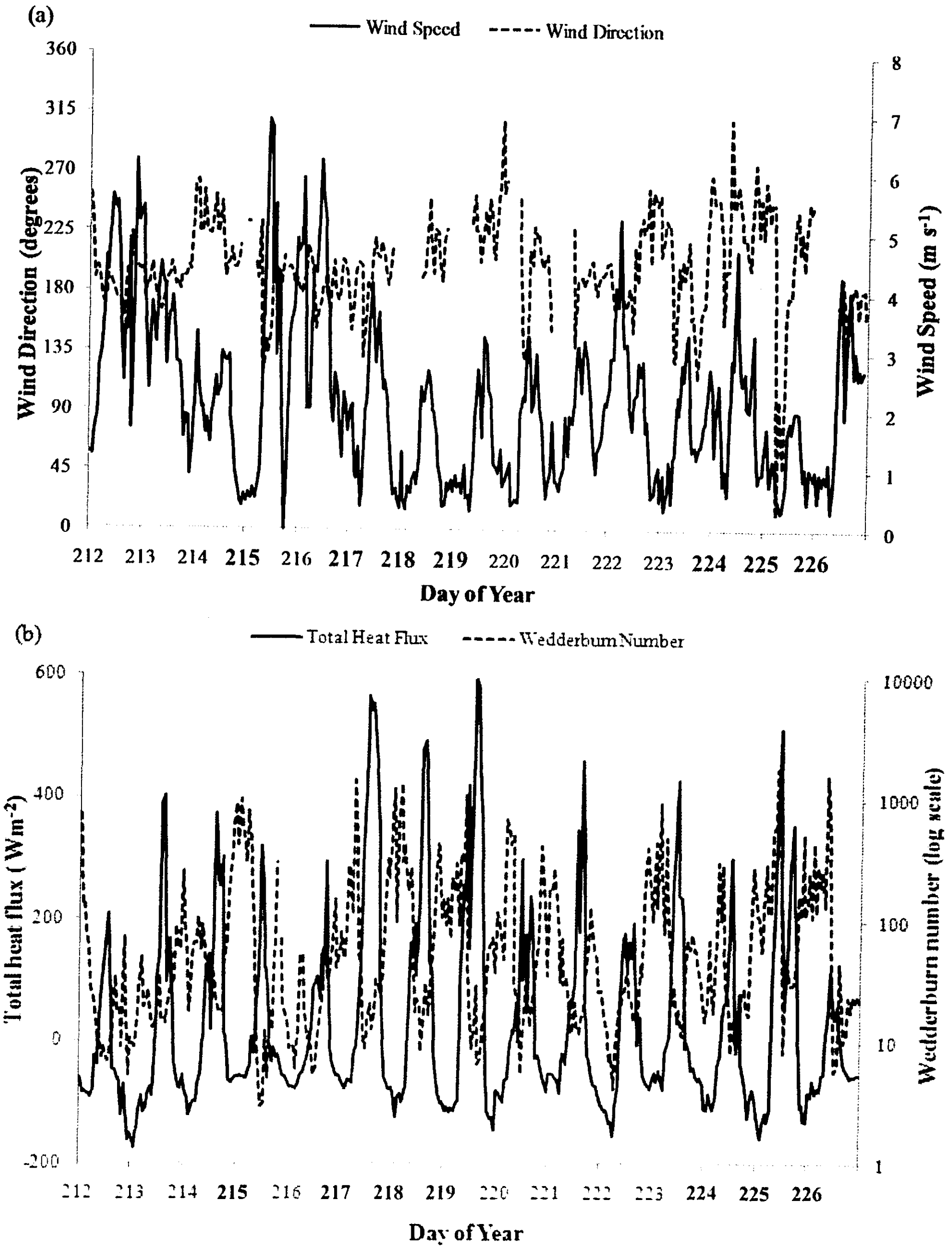

Figure 3.2 a) Hourly wind direction (dashed line) and wind speed (solid line) during the sampling period, **b)** hourly total heat flux (solid line) and Wedderburn number (dashed line) during the sampling period. Sampling days are highlighted in bold.

Table 3.1 Comparison of the averages and standard deviations (stdev) for a range of variables during the sampling period and summer from the CEH fortnightly monitoring campaign on the lake (May to September)

	Sampling period		**Summer**	
Variable	**Average**	**Stdev**	**Average**	**Stdev**
Total Phosphorus (mg m^{-3})	34.3	5.5	18.7	5.2
Chlorophyll *a* (mg m^{-3})	21.9	3.1	26.4	9.3
Temperature (°C)	18.1	0.7	17.5	3.0
Dissolved Oxygen (mg l^{-1})	10.4	0.8	10.3	0.4
Wind speed (m s^{-1})	2.7	1.4	2.5	0.9
Total heat flux (0600 – 1100) (W m^{-2})	110	116	83	96
Total daily heat flux (W m^{-2})	50	151	30	137
Mixed layer depth (m)	3.9	0.8	4.9	1.8

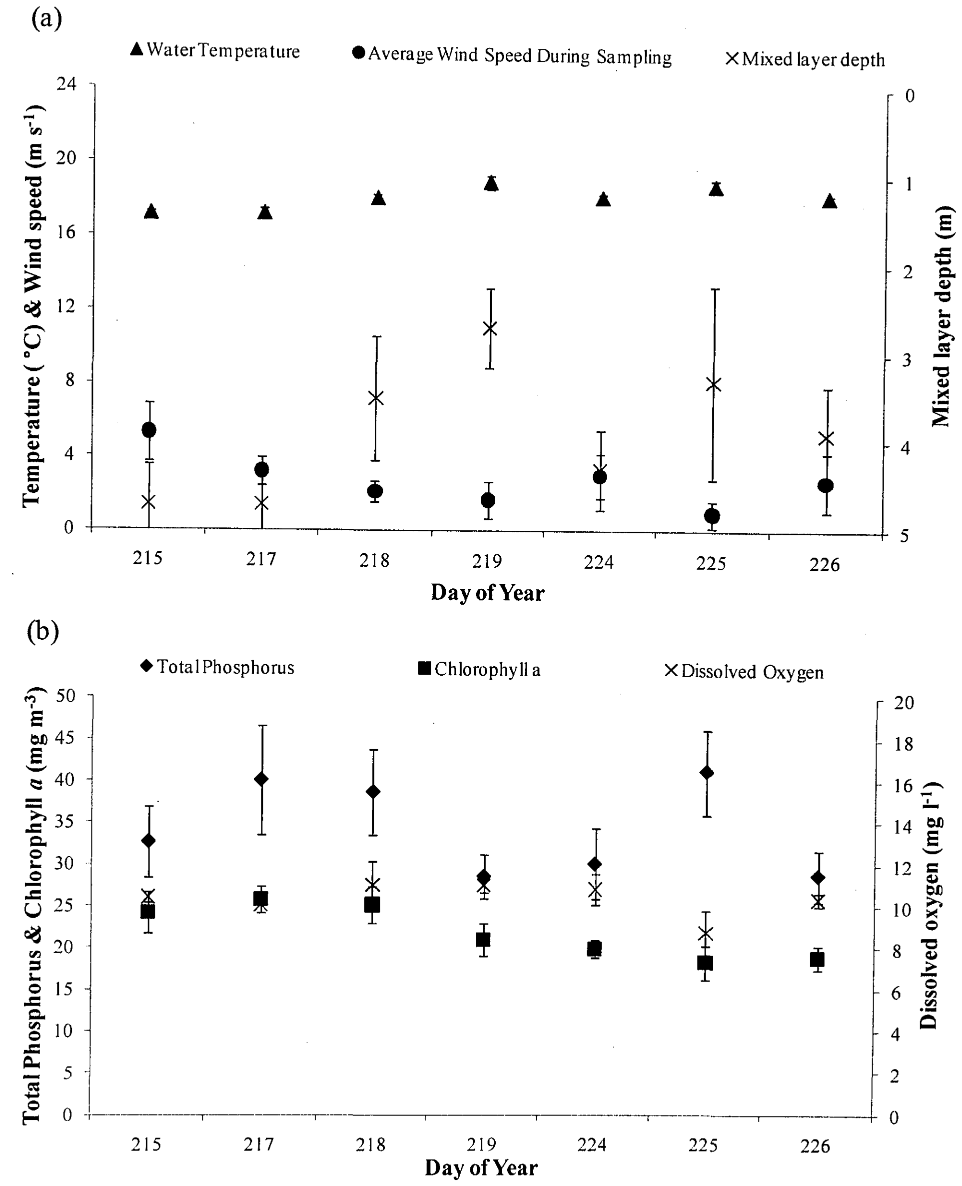

Figure 3.3 a) Daily averages for water temperature, wind speed and mixed depth, **b)** daily averages for total phosphorus, chlorophyll *a* and dissolved oxygen. Error bars show ± 1 standard deviation.

3.4.2 Spatial patterns

Box and whisker plots summarising the correlogram results for the seven sampling days, show a significant positive autocorrelation at short distances (<32 m) for all variables on over half of the sampling days (Fig. 3.4). At mid to longer distances there was a trend towards negative autocorrelation for all the variables. Variability within the data at these distance classes is larger and fewer of the Moran's Index scores have significant *p* values. There is also a noticeable hierarchy in the number of significant *p* values between the physical, and other variables (temperature: 27/63; dissolved oxygen 23/63; chlorophyll *a* 14/63 total phosphorus 12/63). These larger distances over which negative autocorrelation was observed may be between sites in shallow and deep water or one side of the lake and the other, implying a fetch related difference where wind direction is consistent. As the correlogram analysis is isotropic (i.e. it assumes the same pattern of spatial dependency in all directions), the signal due to these morphology-related differences is conflated with general variability between sites, which may account for the relatively unclear results in these mid to longer distance classes.

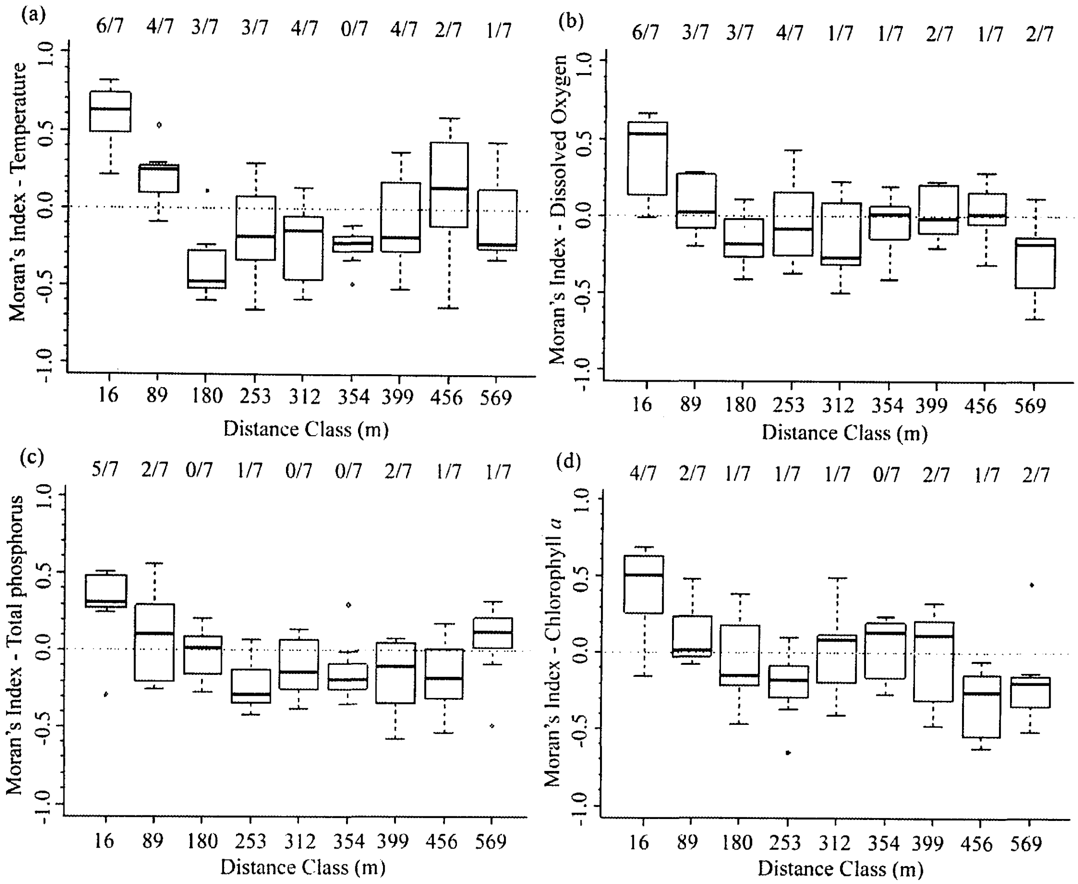

Figure 3.4 Correlograms showing variation in spatial patterns and the number of days (out of 7) in which the adjusted P value of the Moran's Index was <0.05 over the sampling period for (a) temperature (b) dissolved oxygen (c) total phosphorus and (d) chlorophyll *a*. The box and whisker plots show the line as the median, the box enclosing the quartiles and the whiskers as 1.5*inter-quartile range.

3.4.3 Morphological influences

The directional differences and morphometric effects suggested by the correlograms were tested explicitly by analysing the measured variables with respect to effective fetch and water depth. Data were pooled across sampling days and the time-averaged data grouped by depth, into shallow (≤3 m) (sites 1, 5, 6, 7, 8, 11 and 12) and deep (≥12 m) (sites 2, 3, 4, 9 and 10) classes; and by fetch, into short (<500 m) (sites 1, 2, 7, 8 and 9) and long (>500m) (sites 4, 5, 6, 10, 11 and 12) classes. Site three was excluded from the fetch analysis, as it was the central sampling location with a fetch intermediate between the two distance categories used to define short and long fetch.

GLS models were then used to examine differences in variables, with fetch and depth as categorical predictors. In these models, the error structure that best described patterns of autocorrelation in the residuals was the Gaussian variogram. Inclusion of this variogram model significantly improved the fit of the GLS models on the basis of the likelihood ratio tests. The results of the subsequent ANOVA analysis performed with this variance structure showed two significant patterns in the measured variables (Table 3.2). Firstly, temperatures in the averaged data were significantly higher ($p < 0.05$) at shallow sites compared to deep sites and showed a wider range (Fig. 3.5a). The same pattern was found in both the corrected and uncorrected data. Secondly, there was a significant difference in chlorophyll *a* concentrations between fetch classes, longer effective fetches corresponding to higher concentrations (Fig. 3.5b). Neither the corrected nor uncorrected temperature data were significantly related to fetch classes (results not shown for uncorrected data). The dissolved oxygen and the total phosphorus variables were not significantly related to either depth or fetch classes.

Table 3.2 Results of the one-way ANOVA analysis (significant results highlighted in bold)

Variable	Factor	Degrees of Freedom	F statistic	P value
Chlorophyll *a*	Water depth	1, 34	1.513	0.2271
	Effective fetch	**1, 31**	**24.57**	**<0.0001**
Total Phosphorus	Water depth	1, 34	1.035	0.3161
	Effective fetch	1, 31	0.677	0.4169
Temperature	**Water depth**	**1, 34**	**4.3**	**0.0457**
	Effective fetch	1, 31	0.45	0.5072
Dissolved Oxygen	Water depth	1, 34	2.111	0.1554
	Effective fetch	1, 31	2.223	0.1461

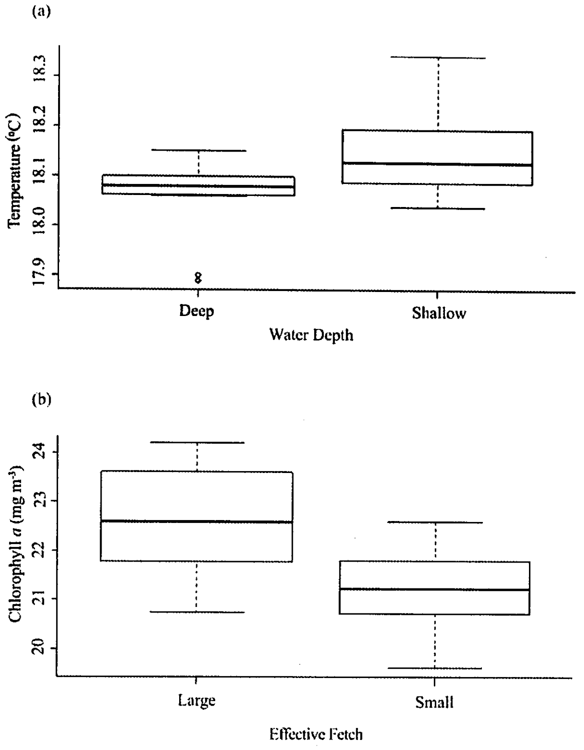

Figure 3.5 Significant results from the GLS ANOVA analysis of lake morphological traits, differences between (a) surface temperature and (b) surface chlorophyll *a* concentrations with respect to depth and effective fetch.

3.5 Discussion

The results show that while physical forcing over the sampling period was relatively weak, spatial structures relating to this forcing and to morphometry were still a feature of the lake. This level of forcing was typical of conditions at Esthwaite Water over the summer (Table 3.1) and potentially indicative of archetypal forcing in other small temperate lakes.

As a temperate system, the heat fluxes were low compared to heat fluxes generated in warmer climes such as the Mediterranean or the tropics. Effective heat fluxes of the order of 1000 and 1500 W m^{-2} were found over the same morning time period in the Sau reservoir in northern Spain in July and September (Serra et al. 2007), while Imberger (1985) reported net radiation alone of between 600 and 900 W m^{-2} over the morning period in the Wellington reservoir, Australia. In both cases wind speeds were low, minimising the effect of cooling in the latent and sensible heat fluxes. Similarly, the typical wind speeds on Esthwaite Water, a lake with a relatively short fetch, were substantially lower than both those of large lakes and those which occur during (often reported) strong physical forcing events. Blukacz et al. (2009), for example, measured average wind speeds during sampling of 13 m s^{-1} in South Arm and 7 m s^{-1} in Annie Bay of Lake Opeongo, while in Lake Constance wind speeds between 6 and 10 m s^{-1} were recorded during the storm event studied (Rinke et al. 2009).

Even though the physical forcing within the lake was relatively weak, small scale patchiness was a consistent feature of the measured variables in Esthwaite Water across physical, chemical and biological attributes (Fig. 3.4). This result is consistent with studies from other lakes, where Lake Geneva, Windermere and Lake Constance showed a significant positive autocorrelation at small scales (Pinel-Alloul et al. 1999, Thackeray et al. 2004, Rinke et al. 2009). Given that the latter studies were focused on much larger lake systems and consequently the distances between sampling sites were much larger than in the present study this positive autocorrelation appears to relate strongly to the sampling scale chosen, with sites close together showing a greater similarity than those further apart. The difference within a small system is that as the distance classes increase, the greater the expected interaction with the lake's morphology and shoreline characteristics (shallow water, deep water, sheltered, and exposed). The result would be a rapid transition to negative autocorrelation on scales that reflect the change in lake morphology (e.g. shallow to deep water) where sites may be expected to have different characteristics. For this study there appears to be some indication of this pattern at mid distance classes (Fig. 3.4), while in the case of the larger lakes, the transition to negative autocorrelation is more gradual and gradient-like.

The effect of depth on the measured variables was restricted to small water temperature differences between shallow and deep sites (Table 3.1 and Fig. 3.5). On average, the measured difference between the surface temperature of the shallow and deep sites was 0.11°C. This horizontal difference is 10% of the average diel temporal temperature change in the lake surface waters measured during the survey period which ranged between 0.5°C to 2.1°C. The small observed morning (0600 – 1100) heat flux of 110 W m^{-2} was sufficient to explain the small horizontal temperature differential (Equation 1.), assuming an average depth of two metres for shallow sites and a mixed layer depth of four metres for deep sites. None of the other variables were overtly influenced by this differential heating due to water depth, suggesting that the strength of the forcing was insufficient to affect the spatial organisation of the measured chemical and biological attributes at these scales, such as differences in algal growth rates. This is also indicated by the lack of a significant correlation between temperature and the other variables. While the temperature differences between deep and shallow water here were small, being the product of small heat fluxes and a relatively shallow mixed layer, it is likely that these variations would be an order of magnitude larger in similar sized lakes in warmer regions, with consequent potential for influencing biochemical variables and the generation of convective motions (Monismith et al. 1990). This emphasises the differences that may be expected in the spatial organisation of variables due to depth between different climatic regions and between smaller and larger, deeper lakes, where the depth of the mixed layer in the latter is likely to be greater, with the potential for a larger temperature differential (Finlay et al. 2001).

Chlorophyll *a* levels were found to be significantly higher on the eastern side of the lake, where fetches were larger (Table 3.1 and Fig. 3.5). The weak but significant correlation between chlorophyll *a* and dissolved oxygen, suggests that photosynthesis may have had some influence on surface water oxygen concentration, however no significant effect with fetch was seen for dissolved oxygen. In terms of biovolume the dominant species of phytoplankton in the lake at the time of this study was the buoyant cyanobacterium *Aphanizomenon*. The potential for vertical migration of the *Aphanizomenon* cells is unlikely to have influenced the horizontal pattern shown by the chlorophyll *a*, because the timing of the sampling avoided the early evening and night time periods when populations have been found to form deepwater maxima (Sellner 1997). In addition, vertical migration of *Aphanizomenon* was not found to occur in Esthwaite Water in a previous study, where the cells were vertically evenly distributed throughout a 24 hour period (George and Heaney 1978).

The chlorophyll *a* pattern appears to agree with the downwind accumulation expected at low wind speeds (1 to 3 m s^{-1}) where cyanobacteria dominate the phytoplankton (George and Edwards 1976). The ratio of plankton concentration length scale to the maximum distance between sites provides a measure of the difference in concentration between one side of the lake and the other (Webster 1990). During the sampling period this ratio was nearly always <1, where assuming a floatation rate for *Aphanizomenon* of $4.0\text{x}10^{-5}$ (Reynolds et al. 1987), confirmed that plankton were strongly concentrated at one end of the lake (Webster 1990). Assuming an estimate of

3% of the wind speed for a surface current speed (Smith 1979), resulted in average surface current speeds of around 0.08 m s^{-1} during the morning sampling. This would imply that the timescale for the water movement from upwind to downwind sites is on average around 1.5 hours. The patterns seen are therefore capable of being established during the lower wind forcing of the morning period and this timescale is analogous with the timescale for the establishment of a circulation pattern within the basin of 1.25 hours based on Webster (1990). An alternative explanation of Langmuir circulation is unlikely as no evidence was seen on the sampling days and wind speeds were nearly always below 5 m s^{-1}, the wind speed required for formation (Kalff 2002, Blukacz et al. 2009). Note these winds were insufficient to generate any wind induced spatial variation in temperatures, but still had a significant effect on phytoplankton location. Other studies have focused on effects at higher wind speeds; Blukacz et al. (2009) found wind speeds >6 m s^{-1} generated temperature differences of more than 1°C and accumulations of phytoplankton at downwind sites while little difference in these variables was found at low wind speeds (<3 m s^{-1}). In Lake Constance, the variation in resource supply for the phytoplankton is thought to be more important in explaining their distribution at lower wind speeds (<6 m s^{-1}), while the effect of upwelling determined the distribution of water temperature and phytoplankton after a storm event (Rinke et al. 2009). Wind speeds in Loch Ness >5 m s^{-1} have also been found by Jones et al. (1995) to generate a 2°C difference in water temperature and higher concentrations of chlorophyll *a* at the downwind end of the lake, with the pattern reversing following a change in wind direction. Warmer water is associated with downwind transport and accumulation at the windward side of the lake, whilst cooler water relates to the resultant upwelling of deeper water at the leeward side and the generation of the epilimnion 'conveyor' (George and Edwards 1976). The difference between the lakes where these large differences are seen and Esthwaite Water is clearly the scales at which the accumulations are occurring over. It appears that even within a smaller system, it is possible to see accumulation and spatial structures develop within the phytoplankton in relation to effective fetches even at low wind speeds where the direction of forcing is consistent.

The fact that large differences in temperature were not seen within the present study suggests that strong upwelling or downwelling was not occurring across the lake. This was confirmed by the Wedderburn number which was above five for virtually the entire sampling period, indicative of a stable system. MacIntyre et al. (1999) found that values of between one and five were necessary to produce tilting of the upper and lower thermocline and persistent periods of strong wind forcing required for boundary mixing. Strong wind forcing on Esthwaite Water is therefore unlikely to have persisted for periods long enough to develop significant up and downwelling. It seems that passive horizontal transport at the near surface and accumulation of buoyant cyanobacteria under stable wind conditions (George and Edwards 1976) is a more probable explanation for the pattern seen in the chlorophyll. The result at these low wind speeds is consistent with the threshold of 2 - 3 m s^{-1} for separating downwind surface algal accumulation for buoyant species at low speeds from entrainment of algal cells into deeper lake water at higher speeds proposed by Webster & Hutchinson (1994). This relatively low level of forcing for both heating and wind mixing, which is typical for this lake during the summer, clearly has a role in the systematic spatial organisation seen within the lake during the morning period.

In this study we targeted the typical modest forcing conditions of a small temperate lake, using a quantitative approach. Other studies have frequently investigated much stronger forcing conditions, either representative of (atypical) storm events or of lakes that are larger or in a warmer climate. Nevertheless, within this lake system, a persistent small scale spatial structure was still found for a range of physical, chemical and biological variables that can be linked to physical forcing and the system's morphology, despite the forcing being relatively weak. Small-scale patchiness was evident. Patterns in surface temperature variation were associated with changes in lake depth, with shallow areas being warmer than deeper water. Spatial variation in chlorophyll *a* was best explained by examining the effective fetch of individual sites, where even under low wind forcing and a lack of significant up or downwelling, buoyant cyanobacteria appeared to be transported downwind. These results for temperature and chlorophyll *a* support the hypotheses that even weak physical forcing will have an influence on spatial patterns (hypothesis 1) and morphometry will interact with the forcing resulting in different patterns for individual variables (hypothesis 2). Therefore, even under typical, modest forcing conditions characteristic of small temperate lakes, small-scale patchiness was detected for all variables. At larger scales, low but consistent wind forcing resulted in a systematic effect on buoyant algae and the expected differential heating of shallow water was found but this was insufficient to result in secondary effects on other variables. Neither fetch nor water depth were found to influence the spatial distribution of total phosphorus and dissolved oxygen.

Chapter 4 Contribution of sediment focusing to heterogeneity of organic carbon and phosphorus burial in small lakes

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4.1 Summary

1. Sediment distributions within lakes are typically heterogeneous. Much of our understanding comes from the study of large and/ or shallow lakes, where wave mixing is the dominant sediment focusing mechanism.

2. We elucidated the heterogeneity of surface sediment distribution in a small lake, Esthwaite Water (UK). We considered multiple focusing mechanisms (downslope gravitational transport, waves, and wind-driven currents) and their effect on multiple sediment variables (water content, organic content, total phosphorus and benthic diatom taxon richness). In particular, we investigated the implications of different focusing processes for calculations of burial rates of organic carbon and total phosphorus. We used a new, high-resolution bathymetric survey of the lake in our calculations and compared the results to those from an earlier low-resolution bathymetric survey.

4. Wave-driven focusing and downslope gravitational transport were not significant in Esthwaite Water. However, calculated wind-induced current speeds were sufficient to mobilise small particles at all depths of the lake and therefore could potentially be an important resuspension process in small lakes.

5. We calculated that approximately half of the phosphorus entering the lake is retained in the sediments. This has important implications for the ability of the lake to recover from eutrophication because of the prolonged internal phosphorus loading capability.

6. Differences in calculated burial rates due to sediment heterogeneity were much larger than those due to the difference in bathymetric resolution. Ignoring sediment heterogeneity when calculating flux-to-lake bed rates for organic carbon and total phosphorus can lead to large inaccuracies, with implications for burial rate and budget studies.

4.2 Introduction

Calculating the store of carbon, phosphorus or other particulates in lake sediments is problematic due to an uneven input of sediment and subsequent reworking within the lake. Lake sediment distribution is widely regarded to be heterogeneous, especially in large lakes, and is determined by several sediment transport, deposition and re-suspension processes, which vary spatially (e.g. Hilton and Gibbs 1984, Cyr 1998) and whose effects vary according to the effective sediment particle size and density (Hilton et al. 1986, Rowan et al. 1992).

This paper is concerned with understanding sediment heterogeneity for the calculation of burial rates of nutrients and organic matter, for which sediments may be active sources or sinks (e.g. Baudo et al. 1989, Søndergaard et al. 2003, Trolle et al. 2008). While spatial heterogeneity in sediment is widely recognised, the estimation of burial rates or lake-wide fluxes of materials such as organic carbon do not often reflect this (e.g. Downing et al. 2008, Anderson et al. 2009, Finlay et al. 2010). Similarly, the general applicability of existing models used to explain this spatial heterogeneity still needs to be demonstrated, particularly in the case of small lakes.

Central to the study of sediment distribution in lakes is the concept of 'sediment focusing', a term used to describe the tendency of fine-grained sediments to be concentrated in deeper parts of the lake. Focusing occurs because the dominant sediment resuspension and transportation processes tend to be strongest near the water surface, and to decay in strength with depth. Thus sediments will tend to be resuspended and transported out of shallower areas until they reach a sufficient depth that these processes no longer affect them significantly. Therefore, this spatial process can be related to near-shore zones of re-suspension and transportation and deep-water zones of accumulation (Håkanson and Jansson 1983, Blais and Kalff 1995). The spatial extent of these zones depends on factors relating to the size and depth of the lake (e.g. fetch, wind speed, water depth and lake slope), which govern the physical processes (waves, currents, gravitational slope failure) controlling resuspension.

In addition to these physical processes, bioturbation of sediments by animals enhances or causes resuspension in some shallow lakes where benthivorous fish populations are high (Breukelaar et al. 1994, Carvalho and Moss 1995, Moss et al. 2002, Tarvainen et al. 2005, Jackson et al. 2010). Lower rates of decomposition in deeper water may also contribute to the sediment distribution patterns of organic matter, however this is likely to be superimposed on the physical focusing processes, rather than an alternative to it (Jones 1980, Wetzel 1983).

One cause of sediment focusing is gravity-driven bed slope failures, whose effect is largely governed by the gradient of the lake bed. Slumping, sliding and turbidity currents are the main processes of this kind (Håkanson and Jansson 1983). Very little active movement due to these processes is expected on slopes with a gradient of <4%, while little accumulation is anticipated for slopes >14% (Håkanson 1977). Therefore mean basin slope has been used to categorise sediment focusing patterns among lakes, where lakes with lower basin slopes are anticipated to have larger sediment accumulation areas (Blais and Kalff 1995). While this provides a means for comparing between lakes, it does not give a clear indication of the within-lake processes, as site slope and mean basin slope between contours have not been found to be significant indicators of the accumulation area (Blais and Kalff 1995). It is reasonable to assume that increased accuracy in lake bathymetry will lead to increased accuracy in predictions of slope-generated resuspension and focussing.

Wave mixing has been suggested to be the dominant process causing sediment focusing for many lakes (Håkanson 1977, Rowan et al. 1992). Wind-induced surface waves have their energy confined to a near-surface layer, whose depth is approximately a half of their wavelength, known as the 'wave mixed layer' (Smith and Sinclair 1972). When the mixing caused by wave motion in this layer interacts with the lake bed, it can resuspend particles. Wave-induced resuspension is important in large lakes where waves are large and energetic, creating deep wave-mixed layers (Håkanson 1977, Rowan et al. 1992, Cyr 2009) and in shallow lakes where wave-mixed layers frequently reach the lake bed (Hamilton and Mitchell 1997, Spears and Jones 2010). However, very few studies have considered whether wave mixing is important in small, deep lakes (on the order of 1 km^2 or less), where fetches are relatively short and thus wave-mixed layer depths relatively shallow. Furthermore, accurate prediction of wave mixing requires detailed knowledge of the wind. As frictional drag over the water surface is sufficiently different from that over land, effective predictions of wave-mixing will require wind speed measurements taken over the lake itself.

Few studies examining sediment focusing have considered whether wind-induced currents might be important for sediment resuspension and focusing, particularly for small lakes. These currents are directly related to the strength of the wind blowing over the lake surface (Smith 1979). At a simplified level, during isothermal conditions, current speed declines exponentially with depth and, as described by the law of the conservation of mass, a return current is generated in the opposing direction (Smith 1979). These currents cause resuspension below the wave-mixed layer and are important in the offshore transport of sediments in large lakes (Lemmin and Imboden 1987, Hawley et al. 1996, Hawley and Lee 1999). Under stratified conditions, currents and mixing below the thermocline are likely to be strongly suppressed (Wüest and Lorke 2003). Seiching has however been found to resuspend sediments, either by breaking against the lake side, or as a 'burst-like' motion at the lake bottom in more central locations (Gloor et al. 1994, Shteinman et al. 1997).

Resuspension potential is also related closely to particle size and composition; smaller and less dense particles are more readily entrained into the water column (Miller et al. 1977, Gloor et al. 1994). Understanding the fate of small particles within lake systems is important because they are often associated with heavy metal contaminants and phosphorus (Williams et al. 1976, Schorer 1997, Andrieux-Loyer and Aminot 2001). The cohesive properties of sediments, such as the behaviour of colloidal particles and the tendency of organic material to form aggregates (Alldredge and McGillivary

1991), can result in an increase in effective grain size, thereby increasing the critical shear required for resuspension (Håkanson and Jansson 1983).

In the past, the definition of sediment accumulation zones has been based on the distribution of a single sediment variable such as water content as a proxy for grain size (e.g. Håkanson 1977, Rowan et al. 1992, Blais and Kalff 1995). The transition from the zones of re-suspension and transport to that of accumulation has then been assumed to be identified by an abrupt change in the depth profile of this variable (Blais and Kalff 1995, Anderson et al. 2008). Here, we hypothesise that these single variable-based focusing models used to predict areas of accumulation do not explain the depth distribution of all sediment variables, particularly those associated with small particle sizes. Furthermore, our understanding of sediment distribution is dominated by results from large and shallow systems. Much less is known in this respect about small, deep lakes, yet their ubiquity (e.g. Downing et al. 2006) makes them important components in global biogeochemical cycles.

In this study, we examined the extent to which estimates of different sediment distribution processes (slope failures, wave mixing and wind-induced current shear) accounted for the heterogeneity observed within the surface sediments of a small lake by testing the adequacy of focusing models. In order to predict wave-mixed depths and wind-induced currents we used continuously monitored wind data measured by a buoy on the lake. To assess the effect of slope processes we used a far more detailed bathymetry of the lake than previously existed. Burial rate and whole lake flux-to-bed rates of organic carbon and total phosphorus were calculated using three methods. The first used the established method of a single site in the deepest part of the lake, the second used the predictions provided by each sediment distribution process, and the third was a depth-integrated measure (taken to be the true estimate). We compared the results of the first two methods to that of the depth-integrated measure to calculate the errors in these predictions and contrasted these errors with the differences between values calculated using two different resolution bathymetries. The work expanded on a previous study of Hilton *et al.* (1986), by providing a directly quantitative approach to elucidating the processes responsible for the distribution patterns of different sediment variables. The total phosphorus burial rate was also compared with previous phosphorus budget measures to examine the lake's capacity for phosphorus retention.

4.3 Methods

4.3.1 Study site

Esthwaite Water (54°21'N, 3°0'W) is a lake of glacial origin, forming a part of the larger Windermere catchment within the southeastern area of the English Lake District. Based on a new bathymetry of the lake (see below), it has a surface area of 0.96 km^2, a total volume of 6.7×10^6 m^3, and an average depth of 6.9 m (Fig. 4.1 and Table 4.1). Esthwaite Water contains three basins, which are separated by sills. The northernmost basin is the largest (0.54 km^2) and deepest (maximum depth 16 m) and was where the sampling for this study took place.

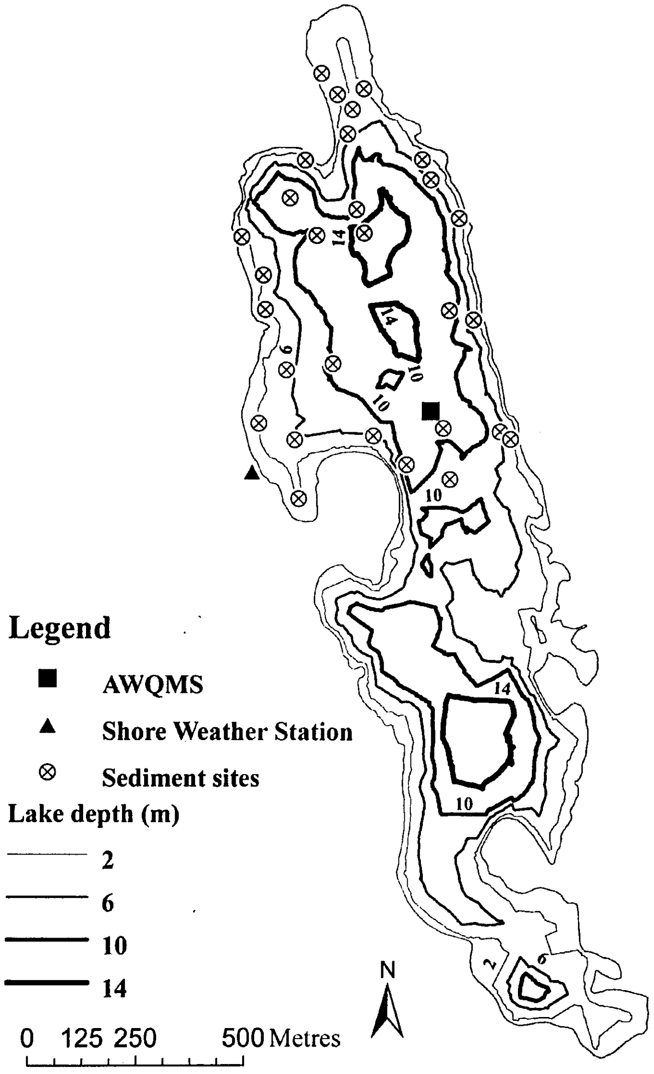

Figure 4.1 Bathymetry of Esthwaite Water, showing position of sediment sampling sites, shore weather station and AWQMS buoy.

Table 4.1 Summary of the bathymetry of Esthwaite Water

Depth (m)	Area enclosed by contours (m^2)	% Total area	Layer (m)	Volume (m^3)	% Volume of layer	% Cumulative volume
0	956565	100	0-1	889513.4	13.30	13.30
1	849502	88.81	1 - 2	810936.5	12.12	25.42
2	773103	80.82	2 - 3	734959.3	10.99	36.41
3	699232	73.10	3 - 4	670431.2	10.02	46.44
4	642365	67.15	4 - 5	612987.7	9.16	55.60
5	584819	61.14	5 - 6	558876.7	8.36	63.96
6	533841	55.81	6 - 7	509740.2	7.62	71.58
7	485632	50.77	7 - 8	458245.4	6.85	78.43
8	430580	45.01	8 - 9	402397.2	6.02	84.44
9	373818	39.08	9 - 10	341333.5	5.10	89.55
10	306442	32.04	10 - 11	270203.2	4.04	93.59
11	233792	24.44	11 - 12	195089.4	2.92	96.50
12	158770	16.60	12 - 13	128789.7	1.93	98.43
13	103929	10.86	13 - 14	77289.41	1.16	99.58
14	51139	5.35	14 - 15	24529.54	0.37	99.95
15	8337	0.87	15 - 16	3234.118	0.05	100.00
16	0	0				

The biological, chemical and physical characteristics of the lake have been previously described (Mortimer 1941, Sutcliffe et al. 1982, Talling and Heaney 1988, George et al. 1990, George 2000). High-resolution meteorological data were provided by the UK Centre for Ecology and Hydrology (CEH) Automatic Water Quality Monitoring Station (AWQMS) in the north basin of the lake and a meteorological station on the shore (see Rouen et al. 2001, Madgwick et al. 2006 for more details), from which data have been collected with hourly resolution from 2005.

4.3.2 Field and laboratory methods

A bathymetric survey of the lake was undertaken on 21 May 2009 using a BioSonics DT-X echo sounder (Biosonics Inc, Seattle, USA) with a 200 kHz split-beam vertical transducer of beam angle 6.5°. The data threshold was set at –70 dB, the pulse rate at

5 pulses s^{-1}, pulse width at 0.4 m and data recorded at a range of 2 m from the transducer. Navigation along 39 transects was undertaken with a Garmin GPSMAP 60CSx GPS (Global Positioning System) (www.garmin.com) with an accuracy to less than 10 m, while a JRC Model DGPS212 GPS (www.jrc.co.jp) with an accuracy to less than 5 m inputted location data directly to the hydroacoustic system to provide spatial position for the data. The detection of the depth of the lake bottom was undertaken using Sonar5-Pro Version 5.9.6 software (Lindem Data Acquisition, Oslo, Norway, www.fys.uio.no/~hbalk/sonar4_5). The lake bottom data were imported into ESRI ArcMap (www.esri.com) where Triangulated Irregular Network (TIN) and raster surfaces were created with the data and contours calculated from the raster surface. This survey represents a much higher resolution and more accurate bathymetry than a previous study by Ramsbottom (1976) undertaken in the 1930s, with an increase of two and half times in the number of transects surveyed.

Sediment cores were collected at 29 sites during the spring and summer of 2009 using a Jenkin corer (Jenkin and Mortimer 1938) for deep sites and manually pushing a core tube into the sediment at very shallow sites. Sites were selected both to cover a wide range of water depths and to provide good spatial coverage of the basin. To avoid discrepancies in accumulation caused by the presence of the stratification, the summer samples were taken only from depths within the epilimnion. The top 2 cm of sediment from the cores were extruded, sliced and then frozen on the day of sampling for later analysis. Water depths were recorded with a Plastimo Echotest II (Southampton, Hampshire, UK) echo sounder in deeper water and a weighted graduated line in shallow water.

Water content for the samples was determined by pre- and post-weighing of well mixed sub-samples dried at 60°C for 24 hours. Organic content was determined as loss-on-ignition (LOI) by ashing at 550°C for three hours. Total phosphorus concentration was determined using the molybdenum blue reaction on a SEAL AQ2 auto analyser (Seal Analytical Ltd., Fareham, Hampshire, UK) following a two hour hot sulphuric acid-hydrogen peroxide digestion (Rowland and Grimshaw 1985). Particle size analysis was carried out on a Malvern Mastersizer 2000 (Malvern Instruments Limited, Malvern, Worcestershire, UK) after heating for three hours in hydrogen peroxide to remove organic material and passing through a 2 mm sieve. Diatom slides were prepared following Battarbee (1986). Counts up to 200 frustules were made on each slide to species or genus level to provide a measure of taxon richness as a simple indicator of the dispersal of benthic (littoral) taxa across the lake.

Wind speed was measured at 2.9 m above the lake's surface with a Vector A100L2-WR cup anemometer with optical rotation sensing (Vector Instruments, Rhyl, Wales) obtained as hourly averages from the AWQMS buoy in the north basin of the lake. As the buoy is a rotating platform, wind direction data were obtained as hourly averages from a Vector W200P-WR wind vane (Vector Instruments, Rhyl, Wales) measured at 4.9 m above the water surface at an unsheltered location on the shore of the north basin of the lake.

4.3.3 Data analysis and statistical methods

The influence of particle size and density on the distribution pattern of different sediment characteristics was examined for a representative range of sediment variables. Water content was taken to characterize typical whole sediment bulk density measures, organic content (as LOI) provided a measure of low-density sediment comprising a range of grain sizes and the distribution of total phosphorus and benthic diatom taxon richness were taken as independent measures of small particle sizes. Phosphorus is often associated with small particles (e.g. Pacini and Gächter 1999) reflecting their large surface area to volume for binding sites (Froelich 1988). In Esthwaite Water, approximately 83% of total phosphorus is labile, reductant-soluble and metal oxide-adsorbed phosphorus (Spears, unpublished data). In a study of Lake Võrtsjärv (Nõges and Kisand 1999), these forms of phosphorus were most associated with finer, soft sediments. Benthic diatoms, are also representative of small size fractions (<40 μm) (e.g. Kelly et al. 2005). They will grow actively only in the photic zone, which extends to ≈2.5 m depth in Esthwaite Water (Maberly et al. 2006). High diatom diversity in this shallow water is associated with the large number of habitat niches present (e.g. epipelic, epilithic, epipsammic and epiphytic) (Round et al. 1990). Occurrence of these benthic taxa in deeper water was therefore interpreted as a tracer of resuspension and transport of the diatom frustules.

Three focusing models and direct measurements of slope were tested to examine whether they can account for the heterogeneity in the surface sediment characteristics of the four variables defined above (water content, organic content, total phosphorus concentration and benthic diatom taxon richness). These are divided into lake bed gradient and wave-mixing models. In addition, the resuspension potential for wind-induced currents was assessed.

Lake bed gradient

Bed slope was calculated at each sampling site from the lake bathymetry using the Spatial Analyst slope analysis function in ESRI ArcMap. In addition, the mean basin slope α'_p (%) was calculated as (Blais and Kalff 1995):

$$\alpha'_p = (l_0/2 + l_1 + l_2 + _{\dots} + l_{n-1} + l_n/2)Z_{max}/10nA_L \,, \tag{1}$$

where l_0 is the length of the shoreline (km), l_i and n are the lengths (km) and number of the contour lines respectively, Z_{max} is the maximum lake depth (m) and A_L is the lake surface area (km^2). This was used to predict the percentage of the lake bed surface occupied by the accumulation area (*%ZA*) using:

$$\%ZA = 49.92(\pm 3.73) - 2.50(\pm 0.31)\alpha'_p \,, \tag{2}$$

from Blais & Kalff (1995). To estimate the average depth of the transition to the accumulation zone, *%ZA* was compared to the hypsometric curve of the lake calculated from the bathymetric data. The calculation of *%ZA* was also carried out using the bracketed standard error estimates in Equation (2) to give a predicted error for the transition estimate.

Wave mixing

Wind data from 2008 were used for all wave mixing and wind-induced current calculations; it was representative of a recent five-year period 2005 – 2009 (average and average maximum wind speeds 2.3 m s^{-1} and 13 m s^{-1}). Wave theory was used to predict wave-mixed-layer depth, Z_c (m), as a function of the maximum wind speed and effective fetch across a lake (Smith and Sinclair 1972). To calculate Z_c, an effective fetch, F_e (m), for each coring site and for sites forming a 100 m grid across the lake was calculated in ESRI ArcMap using the USGS Wind Fetch Model (Finlayson 2005, Rohweder et al. 2008). For a given wind direction, D, F_e represents the weighted average fetch measured along radials centred about D, to account for short-term variability in the wind field (Håkanson 1977). Each measured wind direction was binned into one of 16 classes (N, NNE, NE, ENE, E etc.) and F_e for each site was calculated for each class. Z_c was then calculated as a function of F_e based on Smith & Sinclair (1972) following Spears & Jones (2010):

$$Z_c = 0.0062 F_e^{0.56} W_8^{0.88}, \tag{3}$$

where W_8 is maximum wind speed for 2008 (m s^{-1}) at a height of 8m above the water surface. As wind speed data over Esthwaite Water is measured at a height of 2.9 m above the water surface, the height correction used by Spears & Jones (2010) was applied to the data:

$$W_8 = W_{2.9} \frac{\ln(8/z_0)}{\ln(2.9/z_0)}, \tag{4}$$

where a surface roughness length (z_0) of 3.2×10^{-5} m was used, based on the neutral value of the transfer coefficient (C_d) suggested by MacIntyre *et al.* (2002). The 100 m grid of sites were used to generate an interpolated raster surface of Z_c using inverse distance weighting within ArcMap.

In addition to the calculation of Z_c, the depth at which surface waves cease to resuspend bed sediments can be identified as the depth where there is a transition in the nature of bed sediment from coarse to fine particles: known as the mud energy boundary depth *EBD* (m) (Rowan et al. 1992). The predicted *EBD* was calculated as a function of the maximum fetch for each site F_m (km) following Rowan *et al.* (1992):

$$EBD = 3.076F_m^{0.549}. \tag{5}$$

EBD is valid for sites whose depths (h) satisfy the condition required for the application of deepwater wave theory (Rowan et al. 1992):

$$h > 1.660F_m^{0.5}\ . \tag{6}$$

Thus, *EBD* was calculated for 26 of the 29 sediment sites in this study, since the other three sites were too shallow for this condition to apply. The depths predicted by Z_c and *EBD* were used to delineate the depth of the transition from zones of sediment resuspension and transport to zones of accumulation.

Wind-induced currents

Indicative wind-induced current speeds were calculated from 2008 wind data, using the method of Smith (1979) where surface current speed U_s (m s^{-1}) is assumed to be 3% of the wind speed W (m s^{-1}) and current speed U_z (m s^{-1}) at depth z (m) is calculated as:

$$U_z = U_s\, e^{-kz}, \tag{7}$$

where $k = 6/W^{1.84}$ is a decay coefficient inversely related to wind speed in temperate latitudes.

This exponential decay in current speeds below the lake surface generates a gradient return current of mean velocity $\bar{U}_g$ to ensure the conservation of mass of the water body under isothermal conditions. $\bar{U}_g$ (m s^{-1}) is given by:

$$\bar{U}_g = M_d/Z, \tag{8}$$

where Z is the depth of the water column (m) and M_d is the quantity of water transported by the gradient current:

$$M_d = \frac{U_s}{k}\left(1 - e^{-k(D-b)}\right), \tag{9}$$

where $b = 0.033\,W^{1.63}$ is the thickness of the bottom boundary layer (m). The resultant current speed $U_L = U_z - \bar{U}_g$, represents an average speed at that depth, because channelling and boundaries have not been taken into account. The spatial influence of these effects will result in lower or higher speeds in different areas of the lake, for example, boundaries have been shown to increase return current speeds (Falconer et al. 1991).

Rather than generate a predicted depth for the transition to an accumulation area for the wind-induced current mechanism, the potential for current-induced resuspension was assessed through the comparison of Reynolds number $Re*$ calculated using particle size as the characteristic length scale, and the relative shear stress θ required to resuspend specific-sized particles, following Gloor *et al.* (1994). Estimates of U_L 1 m above the lake bed were calculated for the range of observed wind conditions from 2008. These theoretical current speeds allowed the calculation of the friction velocity at this location u* (m s^{-1}):

$$u^* = (C_{1m}\, U_L^2)^{1/2}\,, \tag{10}$$

assuming a bottom drag coefficient C_{1m} of 1.5 × 10^{-3} (Elliott 1984), which was then used to calculate Re^* as:

$$Re^* = u_* D_p / v, \tag{11}$$

where D_p is particle diameter (m) and v is kinematic viscosity at 5°C (1.5 × 10^{-6}) (m^2 s^{-1}). The relative shear stress θ was calculated as:

$$\theta = \frac{\rho u_*^2}{(\rho_p - \rho) g D_p}, \tag{12}$$

where ρ is the density of water (kg m^{-3}), ρ_p is the density of the suspended particles (kg m^{-3}) and g is acceleration due to gravity (9.8 m s^{-2}). Values of Re* and θ were calculated for different particle sizes and densities, these values were used to compare critical thresholds of resuspension based on the modified Shields diagram (Gloor et al. 1994). Current-induced resuspension was predicted to occur when the critical values of Re* and θ were exceeded.

Sediment burial rate

Sediment burial rate, *BR*, (g $m^{-2}yr^{-1}$) for carbon and total phosphorus were calculated using:

$$BR_i = AR_i * D_i * C_i, \tag{13}$$

where AR_i is the accumulation rate (m yr^{-1}) for each site *i* based on the ArcMap inverse distance-weighted interpolation of accumulation rates calculated by Hilton *et al.* (1986), D_i is the sediment dry bulk density (g m^{-3}) for each site calculated according to Rausch & Heinemann (1984) and C_i is the concentration of organic carbon or total phosphorus (g g^{-1}) . Organic carbon was estimated to be 50% of the weight LOI based on previous analyses of these sediments (Pennington 1974). Predictions of whole lake flux-to-bed rates (tonnes yr^{-1}) were calculated for each of the focusing models (mean basin slope α'_p , mud energy boundary depth *EBD*, wave mixed layer depth Z_c), a single burial rate value from the deepest site and a fully depth integrated measure (representing the true sediment heterogeneity in the lake) using the new bathymetric data. The depth integrated measure was calculated as the total sum of the mean *BR* at 1 m depth intervals multiplied by the area of the lake bed at each corresponding depth interval. For the focusing models with a predicted transition depth to the accumulation zone, the value of *BR* from the deepest site was applied to the lake area below the transition depth, thus assuming a constant burial rate across the accumulation zone. The single-site burial rate value was obtained by multiplying the rate by the whole lake area, following the approach taken in many burial rate studies. This enabled an assessment of the prediction error for the single site and focusing processes compared to the depth-integrated value. The whole lake flux-to-bed rate calculations and the α'_p model were then repeated using the original bathymetric data from Ramsbottom (1976) to assess the effect on the results of using high- and low-resolution bathymetric data. Linear and piecewise regression analysis were conducted in the R statistical package using the base and segmented packages (Ihaka and Gentleman 1996, Muggeo 2008).

4.4 Results

4.4.1 Surface sediment characteristics

Across the sampling sites, there were different degrees of variability in the surface sediment characteristics (Table 4.2). The highest variability (coefficient of variation) between all sites was for the sand particle size fraction, benthic diatom taxon richness and total phosphorus concentrations. Water and silt content were the least variable. The water depth distributions of the four sediment variables of particular interest were very different. The bulk measures of water content and organic content increased approximately linearly at shallower depths, but had a constant value in deeper water (Fig. 4.2). Piecewise linear regression of these plots showed that the correlation was maximised by a breakpoint between regression line segments at 5 - 6 m ($r^2 = 0.50$, $P<0.05$). The distributions of the benthic diatom taxon richness and total phosphorus (the variables associated with smaller particle size fractions) had clear linear relationships with water depth. The former has a significant, negative linear relationship with depth ($r^2 = 0.60$, $P<0.01$) throughout the whole water column (Fig. 4.3a), while the latter exhibited a similarly consistent significant positive linear relationship with depth ($r^2 = 0.82$, $P<0.01$) (Fig. 4.3b).

Table 4.2 Summary of the characteristics of the surface sediments of Esthwaite Water

	Mean	Standard deviation	Range	Coefficient of variation %
Clay (<2 µm) (%)	1.8	0.4	1.2 - 2.7	19.4
Silt (2 - 63 µm) (%)	82.9	10.4	56.6 - 93.7	12.6
Sand (63 - 1000 µm) (%)	15.3	10.6	4.3 – 42.0	69.5
Water content (%)	86.5	4.0	75.4 - 92.1	4.6
Organic content (%)	25.5	6.0	9.9 - 34.0	23.5
Total Phosphorus (mg kg^{-1})	3139.1	1483.6	476 - 6870	47.3
Diatom plankton (%)	61.4	21.8	8.7 - 88.5	35.5
Diatom benthic (%)	38.6	21.8	11.5 - 91.3	56.5

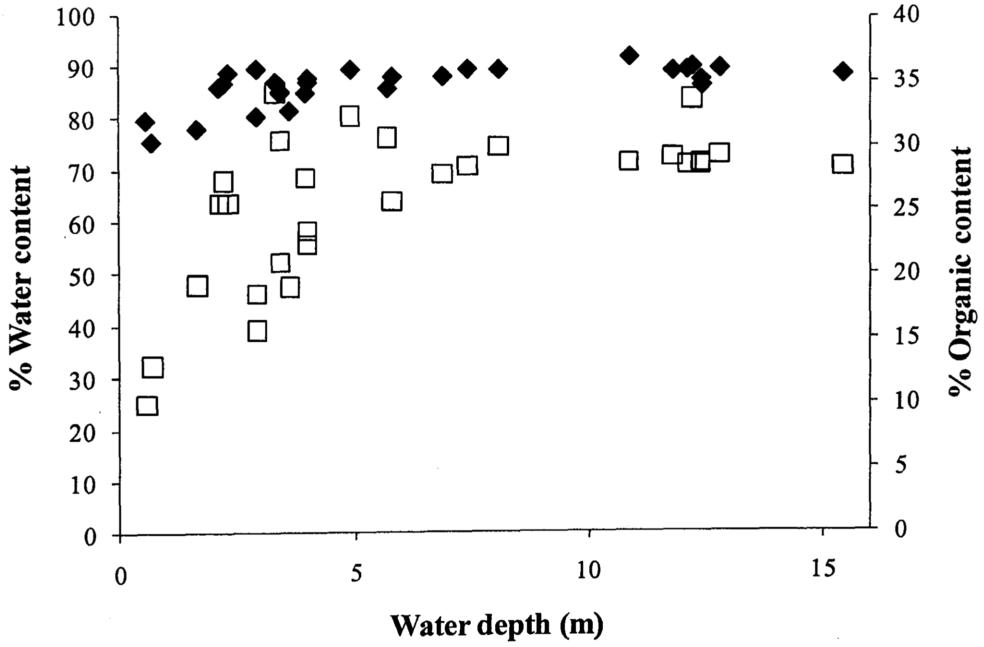

Figure 4.2 Distribution with water depth (m) of % water content (diamonds) and % organic content (squares) in surface sediments of Esthwaite Water.

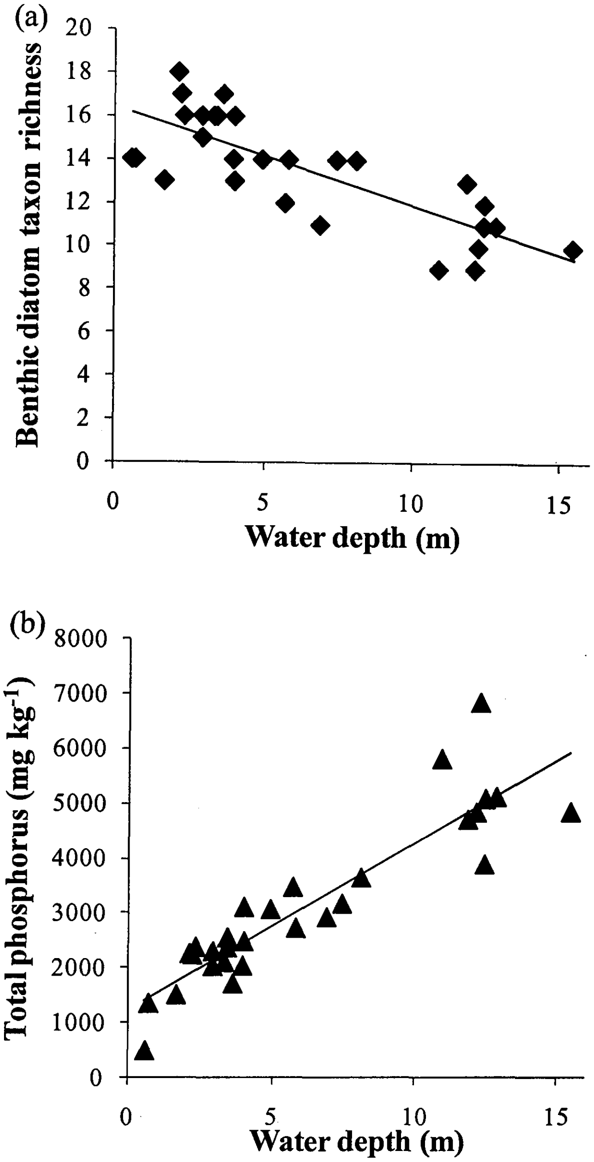

Figure 4.3 Distribution with water depth (m) of small particles in surface sediments of Esthwaite Water: **(a)** benthic diatom taxon richness (number of taxa) and **(b)** total phosphorus (mg kg^{-1}).

4.4.2 Focusing processes

Lake bed gradient

Using the new bathymetry, the mean basin slope for the lake was calculated using Equation (1) as 2.33% which, using Equation (2), gives an accumulation zone of 44% (range of 41% to 47% based on the standard error from the equation) of the lake area. This implies that the transition to the accumulation zone occurs at 8.0 m (±0.5 m) depth, based on the high-resolution bathymetric data. The corresponding results using the old bathymetry were a mean basin slope of 3.2%, an accumulation zone of 42% and a transition depth of 8.0 m (±0.5 m). Site-specific slope measurements for the new bathymetry ranged from 1° - 13° (0° - 10° for the old bathymetry). No significant correlations were found between site-specific slope and any of the sediment variables in Table 4.2 ($P>0.05$), either for specific depth ranges or using the whole dataset, indicating that local slope was not important in determining sediment characteristics in any section of the lake.

Wave mixing

The average and maximum wind speeds of 2.4 m s^{-1} and 13.4 m s^{-1} in 2008, prevailingly from the south (Fig. 4.4) are typical of wind conditions measured over the lake. These winds resulted in a clear gradient in the wave mixed-layer depth, Z_c, across the lake from the interpolated grid data (Fig. 4.5a). Z_c was greatest along the northeastern shorelines and lower in more wind-sheltered bay areas. The average and maximum Z_c for 2008 were 1.6 m and 3.7 m respectively. This map of Z_c (Fig. 4.5a) was compared with the lake bathymetry to identify the area where wave-induced resuspension was likely to occur (Fig. 4.5b), demonstrating that the effect of wave-induced resuspension of bed sediments was predicted to be restricted to a narrow nearshore zone. The *EBD* values calculated at the 26 sites applicable to deepwater wave theory varied between 2.4 and 3.5 m, averaging 3.1 m.

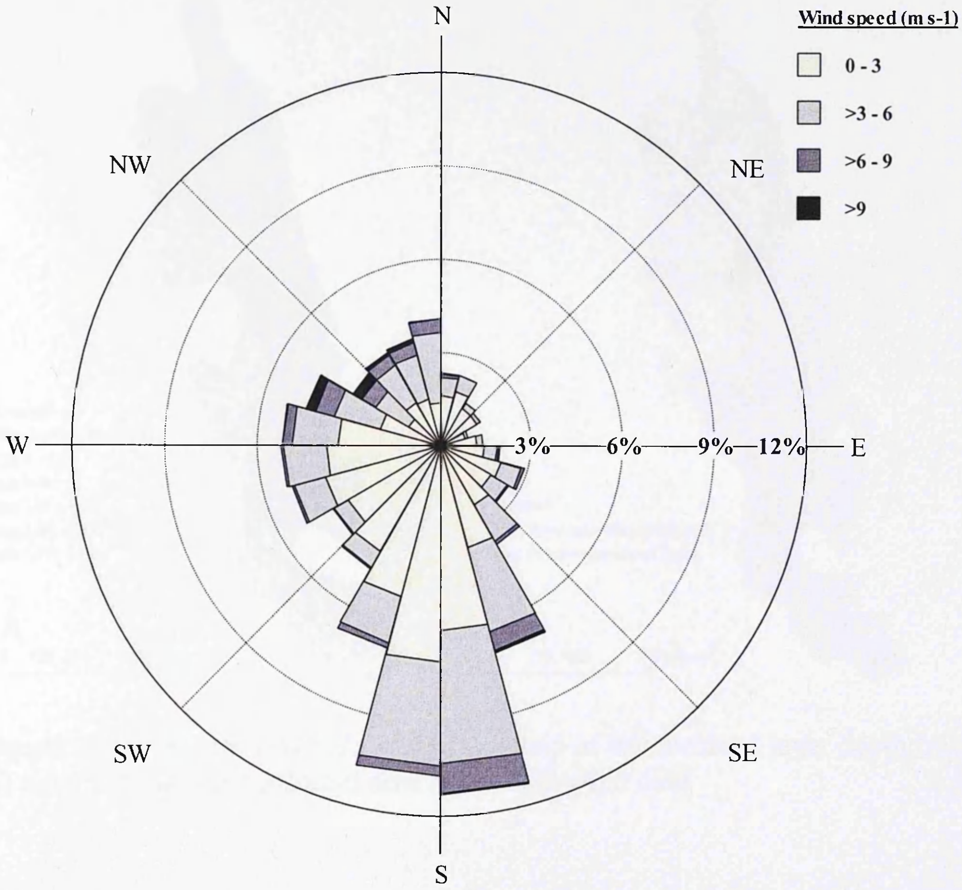

Figure 4.4 Wind speed (m s^{-1}) and direction (15° segments) over Esthwaite Water for 2008.

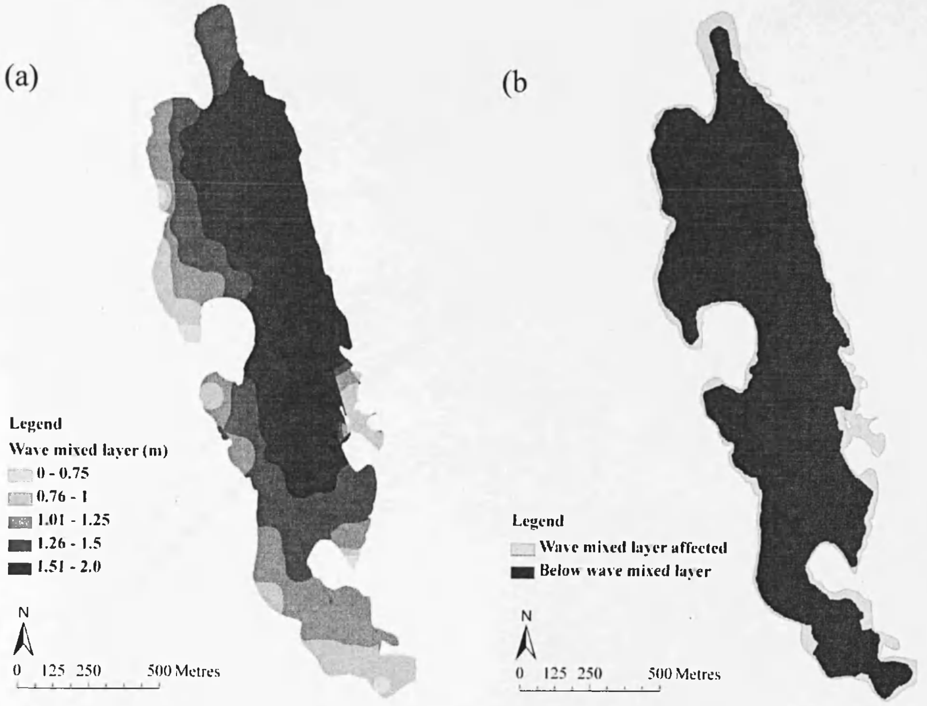

Figure 4.5 Esthwaite Water showing **(a)** a map of wave-mixed layer depth (m) and **(b)** a map of the wave-affected area from 2008 wind data.

Wind-induced currents

Using the method of Smith (1979), a theoretical profile of wind-induced current speed with water depth was generated for different wind speeds (Fig. 4.6). Theoretical wind-induced current speeds calculated at 1m above the lake bed in the deepest part of the lake were up to 0.07 m s^{-1}, with wind speeds of 7 m s^{-1} capable of generating currents speeds at this depth of 0.05 m s^{-1}. Using Equation (10) these currents represent u* values of 2.7×10^{-3} m s^{-1} and 1.9×10^{-3} m s^{-1} respectively. According to the revised Shields diagram of Gloor *et al.* (1994), resuspension of 20-μm diameter organic particles is possible at current speeds of 0.05 m s^{-1} ($\theta = 0.38$, Re* = 0.026), while 0.07 m s^{-1} speeds are sufficient to resuspend quartz grains of 2 μm diameter ($\theta = 0.23$, Re* = 3.6×10^{-3}). This suggests resuspension driven by these currents is sufficient to resuspend these small particles at all depths in the lake, especially as most particles have lower densities than quartz.

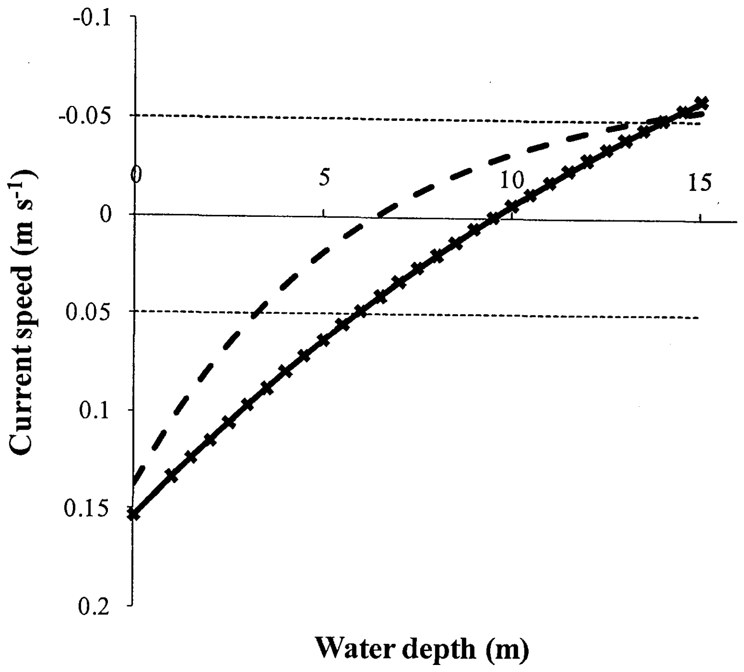

Figure 4.6 Theoretical wind-induced current profiles for wind speeds of 7 m s^{-1} (dashed line) and 13.4 m s^{-1} (solid line with crosses). Dotted horizontal lines denote critical resuspension threshold for organic particles (density = 1050 kg m^{-3}) of 20μm diameter.

The different focusing processes of slope failure, wave mixing and wind-induced current-shear produced a wide range of estimates for the depth of transition to the accumulation zone. Wave mixing predicted the shallowest transition depths (Z_c = 1.6 m and *EBD* = 3.1 m). No relationship was found between local bed slope and sediment characteristics, but using Blais & Kalff's (1995) empirical relationship to predict transition depth from mean basin slope gave a value for the transition depth of 8.0 m (±0.5 m). Wind-induced current shear was predicted to be able to resuspend sediment in the deepest part of the lake, and thus predicts no transition depth and no accumulation zone, at least for small particles. These predictions can be compared to the depth profiles of sediment variables in Figs 4.2 and 4.3. Although benthic diatom taxon richness and total phosphorus concentration show no break in their distribution that might be identified as a transition point (e.g. Blais and Kalff 1995, Anderson et al. 2008), the water content and organic content distributions suggest a transition at 5 - 6 m.

4.4.3 Burial rate estimates

Estimates of the net yearly flux of sediment to the bed (Table 4.3) were calculated for total phosphorus and organic carbon using the methods described above. The range of values calculated for total organic carbon flux to the bed was 41- 62 tonnes yr^{-1}. The different focusing models (wave mixing: *EBD*, Z_c; lake bed gradient: α'_p) and the single site-based calculation lead to over-estimates of between 27% and 54% compared to the depth-integrated true value. Calculated values for the total phosphorus flux using the single-site and focusing model methods were 40 - 110% larger than the value calculated using the depth integration method. This larger variation reflected the linear depth distribution pattern of the total phosphorus compared with the piecewise linear pattern for organic carbon. The latter pattern resulted in a larger area of the lake with similar organic carbon concentrations, reducing the difference in the flux rate estimates from the single-site and focusing models from the depth-integrated value. The difference in total fluxes resulting from the use of different bathymetries (i.e. that of Ramsbottom (1976) and the new one described above) were much smaller than the difference in values calculated using different focusing models: 5 - 11% for organic carbon and 3 - 11% for total phosphorus. Thus the effect of the improved resolution in the bathymetry was secondary to that of the choice of focusing model and transition depth to the accumulation zone.

Table 4.3 Estimates of burial rates and fluxes to the sediments of Esthwaite Water using different accumulation area predictions

	Organic Carbon		Total Phosphorus	
Method	Flux tonnes yr^{-1}	Burial rate g m^{-2} yr^{-1}	Flux tonnes yr^{-1}	Burial rate g m^{-2} yr^{-1}
Depth integrated	40.5	44.3	1.0	1.2
α'_p	51.3	54.8	1.4	1.6
EBD	57.2	61.9	1.8	2.0
Z_c	58.6	63.0	2.0	2.1
One site	62.4	65.3	2.1	2.2

4.5 Discussion

4.5.1 Sediment characteristics

Both organic content (measured as LOI) and total phosphorus concentrations in Esthwaite Water (Table 4.2) were comparable to those found in other lakes such as Bassenthwaite Lake, Wastwater (15% and 25% organic content as LOI, respectively) (Bennion et al. 2000), Lake Rotoiti, New Zealand (3460 mg P kg^{-1}) (Trolle et al. 2008) and Loch Leven, Scotland (2288 mg P kg^{-1}) (Spears et al. 2006). Burial rates of organic carbon (Table 4.3) were also similar in magnitude to small (surface area <100 km^2), natural meso-eutrophic lakes (11 - 198 g C m^{-2} a^{-1}) (Mulholland and Elwood 1982), but lower than man-made impoundments in the USA (148 - 17,000 g C m^{-2} a^{-1}) (Downing et al. 2008).Water content, which is routinely assumed to be inversely proportional to sediment particle size, ranged between 75 - 92%. This would imply that the whole lake was an accumulation zone, as previous work on larger lakes suggests that the transition to an accumulation zone occurs at a depth in the lake where sediments exceed 50% water content (Håkanson and Jansson 1983). However, the results from this study suggested that this was not the case.

The four different sediment variables examined (water content, organic content, benthic diatom taxon richness and total phosphorus concentration), each representing different characteristic densities and particle sizes, showed a different relationship with depth (Figs 4.2 and 4.3). The linear relationship with depth seen in the total phosphorus concentrations and benthic diatom taxon richness implied that they were most closely associated with resuspension all the way to the deepest waters. Hence, classifying lake sediments as accumulation areas on the basis of single or bulk variables such as water content, which do not take account of these specific particle sizes, leads to an oversimplification of the heterogeneity within the sediments.

4.5.2 Sediment focusing predictions

Slope-based models, both site-specific and across the lake basin, did not adequately explain sedimentation patterns in this lake, even after significant improvements to bathymetric data. The transition depth predicted by the mean basin slope calculations (approximately 8m) was closer to the depth of the transition in the piecewise linear fit of the plots of the bulk variables of water content and organic matter (5 - 6 m), but overestimated it by around 30%. These calculations did not predict the distribution of either sedimentary total phosphorus concentration or benthic diatom taxon richness very well, which suggested that the processes assumed to be acting in its calculation were not those which govern the distribution of these variables. Moreover, the site-specific measure of slope was a poor predictor of all of the sediment variables in this study, as was the case for Blais & Kalff (1995).

Although wave action is the dominant focusing process in a number of large or shallow lakes such as Lough Neagh (surface area = 383 km^2) (Douglas and Rippey 2000), Lake Vänern (5655 km^2) (Håkanson 1977) and a typical North American prairie lake (1.04 km^2, mean depth = 1.3 m) (Carper and Bachmann 1984), it is clear that neither the Z_c or *EBD* models was effective at describing the sediment distribution in Esthwaite Water (Figs 4.2 and 4.3). This suggested that lake morphometry, in terms of both water depth and wind sheltering, was important in determining the influence of wave mixing. In lakes such as Esthwaite Water, where Z_c values were low compared to mean water depth, wave-induced resuspension occurred only in a small proportion of the lake. It is therefore clear that neither slope-based models nor wave mixing could account for the sedimentation pattern in Esthwaite Water.

While currents have not been directly measured in Esthwaite Water, theoretical calculations suggested wind speeds during episodic events were sufficient to resuspend small particles throughout the depth of the lake (Fig. 4.6). Current speeds greater than the minimum resuspension threshold values identified here (0.05 m s^{-1}) have been measured close to the lake bottom in a number of lakes, particularly during storms. Aota (2006) recorded current speeds up to 0.3 m s^{-1} and frequently above 0.06 m s^{-1} at 1.8 m above the bottom in 90 m water depth in Lake Biwa during storms (wind speeds >10 m s^{-1}), and currents >0.1 m s^{-1} were measured 1.8 m above the lake bed in 11 m of water in the Salton Sea in response to wind speeds of 10 m s^{-1} (Chung et al. 2009). Resuspension due solely to wind-induced currents occurs in larger lakes below the wave base, during isothermal conditions (Lemmin and Imboden 1987, Hawley et al. 1996, Hawley and Lee 1999). These currents are important for the transport of material from nearshore areas dominated by resuspension due to wave action to the deeper parts of the lake (Hawley and Lee 1999). Current speeds of 0.05 to 0.07 m s^{-1} have also been found to resuspend material in Lake Alpnach, a smaller lake (surface area 4.76 km^2) (Gloor et al. 1994).

The measurement and modelling of wind-induced currents in lakes is complicated by their interaction with the lake morphometry. Boundaries enhance return current speed (Falconer et al. 1991), as can the alignment of a lakes' major axis relative to the wind direction (Bowyer 2001). The presence of islands or an uneven lake bed can also deflect flow (Bowyer 2001). The theoretical calculations presented here cannot account for these effects but did show that current speeds were sufficient to resuspend small particles and therefore represent a potential mechanism for the movement of sediment in the lake. This mechanism for sediment focusing has been overlooked in many previous studies: this study suggests it is important in small lakes like Esthwaite Water. Current speeds in small lakes are likely to be lower than those found in large lakes, but the distribution of total phosphorus concentrations and benthic diatom taxon richness in Esthwaite Water suggested that current-driven resuspension and transport to deeper parts of the lake bed occurred for smaller particles, and thus the sediment variables associated with those particles.

Bioturbation of sediment by invertebrates and fish has resulted in resuspension or increased mobilisation of sediments and the release of nutrients in some shallow lakes (e.g. Moss et al. 2002, Vanni 2002, Jackson et al. 2010). The daily migration of burrowing benthic invertebrates such as *Chaoborus* has been observed to disturb the sediment surface around the burrow, causing sediment mobilisation (Gosselin and Hare 2003) and increasing the propensity of the sediment to be resuspended. There are no contemporary records on the spatial abundance of *Chaoborus* in Esthwaite Water and it is therefore difficult to assess this effect. However, data from a single site suggests that abundance is relatively low compared to other lakes (Reynoldson 1990, Gosselin and Hare 2003) and very few benthic invertebrates were observed in the sediment samples for this study. Benthivorous fish, particularly the common carp (*Cyprinus carpio*) and common bream (*Abramis brama*) increase turbidity at high stocking densities (Carvalho and Moss 1995, Jackson et al. 2010). Esthwaite Water is not a shallow lake and has a low benthivorous fish population, with no record of carp or bream (I.Winfield, pers comm.). It is therefore unlikely that bioturbation played a significant role in sediment resuspension in this lake. Although localised sediment mobilisation effects cannot be excluded, they are likely to be secondary to physical resuspension.

4.5.3 Burial rate calculations

The large overestimation in whole-lake fluxes to the sediments arising from calculations based on single sites (Table 4.3) was also found in a study from Kassjön, where overestimates were between 25% and 85% for different variables (Rippey et al. 2008). In our study, these overestimates, due to assumptions about the distribution of sediment variables with depth, were much larger than the errors from using a low-resolution bathymetry. As many carbon burial rate studies are explicitly sampled at the deepest point in the lake or areas where sediment accumulation is most rapid (e.g. Downing et al. 2008, Anderson et al. 2009, Finlay et al. 2010), these values should therefore be regarded as maximum burial rates and not necessarily representative of the whole lake. This qualification of organic carbon burial is important for comparing between lakes and especially when assessing the overall importance of lakes in global carbon burial (e.g. Buffam et al. 2011).

The total annual phosphorus efflux from Esthwaite Water estimated from four years of routine monitoring data amounted to ~1 tonne yr^{-1}, whilst Hall *et al.* (2000) estimated an annual phosphorus influx of ~2 tonnes yr^{-1}.The importance of accurate burial rate estimates was therefore underlined by the depth-integrated method value (~1 tonne yr^{-1}: Table 4.3) which balanced the phosphorus budget of the lake. All other calculations would have left a large discrepancy in the budget and consequent uncertainty in appropriate management strategies. That approximately half of the phosphorus entering the lake was retained in the sediments is likely to affect the lake recovery from eutrophication because of the potential for prolonged internal loading (Jeppesen et al. 2005).

The findings of this study demonstrated that different sediment variables have different distributions with water depth, and implied that this can be explained by consideration of the particle size fraction with which each variable is most closely associated. Thus, these distributions cannot be explained by measures of single sediment variables. Moreover, previously developed focusing models for wave mixing and slope processes have been found not to be relevant to Esthwaite Water and, by extension, are hypothesised to be similarly irrelevant to other small lakes. We did however find evidence for the resuspension and focusing of small particles, which was inferred to relate to bed-shearing of wind-induced currents. This has not been widely considered as a focusing mechanism in previous studies, particularly in small lakes. Our comparison of flux rate predictions demonstrated that those derived from the different focusing models or a measurement at a single, deep site, suggested that whole lake fluxes to the bed for total phosphorus are up to twice that of a depth-integrated value. Therefore, the calculation of fluxes of materials such as total phosphorus or organic carbon should routinely take into account the specific different depth distribution of these variables.

Chapter 5 Transition zones in small lakes: the importance of dilution and biological uptake on lake-wide heterogeneity

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5.1 Abstract

Stream inflows are frequently the dominant route for nutrients from catchments to lakes. Studies on large, deep reservoirs and lakes have shown the importance of the fate of inflow plumes for nutrient accessibility to phytoplankton. However, few studies have considered shallow water transition zones between streams and lakes, often a feature of small lakes. This study examined the spatial and temporal dynamics of phosphorus in a shallow stream-lake transition in a small lake to improve our understanding of how phosphorus reaches the pelagic zone. Despite the high discharge levels, and the importance of dilution in explaining observed spatial gradients in soluble reactive phosphorus (SRP), total phosphorus (TP) and chlorophyll *a*, we found evidence for significant biological uptake of SRP in the inflow embayment during the growing season. This may represent an additional mechanism for the dispersal of phosphorus from the embayment into the lake. The length scale for the transition zone was short (~150 m) which indicated that the direct influence of the inflow on the wider lake was small. However, SRP measurements taken only from the pelagic site underestimated mean lake-wide concentrations when including transition zones by up to 18% during the growing season.

5.2 Introduction

The importance of stream inflows as conduits for catchment material to lakes is well established. Catchment-derived nutrients often represent a significant fraction of those required to support the total productivity of lake, and anthropogenic inputs can greatly enhance this productivity (e.g. Likens 1972). Previously, much attention has focused on either the catchment sources of nutrients (e.g. Heathwaite et al. 2003, McDowell et al. 2004, Haygarth et al. 2005, Wood et al. 2005) or the response of the biota, particularly the phytoplankton, to the nutrients in the lake water (e.g. Likens 1972, Reynolds and Walsby 1975, Schindler 2006, Conley et al. 2009). However, little research has focused on nutrient dynamics within the interface between the riverine (catchment) and lacustrine environments.

Chemical and biological gradients are often associated with this inflow interface in lakes. Transition zones are defined as regions where hydrological conditions transform from river-dominated flow to lake mixing processes (Thornton 1990). Mixing regimes in the transition zone have important implications for lake nutrient dynamics and budgets. The assumption of instantaneous mixing made by most phosphorus budget models is an oversimplification of within-lake processes and the horizontal and vertical heterogeneity found in lake mixing (e.g. MacIntyre and Melack 1995, Imberger 1998, Wüest and Lorke 2003). In addition, the form and bioavailability of nutrients such as phosphorus within the inflowing water will affect the impact they have on the lake (Reynolds and Davies 2001).

Hydrological processes in the transition zone are well understood for large, deep river-lake systems where pronounced density differences between inflow and lake water combined with significant water depth can result in vertically-structured over-, under-, or interflows of the river water (e.g. Carmack et al. 1979, Fischer et al. 1979, Pickrill and Irwin 1982, Fischer and Smith 1983, Stevens et al. 1995, Vidal 2006).

Entrance mixing prior to this flow separation and initial dilution due to channel expansion at the river-lake interface is also associated with entrainment of water in the transition zone (Spigel et al. 2005) but has received little attention in the literature, where most studies have focused on mixing at the plunge point, the area where denser influent water sinks to form an under- or interflow (Rueda et al. 2007). However, this initial dilution and entrainment was found to be a particularly important mixing process in the shallow water of some artificial cooling ponds, where flow separation is not observed and water columns remain partially or fully mixed (Jirka and Watanabe 1980). Understanding the importance of dilution in the transition zones of natural systems is lacking, particularly where water is shallow and vertical flow structuring does not occur.

In addition to hydrological dispersion of nutrients, other chemical and biological processes have been found to affect nutrient concentrations across mixing or transition zones. Sediment uptake of phosphorus has been found to be an important component of phosphate removal from inflowing water (Twinch 1984). Epiphytic algae have been identified as important moderators of phosphorus concentrations in lake and river water (McColl 1974, Björk-Ramberg 1985, Vandenberg et al. 2005, Aldridge et al. 2010) and high bacterial abundances have been related to high nutrient uptake rates in close proximity to inflows (Rigler 1956, Moll and Brahce 1986, Kapustina 1996). Areas of enhanced phytoplankton productivity have also been found around inflows or inflow embayments where high concentrations of inflowing nutrients combine with relatively shallow and warm waters (Auer and Bub 2004, Izydorczyk et al. 2008). Inflows and the area surrounding them can then be a source of phytoplankton for the wider lake (Pickrill and Irwin 1982, Izydorczyk et al. 2008) acting as an alternative nutrient dispersal route moderated by the differing levels of phytoplankton motility and internal cycling within the biota (Reynolds 1984b, Reynolds et al. 1987, Carpenter et al. 1992, Ejsmont-Karabin et al. 1993, Schindler and Scheuerell 2002). Spatial patchiness in phytoplankton concentrations has also been linked to inflow intrusions forming discrete layers of nutrient rich waters (MacIntyre et al. 2006) or nutrient release from isolated inflowing water by enhanced mixing at the plunge point (Vidal 2006). At large scales, along river-lake profiles, an increase in phytoplankton biomass occurs as hydrological conditions change from river-dominated to the lake-transition zone, where algal growth conditions are closer to the optimal (Kimmel et al. 1990). The algae along this gradient are increasingly able to utilise the high inflowing nutrient concentrations under an improving light climate and lengthening residence time, allowing for rapid cell division. It is unclear how these gradients, which are reported for larger lake systems, are likely to influence phosphorus uptake across the small transition zones of small lakes or how important they may be relative to the physical dilution processes.

The time- and length-scales over which phosphorus dilution or uptake by the biota occurs has been extensively studied along river reaches. Biotic uptake rates have been found to be highest in nutrient poor or unmodified streams and lower where streams have high nutrient concentrations or are degraded or modified (McColl 1974, Aldridge et al. 2010). Uptake rates can be rapid but are highly variable depending on previous flow conditions and nutrient loadings (McColl 1974). Seasonality is also important in terms of uptake rate (both biotic and abiotic) (Aldridge et al. 2010) which in turn affects the length-scale over which uptake occurs (Vandenberg et al. 2005, Lohman and Jones 2010). Few studies have attempted to quantify the time- or length-scales for phosphorus dilution or the importance of uptake across a shallow river-lake transition zone.

The size of transition zones is clearly scale dependant. At large scales, coastal regions of freshwater influence can extend many kilometres into oceans (e.g. Le Pape et al. 2003, Liu et al. 2009, Lihan et al. 2010) and in large lakes and reservoirs, inflows may have an important role in circulation patterns or potentially influence large regions of the water body (e.g. Carmack et al. 1979, Botelho and Imberger 2007, Laborde et al. 2010). Transition zones in small lakes with small inflows are likely to exert less influence over the lake, however the extent of this zone is still of interest when considering pathways of nutrient dispersal and the horizontal heterogeneity of the lake.

Much of our knowledge of transition zones is dominated by studies on large, deep lakes, with little attention paid to shallow water transitions where flow separation does not occur, which are more common in smaller lake systems, which represent a large proportion of the global total number of standing waters (Downing et al. 2006). Therefore, this study explicitly focuses on an inflow transition across a shallow embayment in a small lake. We examine spatial and temporal phosphorus dynamics within the river-lake transition zone of a small temperate lake in order to determine the extent of its influence and the nature of phosphorus inflow to the lake. Based on understanding from the literature presented above, we focussed our study on testing the hypotheses that:

i. hydrological dilution effects would be the dominant mechanism responsible for the dispersal of phosphorus in the lake;

ii. there would be a discernible effect of biological (phytoplankton) uptake on phosphorus concentrations in the transition zone;

iii. the transition zone would be small but still exert a significant influence on the horizontal spatial heterogeneity of the lake, and therefore estimates of mean lake-wide nutrient concentrations

5.3 Materials and Methods

5.3.1 Study site

Esthwaite Water (54°21'N, 3°0'W) is a small lake within the southeastern area of the English Lake District in the United Kingdom. It has a surface area of 0.96 km^2, total volume of 6.7×10^6 m^3 and an average depth of 6.9 m (Mackay et al. 2011a). The catchment area is 17 km^2 with an underlying sedimentary geology of Silurian shales, mudstones and sandstones. A significant portion of the phosphorus input to the lake is of catchment origin (Hall et al. 2000). The main land use is pastoral agriculture, with forest on steeper slopes; settlements are small and the relatively low resident population is substantially enlarged by seasonal tourism. Esthwaite Water has six main tributaries draining the catchment, the largest of these, Black Beck, accounts for around half of the overall discharge into the lake (Davison et al. 1980) and drains ~80% of the catchment area. Black Beck flows into an embayment with a surface area of 0.036 km^2 and an average depth of 1.5 m, in the northernmost basin of the lake, and this is where the sampling for this study took place (Fig. 5.1).

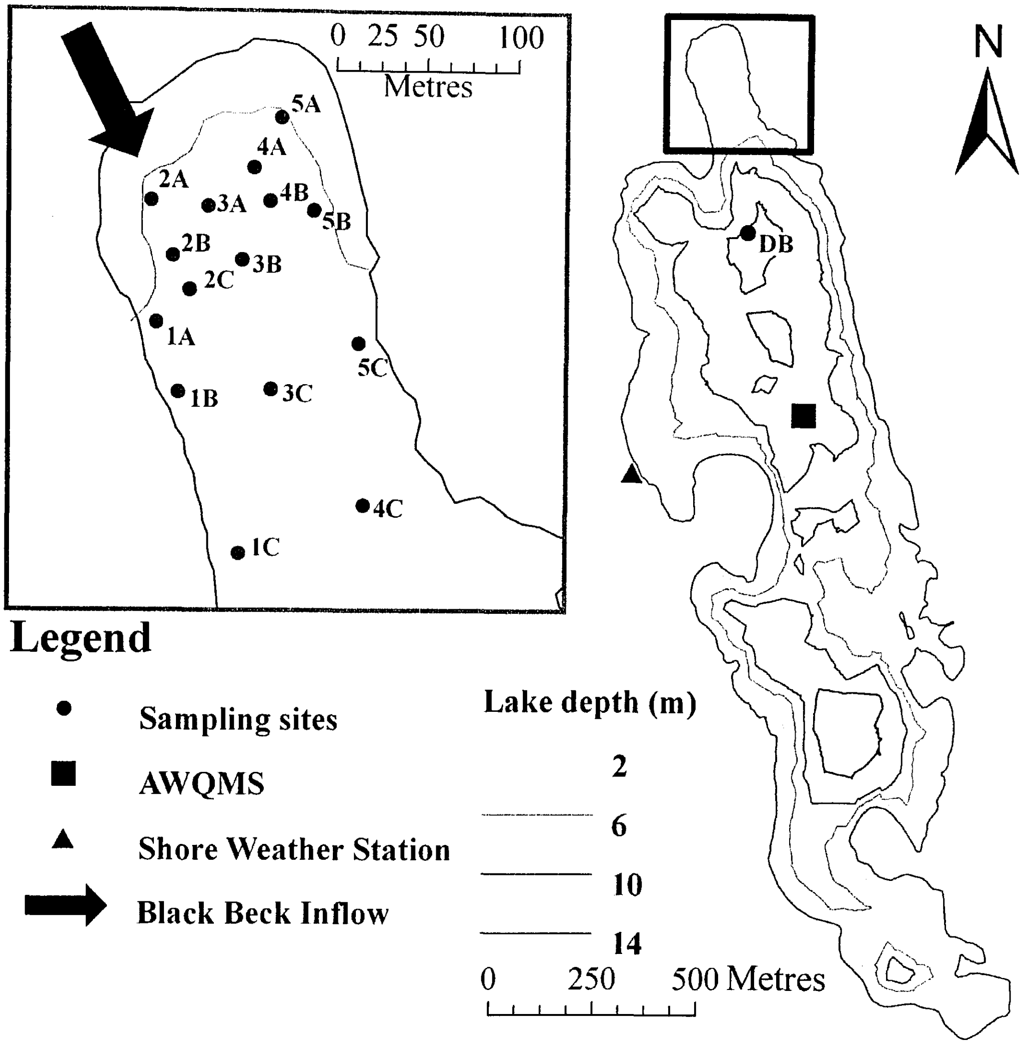

Figure 5.1 Location of Black Beck inflow to Esthwaite Water and sampling sites.

5.3.2 Field and laboratory methods

Sampling took place over four consecutive days on four occasions: May, July, September and November 2009. Surface water samples were taken from a grid of 15 sites covering the spatial extent of the shallow embayment close to the inflow (Fig. 5.1) and also above the deepest point of the lake at 0.5 m depth (referred to as the "pelagic site" hereinafter), which has been shown to be representative of the surface pelagic zone of the lake (Miller 2008). On all four days, samples were taken for total phosphorus (TP) and chlorophyll *a* analysis (taken to represent a measure of phytoplankton biomass). In the case of the latter, during the July, September and

November studies a Chelsea Instuments Minitracka II C In-situ fluorimeter (West Molesey, Surrey, UK) was used to measure fluorescence at each site. This was calibrated by the comparison with the results of chlorophyll *a* extractions of water samples taken from 15 sites on the first sampling day and five sites for each of the remaining three days. Due to logistical limitations, SRP samples at all sites were taken on only half the days (the second and fourth days in each month).

SRP samples were filtered in the field using Whatman GF/C filters and transferred into pre-acid washed bottles for analysis on the same day using the molybdenum blue method of Murphy and Riley (1962) following Stephens (1963). TP samples were stored in the fridge until analysis and concentrations were determined using the molybdenum blue reaction on a SEAL AQ2 auto analyser (Seal Analytical Ltd., Fareham, Hampshire, UK) following an autoclave digestion in potassium persulphate and sulphuric acid. Chlorophyll *a* samples were filtered using Whatmann GF/C filters and frozen on the day of sampling for later analysis. Samples were extracted in hot methanol following the method of Talling (1974).

Temperature, specific conductivity (SpC) and pH were also measured at all sites using a Hydrolab Quanta® Water Quality Measurement System (Loveland, Colorado, USA). For the July, September and November sampling days, the Hydrolab was attached to a Campbell CR10X datalogger (Loughborough, UK) along with the Minitracka fluorimeter for chlorophyll *a* estimation. Approximate water depths were recorded with a Plastimo Echotest II (Southampton, Hampshire, UK) echosounder.

Daily discharge data were provided by the Environment Agency for Eel House Bridge on Cunsey Beck (outflow of Esthwaite Water). A correction factor of 0.92 was calculated to adjust the discharge at Eel House Bridge to that of the outflow from the lake based on the difference in the two catchment areas weighted by rainfall. Assumptions were made that the total inflow to the lake was equal to the outflow and that Black Beck comprised 50% of the inflow (Davison et al. 1980).

5.3.3 Data analysis and statistical methods

For each of the sites at which chlorophyll *a* concentration had been determined, fluorescence values were linearly regressed against the measured chlorophyll *a* water samples ($r^2 = 0.61$; $p < 0.01$; $n = 54$) . The regression equation was then used to calculate chlorophyll *a* concentrations from fluorescence readings for the remaining sampling sites.

Phosphorus dispersal mechanisms

In order to test whether hydrological dilution was the only mechanism responsible for the observed gradients in phosphorus around the inflow, we used a simple river-lake water mixing model incorporating both temperature and SpC as conservative tracers of influent water. SpC has been used in previous studies as a tracer of effluent mixing in streams (e.g McColl 1974, Vandenberg et al. 2005, Lohman and Jones 2010) and is considered conservative when pH <8.5 and it is therefore not affected by photosynthesis (George and Heaney 1978), a condition satisfied during all sampling days in this study. Temperature has also been used as a tracer in lakes (e.g. Monismith et al. 1990, Thackeray et al. 2004), and is used here to improve our representation of dilution in the inflow.

Conceptually, the measured gradients in phosphorus and chlorophyll *a* across the transition zone should show the opposite response to an increase in distance from the river (Fig. 5.2). The hydrological dilution of the inflow entering the lake was therefore calculated in terms of a dilution factor for SRP and TP and a concentration factor for chlorophyll *a* (since phytoplankton biomass will be higher in the lake than the river) R_c for each embayment sampling site ($i = 1 \ldots 14$), excluding the site where the stream joins the lake, from the measurements of both the SpC and temperature (Fischer et al. 1979, Vandenberg et al. 2005):

$$R_{ci} = \frac{C_i - C_l}{C_r - C_l} \;, \tag{1}$$

where C_i is the measured value of SpC or temperature, C_l is the background value in the lake (taken as an average of the values at the deep site and the two sampling sites within the embayment furthest from the inflow) and C_r is the value where the stream joins the lake. The dilution or concentration adjusted concentrations, *D*, of SRP, TP and chlorophyll *a* were then calculated for each embayment sampling site ($i = 1 \ldots 14$) using the dilution or concentration factors calculated from both SpC and temperature data:

$$D_i = D_l + R_{ci}(D_r - D_l) \;, \tag{2}$$

where D_l is the concentration in the lake and D_r is the concentration where the stream joins the lake.

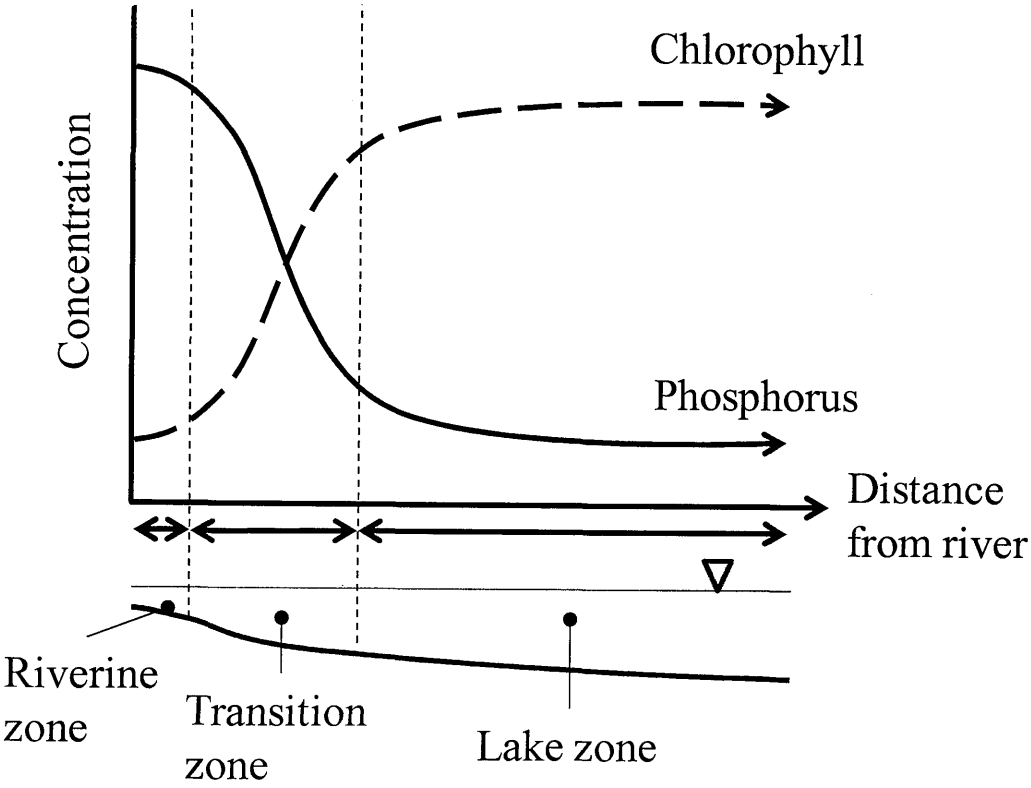

Figure 5.2 Conceptual diagram of an inflow transition zone in relation to phosphorus and chlorophyll concentrations with increasing distance from the river mouth.

The extent to which this river-lake water mixing model could explain the variance in the measured concentrations of SRP, TP and chlorophyll *a* was examined for the entire dataset. Measured concentrations at each site were regressed against corresponding modelled concentrations, and the difference of the slope of the regression equation from unity (indicating measured concentrations = modelled concentrations) was then tested for significance using a Student's *t*-test. A linear mixed effects model (LME) was used to calculate the regression slope. The LME included a fixed effect of the predicted value of each variable and a random effect of date to calculate the regression slope and standard error, while respecting the nested structure of the dataset i.e. groups of measurements from a series of different sampling days. Residual spatial autocorrelation found within the data was modelled by fitting an exponential variogram structure in the LME. The null hypothesis was that the modelled concentration could statistically explain variability in the measured concentrations (slope not different from one) i.e. hydrological dilution could explain the observed pattern in the data. Where regression slopes were significantly different from one, we concluded that hydrological dilution could not account for all of the observed variation. Due to a malfunction of the data logger during the July sampling, all temperature and SpC data were lost. Therefore the use of the river-lake mixing models was only possible for the May, September and November data.

To test whether biological uptake explained any remaining structure in the measured SRP concentrations, we added hydrological dilution-independent chlorophyll *a* values as an explanatory variable to the whole dataset SRP models in the LME. These hydrological dilution-independent chlorophyll *a* values were calculated as the difference between values measured in the lake, and values calculated using the model described above. The addition of chlorophyll *a* was carried out both with and without the variogram structure and the best option chosen on the basis of the Akaike Information Criterion (AIC).

Hydrological dilution-independent SRP and chlorophyll *a* values could be positive or negative, depending on whether dilution alone under- or overestimated observed values at the sampling sites, respectively. We therefore examined the sign of the hydrological dilution-independent SRP and chlorophyll *a* values to understand the overall and seasonal variation in the values of these variables. This assessment provided additional information on whether there were likely to be other processes affecting SRP or chlorophyll *a* concentrations in the embayment which were not associated with hydrological dilution effects. Positive values are indicative of more

SRP or chlorophyll *a* being present than being removed by dilution, whereas negative results indicate that loss processes in addition to dilution are affecting the SRP concentrations or phytoplankton. The test for significance of the difference from zero of the averaged hydrological dilution-independent values was carried out using a 1-sample *t*-test in Minitab 16.1.0. All regression and linear mixed effects models were carried out using the stats and nlme packages in R (Ihaka and Gentleman 1996, Pinheiro and Bates 2000).

Inflow area of influence

To determine the areal extent of the transition zone, the length-scales over which the mixing of the inflow water with the lake water took place were calculated for an average of the whole dataset and by month for SRP, TP and chlorophyll *a*. The concentration data for each site were expressed as a percentage of the lake pelagic site value for each sampling day and then averaged, both over each month and over the whole dataset. The inflow was determined to have been fully mixed with the lake water when its concentration fell to within the average percentage difference between the pelagic site and the two sampling stations within the embayment furthest from the inflow point (sites 1C and 4C). This difference was 5% for SRP and TP and 15% for chlorophyll *a*. The percentage concentration data were linearly regressed onto the distance from the stream mouth for each variable.

Concentration measurements taken at single sampling sites in pelagic zones are frequently assumed to be representative of lake-wide average concentrations. To examine the potential implications of heterogeneity due to inflow transition zones on such assumptions, the mixing distances were used to calculate the proportion of lake area occupied by the transition zone studied. We up-scaled this to represent all inflows to the lake by assuming that the ratio of the Black Beck inflow to the total inflow to the lake (0.5) is equal to the ratio of the Black Beck inflow transition zone surface area to the total lake surface area occupied by inflow transition zones. The percentage over- or underestimation of the lake-wide concentration of the pelagic site was calculated as the percentage difference from the pelagic concentration of an area-weighted average concentration of TP, SRP and chlorophyll *a*. The calculated transition zone surface area and the remaining lake surface area were used to weight the concentration values of an average of all transition zone sites and the pelagic site, respectively.

5.4 Results

The discharge of Black Beck into Esthwaite Water showed strong seasonal variation in 2009 (Table 5.1). On three of the four sampling occasions, discharge levels were above the 30-year averages for the inflow (Fig. 5.3). The instantaneous lake retention time, that is retention time for that day's flow (i.e. the ratio of lake volume to discharge rate), for the sampling days varied from an average of 350 to 15 days (Table 5.1). Lake retention times for the May, September and November sampling days were all less than the 30 year annual average retention time of 90 days. Although variable, average concentrations for the embayment of SRP and TP were highest in November, while chlorophyll *a* concentrations were lowest at this time (Table 5.1). The transition from the stream mouth to lake was characterised by a strong decreasing chemical (phosphorus) and increasing biological (chlorophyll *a*) gradient which varied by season (Fig. 5.4a, b, c).

Table 5.1 Summary of the main hydrological and surface water characteristics in the northern inflow embayment of Esthwaite Water during sampling in 2009.

Date in 2009	Inflow discharge	Lake retention time	SRP[a]	TP[a]	Chorophyll *a* [a]	Water temperature[a]	SpC[a]
	($m^3 s^{-1}$)	(days)		($mg\ m^{-3}$)		(°C)	($\mu S\ cm^{-1}$)
18/05	0.55	71		48.2	12.1	10.7	90.1
19/05	0.55	71	7.8	27.5	8.7	10.8	103.3
20/05	0.50	77		35.8	10.1	11.1	106.8
21/05	0.45	87	4.6	35.1	16.7	12.1	101.4
13/07	0.11	350		46.9	14.7	-	-
14/07	0.12	324	9.8	56.1	-	-	-
15/07	0.12	333		38.6	-	-	-
16/07	0.12	334	7.0	37.8	-	-	-
07/09	0.95	41		45.3	17.0	13.9	91.4
08/09	1.02	38	7.9	40.0	17.1	14.2	98.6
09/09	1.98	40		37.8	12.2	14.1	94.8
10/09	0.76	51	5.4	31.3	11.6	14.2	96.3
02/11	2.31	17		62.9	6.5	10.2	85.8
03/11	2.51	15	13.5	61.9	6.9	10.0	81.8
04/11	2.07	19		52.3	7.8	10.0	93.2
05/11	1.46	27	8.3	49.0	13.6	10.2	92.9

[a] values are averages of the 15 sites in the embayment.

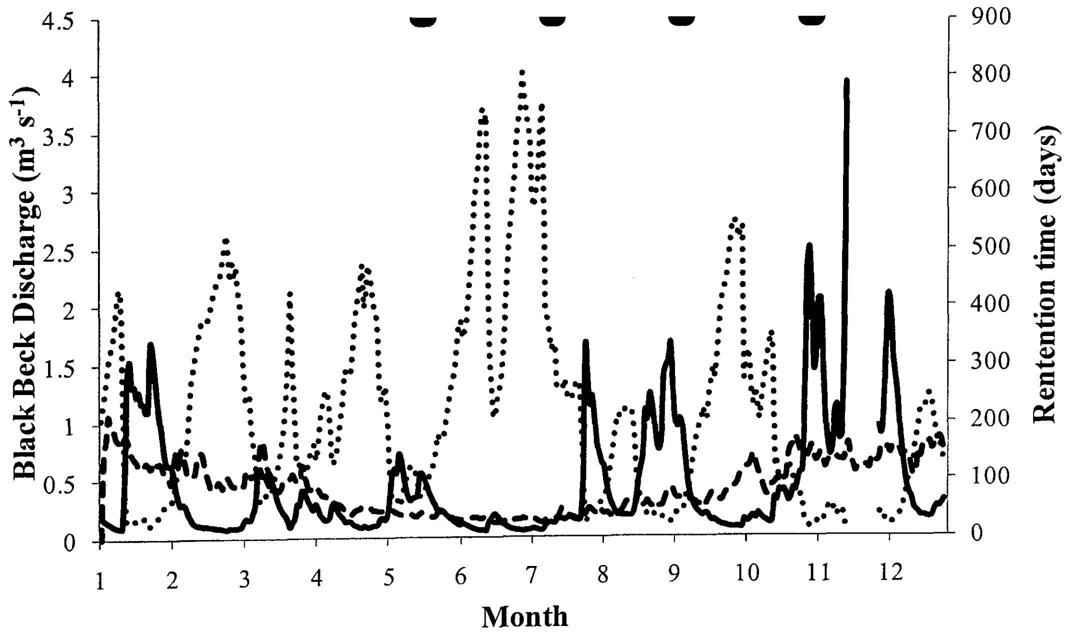

Figure 5.3 Black Beck inflow data: discharge (solid line) and lake retention time in 2009 (dotted line), and 30-year average discharge (dashed line). Bars at the top of the graph indicate sampling dates.

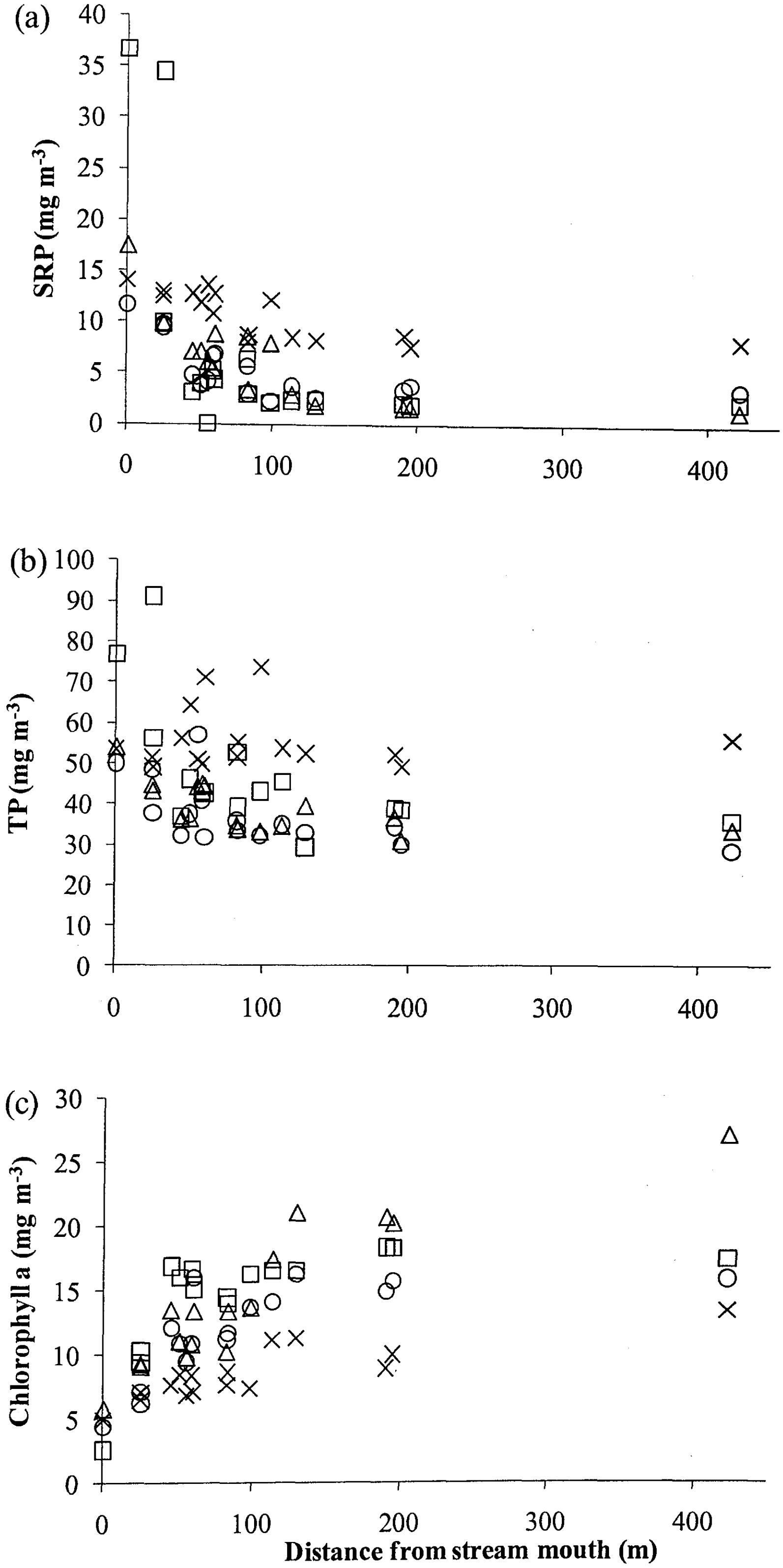

Figure 5.4 Transition zone and lake pelagic site (site at 420 m) concentrations of (a) SRP (b) TP and (c) chlorophyll *a*. Site-averaged May values are represented by circles, July by squares, September by triangles and November by crosses.

5.4.1 Phosphorus dispersal mechanisms

The results from the whole dataset showed that, for all variables (SRP, TP, chlorophyll *a*), LME slopes were significantly different from one (*t*-test, $p<0.05$) for both SpC and temperature proxies of dilution. This indicates that dilution could not account for all of the variation in the measured data. When the dilution-independent chlorophyll *a* data was added to both models (based on SpC and temperature proxies), this improved the model fit, suggesting that biological uptake was having a significant effect on the SRP concentrations in the inflow. However, the effect of the chlorophyll *a* was always weaker than that of the dilution proxy, suggesting that the latter was the dominant effect (Table 5.2).

Table 5.2 LME model of the effect of SpC and water temperature dilution proxies and chlorophyll *a* on SRP concentrations around the inflow.

		AIC	SE	Slope	N	*t* statistic	*p*-value
SpC	Dilution	338.31	0.05	0.87	79	17.10	<0.00
	Chlorophyll *a*		0.05	-0.24	79	-4.72	<0.01
Temperature	Dilution	339.14	0.05	0.88	79	16.48	<0.02
	Chlorophyll *a*		0.07	-0.17	79	-2.48	<0.05

Dilution-independent values of chlorophyll *a* concentration were negative and significantly different from zero when averaged for all data for both dilution proxies (SpC: [chl *a*] = -1.51 mg m^{-3}, $p<0.05$; temperature: [chl *a*] = -0.92 mg m^{-3}, $p<0.05$) – i.e. there was less chlorophyll *a* than predicted assuming dilution alone was acting. A similar result was found for SRP values, though the result for the SpC dilution proxy was not significant (SpC: [SRP] = -0.16 mg m^{-3}, $p>0.05$; temperature: [SRP] = -0.75 mg m^{-3}, $p<0.05$). Seasonal variation was apparent in this comparison: measured chlorophyll *a* values were significantly larger than those calculated assuming dilution alone in May, the opposite case was found in September and no significant difference was found in November (Fig. 5.5). Measured SRP values were significantly lower than dilution-only values in May and November, and not significantly different in September.

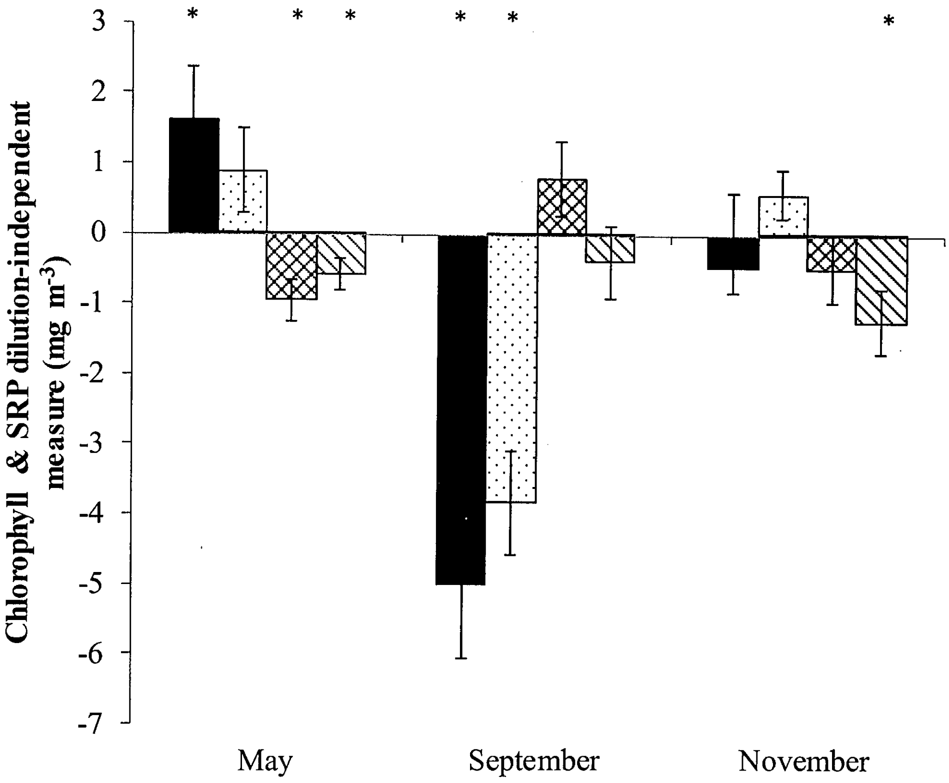

Figure 5.5 Seasonal variation in dilution-independent chlorophyll *a* and SRP values for the two dilution models of SpC (solid bars are chlorophyll *a* and cross-hatched bars SRP) and temperature (stippled bars are chlorophyll *a* and upward diagonal line bars SRP). * values indicate that the result was significantly different from zero and the error bars are ± 1 standard error.

5.4.2 Inflow area of influence

The distance at which the concentrations fell to within the defined variation from the background lake concentration (5% for SRP and TP, 15% for chlorophyll *a*) was ≈100 - 220 m for TP, and ≈110 - 225 m for SRP and chlorophyll *a* based on the 95% confidence intervals (Fig. 5.6). The average mixing distance for all variables was approximately 150 m. This analysis was repeated excluding July dates, as there were missing values for the chlorophyll *a* data, and the pattern remained approximately the same.

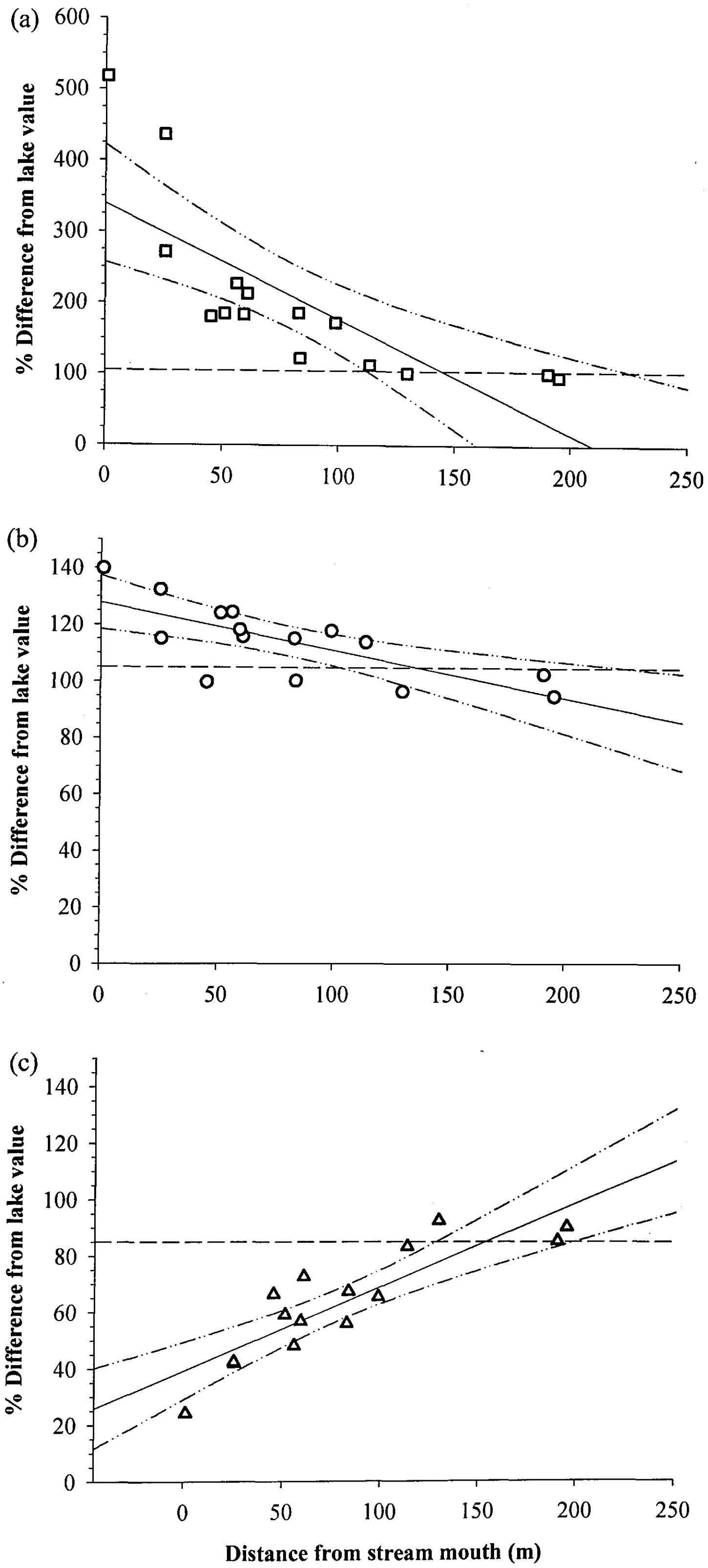

Figure 5.6 Average mixing distances on all dates for **(a)** SRP **(b)** TP **(c)** chlorophyll *a*. Dashed line represents 105% of the lake value for SRP and TP and 85% of the lake value for chlorophyll *a*, the solid line shows the linear fit through the data and the dashed-dotted lines represent the 95% confidence intervals.

The size of the difference between the single pelagic zone concentration measurements and those in the transition zone was variable dependent. On average, SRP concentrations in the transition zone were 2.1 times greater than those at the pelagic site, TP concentrations were 1.1 times greater, and chlorophyll *a* concentration was smaller by a factor of 0.6. Seasonal averages of this ratio varied between 1.3 – 4.5 for SRP, 1.0 – 1.3 for TP and 0.5 – 0.8 for chlorophyll *a*. Using the mixing distances to estimate the area of the inflow transition zone for Black Beck, and scaling this up to derive an estimate of the total transition zone area in the lake (as described in the Methods section), transitions zones were estimated to occupy 5 ±2% of the total lake surface area. Comparison of lake-wide average concentrations taking transition zone heterogeneity into account with the pelagic site values show that the latter underestimate the former by ~5% for SRP, ~0.6% for TP and overestimated chlorophyll *a* concentrations by ~2% (Table 5.3). These estimates were largely consistent across the months for TP and chlorophyll *a*, however there was considerable seasonal variation for SRP with the pelagic site underestimating the transition zone average by nearly 18% in September.

Table 5.3 Pelagic sampling site percentage over- or underestimation of lake SRP, TP and chlorophyll *a* concentrations where transition zone heterogeneity has been taken into account.

	SRP	TP	Chlorophyll *a*
Total	4.7 %	0.6 %	-1.7 %
May	2.4 %	1.7 %	-1.0 %
July	11.4 %	1.0 %	-0.5 %
September	17.5 %	0.5 %	-3.6 %
November	1.4 %	-	-2.0 %

5.5 Discussion

Nutrient concentrations in river-lake transitions zones are often implicitly assumed to be affected by physical processes only (e.g. Spigel et al. 2005, Rueda et al. 2007). However, biological uptake of point source nutrients such as sewage effluent in rivers has been clearly established (McColl 1974, Marti et al. 2004), and enhanced growth of algae in lakes has also been shown to occur near river inflows and attributed to nutrient-enriched waters (Auer and Bub 2004, MacIntyre et al. 2006). In this study, despite the presence of relatively strong physical forcing, due to discharge conditions during most of the sampling being above average for the stream (Fig. 5.3), our results suggest that there was a significant influence of biological uptake on SRP concentrations (Table 5.2).

Annual averages of SRP and chlorophyll *a* concentrations were less than those predicted by conservative tracer-based hydrological dilution calculations, suggesting that at an annual level, depletion processes in addition to hydrological dilution were occurring in the embayment for both variables. In addition to biological uptake by phytoplankton for SRP, sediment chemical or bacterial uptake (e.g. Twinch 1984, Moll and Brahce 1986) and sedimentation of phosphorus through adsorption to particles (Stabel and M 1985, Istvánovics 1994), which were not explicitly considered in this study, may also occur. Seasonal averages of measured SRP and chlorophyll *a* concentrations varied between being greater and less than values predicted using our river-lake water mixing model, further suggesting that biological uptake by phytoplankton was affecting the SRP concentrations. It is not possible to tell directly from the data whether enhanced chlorophyll *a* concentrations were caused by algal growth within the transition zone or by transport of phytoplankton into the embayment by the prevailing winds. However, chlorophyll *a* values in May were higher than predicted by the model, perhaps indicating growth was occurring on this occasion (Fig. 5.5). While there may be some suggestion of in-situ growth in the embayment, it is not a consistent feature, as the September results indicated that loss processes in addition to dilution effects were occurring. This may be due to additional sedimentation of cells, enhanced grazing or the flushing of phytoplankton from the embayment due to the wind direction which was from the west to north-west during the September sampling. This seasonal variability serves to highlight the dynamic nature of the inflow environment, and that understanding the seasonal context is important when interpreting the annual net result. Inflow embayments in large reservoir systems have previously been found to act as periodic sources for algal blooms which can have serious implications for water quality (Izydorczyk et al. 2008, Hart and Wragg 2009). Biological uptake of phosphorus and its subsequent potential for transport and recycling in the wider lake in a biological form is rarely explicitly considered as a mechanism for the spatial dispersal of inflow phosphorus which is largely assumed to be a physical process (e.g. Rueda et al. 2007). However, our results suggest that it may represent an additional pathway to that of dilution.

Our dilution proxies, SpC and temperature, confirmed that hydrological dilution was the dominant process to explain the observed decreasing gradients in phosphorus (both SRP and TP) and the increasing gradient of the chlorophyll *a* in the lake. This is probably not surprising as discharge levels, for the dilution analysis, were above average for the lake (Fig. 5.3). Under high flow conditions, the delivery of phosphorus from the catchment will be enhanced. However, in a lake system the implications of this delivery for biological productivity will depend on what form the phosphorus is in and whether settling particles are likely to be liberated from sediments at a later date (Stabel and M 1985, Pacini and Gächter 1999); the seasonality of the high discharge, whether the influent water affects the light climate through turbidity (Cuker et al. 1990, Bormans et al. 2005); and whether discharge levels affect the thermal structure or reduce the residence time below that required for biomass growth (Jones and Elliott 2007, Jones et al. 2011). In this study, the highest discharges occurred in September and November. In November, there is clearly lower growth potential for phytoplankton and such nutrient loading events will either be flushed through the lake or retained in the sediments for subsequent internal loading. In September however, higher nutrient loading, associated with short term storm events, may provide a pulse of nutrients for sustaining phytoplankton growth, particularly that of the Cyanobacteria which can form a dominant component of the total biomass of the lake in late August and early September (Madgwick et al. 2006).

The transition zone for the Black Beck inflow to Esthwaite Water was small and average mixing distances over which the phosphorus concentration was reduced to pelagic zone levels were short (on the order of 100 – 200 m). This implied that the inflow area of influence was also only a small part of the total lake surface area (~3 - 7%). The influence of large river inflows can extend across large parts of lake basins, thus strongly influencing lake hydrodynamics (Ford 1990, Laborde et al. 2010) and the supply of nutrients or oxygen at large distances from the river mouth (Loizeau and Dominik 2000, von Westernhagen 2010). In the case of Esthwaite Water, these zones are relatively small, and thus have limited influence on lake hydrodynamics. Lake morphology around the inflow is also likely to influence the size of the transition zone. It may be anticipated that embayments, such as the one considered here, will have a more constraining effect on river-lake water mixing than an inflow without an embayment, thereby increasing the size of the transition zone. The relatively rapid assimilation of the inflow into the lake is likely to relate to the shallow nature of the embayment into which the stream flows and the consequentially short residence time of this part of the lake. This implies that influent nutrients are rapidly mixed into the lake and accessible to the phytoplankton, particularly during the growing season.

The spatial heterogeneity in concentrations of phosphorus and chlorophyll *a* introduced by the inflow suggested that using the single pelagic site would lead to small under- and overestimates of lake wide TP and chlorophyll *a* concentrations, respectively. However, the underestimate for SRP was larger, particularly during the summer growing season, indicating that a single pelagic sample cannot adequately represent lake-wide average SRP concentrations. This larger difference in pelagic and transition zone concentrations of SRP likely reflects the 'reactive' nature of this phosphorus fraction which would be used by algae or adsorbed to particles rapidly after entering the lake. This seasonal effect on variables affected by lake productivity has also been found in a study of the chemical representativeness of single sampling sites in 34 Swedish lakes (Göransson et al. 2004). It also implies that understanding the SRP dynamics in the inflow transition zone is required during the summer period in order to capture lake spatial heterogeneity of the variable and provide a more accurate measure of the phosphorus available for phytoplankton growth.

5.6 Conclusion

Despite seasonally high discharge levels from the inflow and the dominant influence of hydrological dilution in the transition zone, we found that biological uptake was likely to be responsible for some of the observed dispersal of SRP in the embayment.

The length-scales for the transition zone are on the order of 100 - 200 m, which represents only a small proportion of the lake. This implies that a single pelagic site could adequately account for the spatial heterogeneity in TP and chlorophyll *a* found by including the inflow transition zone; however SRP concentrations were underestimated, particularly during the growing season.

Chapter 6 Variability in phosphorus supplies during the growing season in a small eutrophic lake

(Mackay, E.B., Jones, I.D. and Folkard, A.M. Variability in phosphorus supplies during the growing season in a small eutrophic lake. To be submitted to Water Research)

6.1 Abstract

Recycling of phosphoric material stored in bed sediments can provide the dominant supply of phosphorus to phytoplankton in many lakes. This internal supply is a function not only of the processes that release phosphorus from the sediments, but also those which transport it into the surface mixed layer where it can be accessed by the phytoplankton. Traditionally, studies of this process have tended to assume constant supply rates, or used a single year's data to estimate the internal supply of phosphorus. Moreover, frequently these budgets have relied on measurements of total phosphorus, thus overestimating the proportion that will be bio-available. In this study, we calculated weekly internal fluxes of the bio-available soluble reactive phosphorus (SRP) for 2008 and 2009 in a small, temperate lake, Esthwaite Water, UK and compared them against the fluxes of phosphorus from external sources. We found that there was a large inter-annual variability in phosphorus loading in the lake. Most of the difference in the load between the two years was associated with the difference in supply from the hypolimnion. Internal and external sources were of a similar magnitude during the summer (June – August), whereas internal entrainment was the dominant SRP source during the autumn until overturn (September – October). We infer that the inter-annual differences in the hypolimnetic supply were caused by differences in the build-up of phosphorus during the stratified period, which was related to lower thermal stability and a greater number of mixing events in the early- to mid-summer of 2009.

6.2 Introduction

The enrichment of phosphorus in lakes, which can trigger problems such as algal blooms, is a major issue in lake management. Tackling this has required the development of our understanding of lake phosphorus budgets (e.g. Dillon 1975, Bennett et al. 1999, Hargan et al. 2009). Much attention has focused on reducing external loads from catchments by the widespread application of tertiary treatment in sewage treatment works and programmes to address diffuse sources (Heathwaite et al. 2003, Environment Agency 2007, Le et al. 2010, Neal et al. 2010). While the reduction in external loads has in some cases resulted in in-lake improvements (Sommer et al. 1993, Evans et al. 2011), many lakes have failed to show reductions in aqueous concentrations of phosphorus or an improvement in lake trophic status and reduction in phytoplankton biomass over the short-term (Marsden 1989, Anderson et al. 2005). This is primarily because of internal loading of phosphorus from nutrient-enriched sediments, which has been found to prolong eutrophic conditions for a number of years (Jeppesen et al. 2005).

Internal loading in some lakes has been found to form a potentially significant fraction of the whole lake phosphorus budget, particularly in eutrophic or hypereutrophic lakes (Larsen et al. 1981, Søndergaard et al. 1993, Soranno et al. 1997). However, the quantification of the internal load has in the past been neglected (Nürnberg 2009) or calculated only as a residual of the external input-output budget. In many cases phosphorus budget studies have determined the lake internal load of total phosphorus (TP) by a mass balance approach (Vollenweider and Kerekes 1980, Larsen et al. 1981, Welch and Jacoby 2001). While this may be a useful measure for the total load, it gives no indication of the form of the phosphorus, or the time of the year when it is released and therefore whether it is available for use by the lake biota. Understanding the bioavailable component of the phosphorus budget is clearly essential when assessing the value of mitigation measures for phosphorus with the objective of reducing algal biomass. The importance of internal sources in this context is that they are often in a highly bioavailable form (Boström 1984, Nürnberg 1988). Seasonal input of phosphorus from the internal load is important since many of the processes which result in phosphorus release from sediment only occur under anoxic, reducing conditions (Mortimer 1941, Nürnberg 1984, Golterman 2001, Prairie et al. 2001). These will only occur when lakes are stratified, in hypolimnia where the dissolved oxygen concentration has been sufficiently depleted. Phosphorus release from oxic sediments (for example from the bed at depths within the surface mixed layer of a lake) require specific temperature or pH conditions (Lee et al. 1977, Drake and Heaney 1987, Jensen and Andersen 1992, Gerhardt et al. 2010).

The liberation of phosphorus from sediment does not necessarily mean that it can be instantly accessed by the lake biota, instead a number of temporally heterogeneous physical pathways exist which transfer phosphorus into the pelagic, epilimnetic lake waters. Where sedimentary phosphorus is released into the hypolimnion, the phosphorus source is relatively isolated from the epilimnetic mixed layer, and thus a large proportion of the phytoplankton biomass, by the seasonal thermocline. The supply mechanisms for this source, once stratification is established have been found to include vertical diffusion, boundary mixing from the breaking of internal waves and the entrainment of hypolimnetic waters through deepening of the mixed layer (Wodka et al. 1983, Soranno et al. 1997, MacIntyre et al. 1999). The importance of these supply mechanisms is dependent not only on their frequency and magnitude but also on the rate of release and build up of phosphorus in the hypolimnion. A strong controlling factor on the concentration of SRP in hypolimnetic waters is the concentration of dissolved oxygen below the thermocline (Mortimer 1941, Nürnberg 1984), which is determined by the rate of both its hypolimnetic consumption, and its replenishment. Following stratification, the replenishment of hypolimnetic dissolved oxygen is controlled by the strength of stratification and the number of mixing events which cause entrainment of oxygen from the epilimnion (Lam et al. 1987). In addition, influent sources of phosphorus from catchment tributaries will supplement either the epilimnetic or hypolimnetic phosphorus supply depending on the mixing processes associated with river plume emplacement (Vincent et al. 1991, Rueda et al. 2007).

Previously, internal loading processes and pathways have largely been considered individually and few studies have compared the relative importance of different internal sources and pathways in a single lake. This comparison is important for lake managers, as understanding which processes are the most significant for an individual lake is important in the context of changing environmental conditions such as land use and climate change and are also likely to inform remediation efforts. In addition, it is likely that different sources will be more important at different times of the growing season and therefore have different effects on both overall algal biomass potential and community composition (Soranno et al. 1997, Nowlin et al. 2005, Steinman et al. 2009).

This study examines the relative importance of different internal loading mechanisms and pathways of bioavailable soluble reactive phosphorus (SRP) to the epilimnetic, pelagic phytoplankton in a small, temperate, eutrophic lake over the summer stratified period (June to October) for two consecutive years. In addition, we compared these fluxes to those from the external catchment sources, and we tested the following hypotheses:

(i) Interannual variability in phosphorus loading is large and has an important impact on the total load received by the epilimneitc pelagic phytoplankton;

(ii) Phosphorus sources will vary in importance over a seasonal timescale; and

(iii) Variability in the lake thermal structure over time has a strong control over the importance of phosphorus supply from hypolimnetic bed sediments.

6.3 Methods

6.3.1 Study site

Esthwaite Water (54°21'N, 3°0'W) is a small glacially scoured lake, surface area 0.96 km^2, total volume 6.7×10^6 m^3, average depth 6.9 m (Mackay et al. 2011a), within the southeastern area of the English Lake District. The catchment area is 17 km^2 with an underlying sedimentary geology of Silurian shales, mudstones and sandstones. Land uses are predominantly pastoral agriculture surrounding small settlements with some forest on steeper slopes (Reynolds and Irish 2000); the relatively low resident population is substantially enlarged by seasonal tourism. Previous studies have found that external sources alone cannot account for the phosphorus concentration in the lake water (Hall et al. 2000), implying that internal loading forms an important component of the phosphorus budget of the lake. Recent analysis has classified the lake as eutrophic (Maberly et al. 2006).

6.3.2 Field and laboratory methods

Sampling of the external SRP load was carried out on the main lake inflow, Black Beck, which accounts for around half of the overall discharge into the lake (Davison et al. 1980) and drains ~80% of the catchment area. A distinction was made between point and diffuse sources of phosphorus in the Black Beck inflow by sampling up- and downstream of the main point source discharge at Hawkshead Sewage Treatment Works (STW) which discharges into Black Beck just upstream of the lake (Fig. 6.1). Water samples were taken on an approximately fortnightly basis for each site from June to October 2008 and 2009. SRP samples for the vertical load calculations were collected at three different depths (0.5 m, 11 m, 14 m) in the water column at the deepest point in the lake, where vertical pH and temperature profiles were also carried out at 1 m intervals using a Hydrolab Quanta® Water Quality Measurement System (Loveland, Colorado, USA). Samples were taken on a weekly basis during 2008 and in September and October 2009; while sampling frequency was fortnightly during June to August 2009. SRP samples were filtered in the field using Whatman GF/C filters and transferred into pre-acid washed bottles for analysis on the same day using the molybdenum blue method of Murphy and Riley (1962) following Stephens (1963).

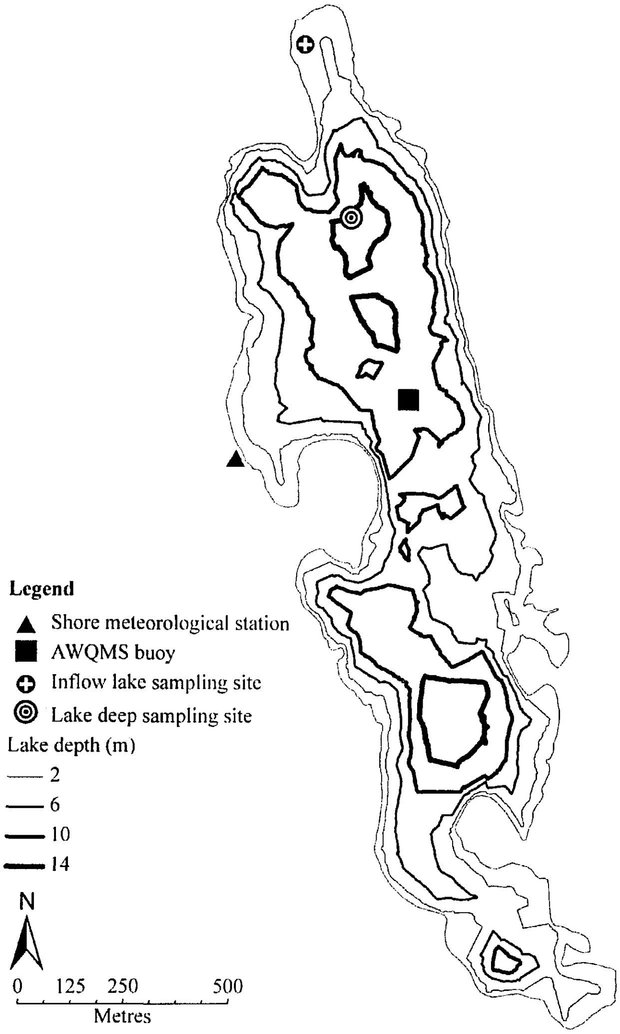

Figure 6.1 Esthwaite Water showing sampling sites and the location of the shore weather station and AWQMS buoy.

Daily discharge data were provided by the Environment Agency for England and Wales from the gauging station at Eel House Bridge, located shortly downstream from the lake on Cunsey Beck, the primary outflow. To adjust the discharge at Eel House Bridge to that of the outflow from the lake, a correction factor of 0.92 was used, based on the difference between the catchment areas of the outflow point and that of the gauging station, weighted by rainfall. An assumption was made that the total inflow to the lake was equal to the outflow, and that Black Beck constituted 50% of the total inflow (Davison et al. 1980).

High resolution meteorological and hydrographic data were provided by the UK Centre for Ecology and Hydrology (CEH) Automatic Water Quality Monitoring Station (AWQMS) in the north basin of the lake and a meteorological station on the shore (see Rouen et al. 2001, Madgwick et al. 2006 for more details). Wind speed was measured with a Vector A100L2-WR cup anemometer with optical rotation sensing (Vector Instruments, Rhyl, Wales) and solar radiation was measured using a Kipp & Zonen CNR1 Net Radiometer (Kipp & Zonen B.V, Delft, Holland), both obtained as hourly averages from the AWQMS in the north basin of the lake. As the buoy is a rotating platform, wind direction data were obtained as hourly averages from a Vector W200P-WR wind vane (Vector Instruments, Rhyl, Wales) in an unsheltered location on the shore of the north basin of the lake. Additional data on the thermal structure of the lake were obtained as two minute averages from a thermistor chain attached to the buoy, consisting of 12 Platinum resistance thermometers (PRTs) (Labfacility Ltd, Bognor Regis, UK) spaced at one metre intervals to a depth of 11.5 metres.

6.3.3 Data analysis and statistical methods

A number of different phosphorus fluxes have been quantified to allow the comparison of different internal and external loads to the lake over two years (Fig. 6.2). The external load is assumed to be solely from the inflowing streams, because wind-blown areal deposition is considered to be low away from urban areas (Pitois et al. 2001) and previous estimates assume it to be a very small proportion of the total load (Hall et al. 2000). Internal loads comprise hypolimnetic and epilimnetic sources. Vertical loading of phosphorus from the hypolimnion is conceptualised as the result of two processes: mixed layer entrainment and vertical diffusion. The first is the physical deepening of the mixed layer, entraining phosphorus rich hypolimnetic water upwards and the second is the vertical diffusion of phosphorus across a vertical concentration gradient between the hypolimnion and epilimnion. Epilimnetic loads comprise the oxic release from the sediment area above the mixed layer depth. All calculated loads are stated in kilogrammes.

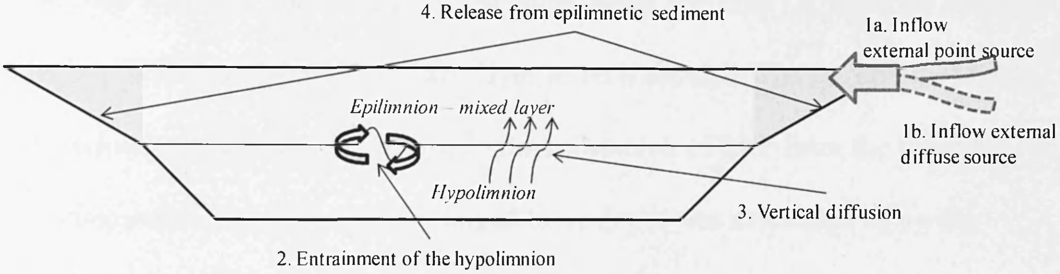

Figure 6.2 The different external and internal phosphorus fluxes considered in Esthwaite Water.

External load

The fortnightly SRP concentration data measured in Black Beck were interpolated to daily values by regressing them onto the corrected daily discharge data inferred from the Eel House Bridge station. For each day, the total external load, E (mg d^{-1}), was calculated as $E = E_d + E_p$ where E_d is taken to represent the load from diffuse sources and E_p the load from the STW, and these terms are given by:

$$E_d = C_{us} \times D_l \, , \tag{1}$$

$$E_p = (C_{ds} - C_{us}) \times (D_l \times 0.5) \, , \tag{2}$$

where C_{us} is the concentration of SRP upstream of the STW (mg m^{-3}), D_l is the discharge for all the lake inflows (m^3 d^{-1}) and C_{ds} is the SRP concentration downstream of the STW (mg m^{-3}). Thus, C_{us} is taken as the SRP concentration from diffuse sources for all the stream inflows.

Hypolimnetic load

Entrainment

The change in the depth of the mixed layer was inferred to represent either an addition of an SRP load to the mixed layer when entrainment occurred i.e. the layer deepened, or a loss of SRP load from the mixed layer when it shoaled. The net effect of these two processes represents the loading to the epilimnion of SRP from the hypolimnion by entrainment. The daily-average mixed-layer depth was calculated using the AWQMS PRT chain, as the minimum depth where water temperature had >1 °C difference from the top thermistor (0.5 m) (following Mackay et al. 2011b). The concentration profile was calculated in three steps. Firstly, it was assumed that the phosphorus concentration through the whole depth of the mixed layer was the same as that measured at 0.5 m depth. Secondly, a linear interpolation of values was carried out between the mixed layer value at the bottom of the mixed layer and the measured value at 11 m. Finally, a linear interpolation was carried out between the 11 m and 14 m values. The loading or loss caused by mixed layer deepening or shallowing, l_{ent} (mg d^{-1}), was then calculated as:

$$l_{ent} = \Delta V_{ml} \times C' , \tag{3}$$

where ΔV_{ml} is the daily change in volume of the mixed layer (m^3 d^{-1}, calculated from the daily change in mixed layer depth and the lake bathymetry taken from Mackay et al. (2011a)) and C' is the previous day's SRP concentration of the layer which is entrained or detrained (mg m^{-3}).

Vertical diffusion

The daily mixed layer depth, top of the hypolimnion and centre of the metalimnion were calculated for the study period in both years. The mixed layer depth was calculated as previously described, the top of the hypolimnion was calculated as the maximum depth at which there was a >1°C temperature difference from the bottom thermistor (11.5 m) and the centre of the metalimnion was the mid-point between these two values. The two-year averages of these values: mixed layer depth = 5.4 m, centre of the metalimnion = 7.2 m and top of hypolimnion = 9.0 m, were used as the basis for calculating the vertical diffusion of SRP across the metalimnion from the hypolimnion to the mixed layer. The depths at which the diffusion was calculated were assumed to be fixed for the study period, being the centre of the epilimnion or mixed layer (5.4 / 2 = 2.7 m) and a point at the same distance from the centre of the metalimnion (7.2 m) in the hypolimnion (7.2 + (7.2 – 2.7) = 11.7 m). The SRP load attributable to vertical diffusive flux, I_f, (mg d^{-1}) was calculated as:

$$I_f = K_z \frac{\Delta C}{\Delta z}, \tag{4}$$

where ΔC is the difference in SRP concentration (mg m^{-3}) between the hypolimnetic (11.7 m) and epilimnetic (2.7 m) points equi-distant from the centre of the metalimnion, Δz is the difference in depth between those two points (9 m), and K_z is the vertical eddy diffusivity (m^2 d^{-1}), at the centre of the metalimnion (7.2 m). Previous work (Miller 2008), has indicated that the effect of surface heating is <1 W

m^{-2} at this depth and therefore the heat flux method of calculation of K_z at this depth can be applied (Jassby and Powell 1975). K_z is highly spatially and temporally variable in Esthwaite Water. For the purposes of these calculations, we have taken an average value for the lake calculated over two years by Miller (2008), 0.07 $m^2\ d^{-1}$ ($8.6 \times 10^{-7}\ m^2\ s^{-1}$), and a representative maximum and minimum range also based on lake observations 0.86 $m^2\ d^{-1}$ and 0.01 $m^2\ d^{-1}$ ($1 \times 10^{-5}\ m^2\ s^{-1}$ and $1.4 \times 10^{-7}\ m^2\ s^{-1}$) the latter being the coefficient of molecular diffusivity, which pertains to the complete absence of turbulence to examine the dependency of vertical diffusive loading on the value of K_z.

Epilimnetic load

Oxic sediment release

A number of studies have examined the sediment release rate for phosphorus under oxygenated conditions (Ryding and Forsberg 1977, Mawson et al. 1983, Drake and Heaney 1987, Penn et al. 2000, Steinman et al. 2009). We were unable to measure directly the phosphorus release rate K (mg P $m^{-2}\ d^{-1}$) in the shallow regions of the lake where the mixed layer reaches the bed, but we have calculated values for this as a function of pH, derived from a previous study of Esthwaite Water (Drake and Heaney 1987):

$$\log K = 0.54pH - 3.94, \qquad (6)$$

to enable estimates of the internal load from oxic sediments. pH values were taken from the lake deep sampling site at the surface (0.5 m depth). In addition, we have used representative values of K from the literature (Ryding and Forsberg 1977, Steinman et al. 2009) to examine the potential variability in this source. Using the information on the mixed layer depth and lake bathymetry, we calculated the area of sediment above the mixed layer depth, S_m, (m^2) for each day and multiplied this by published release rates, K, (mg P m^{-2} d^{-1}) to provide an estimate for the potential total daily load, I_{epi}, (mg P d^{-1}) from sediments within the epilimnion:

$$I_{epi} = S_m \times K \,. \tag{7}$$

Water column stability

To investigate the effect of water column stability on the variability of SRP supply to the epilimnion, we calculated the Schmidt stability, S (J m^{-2}), a measure of the strength of stratification in the lake (Hutchinson 1957, Madgwick et al. 2006) as:

$$S = -\frac{g}{A_0}\int_0^{z_{max}} (z - z_v)A_z(\rho_{max} - \rho_z)dz \,, \tag{8}$$

where g is the acceleration due to gravity (m s^{-2}), z and z_{max} are the water depth and maximum water depth (m), respectively, A_0 and A_z are the lake surface area and cross-sectional area at depth z (m^2), respectively, ρ_{max} and ρ_z (kg m^{-3}) are the maximum density of freshwater and density of water at depth z, respectively and z_v is the centre of volume of the lake:

$$z_v = \frac{1}{V}\int_0^{z_{max}} zA_z dz \,, \tag{9}$$

where V (m^3), is the lake volume. Water temperature data were provided by the AWQMS PRT chain and bathymetric data were taken from Mackay et al (2011a).

6.4 Results

6.4.1 Interannual variability

The internal load and flux rate were, respectively, on average higher than the external load and flux rate in the lake. There was however a clear difference between the two years in the internal flux rate from anoxic sources (Table 6.1, Fig. 6.3). This contrasts with the relatively consistent flux rates and loading from external and internal oxic sources in both years (Fig. 6.4). This difference leads to large differences between years in the relative proportion of the SRP load from the various sources (Table 6.1). The contribution of internal anoxic and external loads varies by 24% and 17% between years, respectively. Lower internal anoxic loading in 2009 resulted in a reduction in total loading to the epilimnion of ~160 kg or 34% during the study period (Fig. 6.4).

Table 6.1 Summary of total and proportional SRP loading to Esthwaite Water from different sources in 2008 and 2009

Source	**Origin**	**Type**		**2008**	**% of total**	**2009**	**% of total**	**2008 - 09 Average**	**% of total**
External	Inflow	Point		60.1	12.6	35.7	11.3	47.9	12.1
			30 year flow	55.8	11.7	44.0	13.9	49.9	12.6
		Diffuse		99.7	21.0	124.4	39.4	112.1	28.3
			30 year flow	60.5	12.7	80.1	25.4	70.3	17.8
	Total External			**159.8**	**33.6**	**160.1**	**50.7**	**160.0**	**40.4**
Internal	Anoxic	Entrainment		211.5	44.5	74.2	23.5	142.9	36.1
		Diffusion	Average	41.5	8.7	19.2	6.1	30.4	7.7
			Range	6.8 - 482.7		3.1 - 223.2		4.9 - 353.0	
		Total		***253.0***	***53.2***	***93.4***	***29.6***	***173.2***	***43.8***
	Oxic	Sediment release	Average	62.8	13.2	62.2	19.7	62.5	15.8
			Range	14.8 - 98.5		14.7 - 97.8		14.7 - 98.2	24.8
		Total		***62.8***	***13.2***	***62.2***	***19.7***	***62.5***	***15.8***
	Total Internal			**315.8**	**66.4**	**155.7**	**49.3**	**235.7**	**59.6**
Total for stratified period				**475.5**		**315.8**		**395.7**	

Note % of total columns do not add up to 100%.

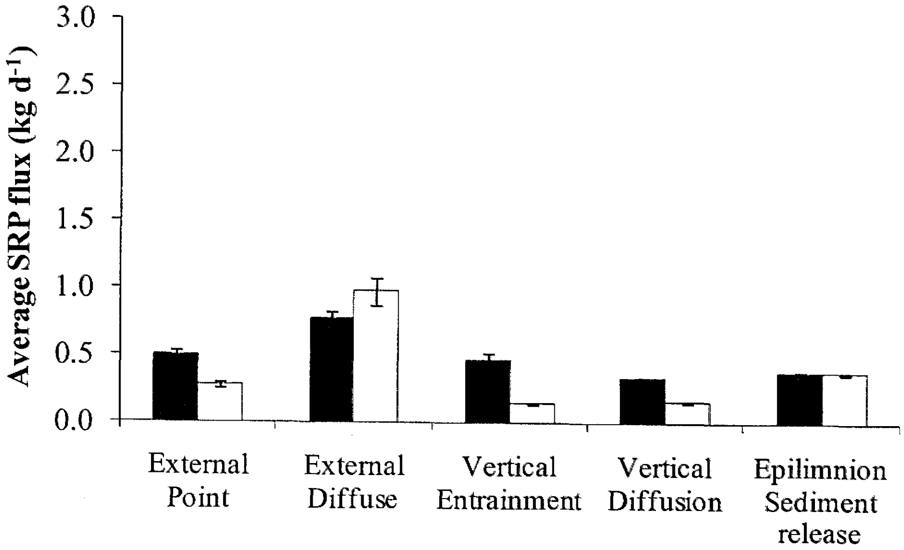

Figure 6.3 Average daily SRP flux (kg d^{-1}) for the different phosphorus sources over a) the study period for 2008 (grey bars) and 2009 (white bars). Error bars show ± 1 standard error.

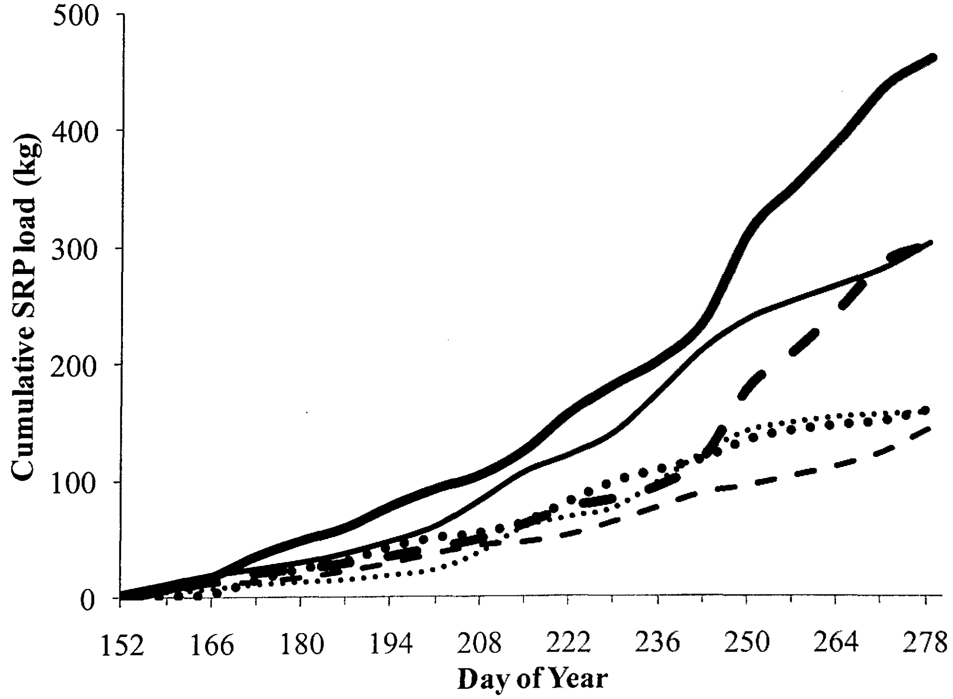

Figure 6.4 Cumulative SRP load (kg) from internal sources (dashed lines), external sources (dotted lines) and total load (solid lines) in 2008 (thick lines) and 2009 (thin lines).

Average stream discharge levels during the study period in 2008 and 2009 were 0.8 m^3 s^{-1} and 0.7 m^3 s^{-1} respectively, both of which are higher than the 30-year average for the stream of 0.5 $m^3 s^{-1}$. The discharge pattern in both years resulted in the SRP delivery being dominated by short time-scale discharge events, and consequently, the flux rates from diffuse sources were larger than those of the point source in both years (Fig. 6.3). Recalculating the SRP load based on the 30 year average discharge resulted in an average reduction in loading of 25% (Table 6.1).

6.4.2 Variability and uncertainty in flux estimates

The range of K_z values used reflects the large potential uncertainty in the estimation of the vertical diffusive load (Table 6.1). The range of values for this load implies that its importance may vary from being negligible (~1% of total) to representing the dominant source of SRP in the lake (~50%). The average difference in the diffusive flux rates between the high and low K_z values used was 3.8 and 1.8 kg d^{-1} in 2008 and 2009, respectively. Similarly, the range in estimates of the oxic sediment loading rate differ by approximately an order of magnitude which again results in a large variability in the potential importance of this source (~4% – 25%) (Table 6.1).

6.4.3 Importance of fluxes during the study period

During the summer (June – August), on average, no single phosphorus source was dominant (Figs 6.5a, 6.5b and 6.6) and internal and external sources were of approximately equal importance in the total flux rate. Vertical entrainment flux rates during 2008 and 2009 were very similar for the first half of the study period, where net loading was small (Fig. 6.4). However, while the flux rate in 2009 remained relatively static until day 264, in 2008 it rapidly increased after day 236 (Figs 6.5a and 6.5b) resulting in a higher overall loading from internal sources (Fig. 6.4). As a proportion of the total flux rate, entrainment becomes most important during

September and October (Fig 6.6). In contrast, the vertical diffusive flux is relatively small overall and proportionally more important from June to August.

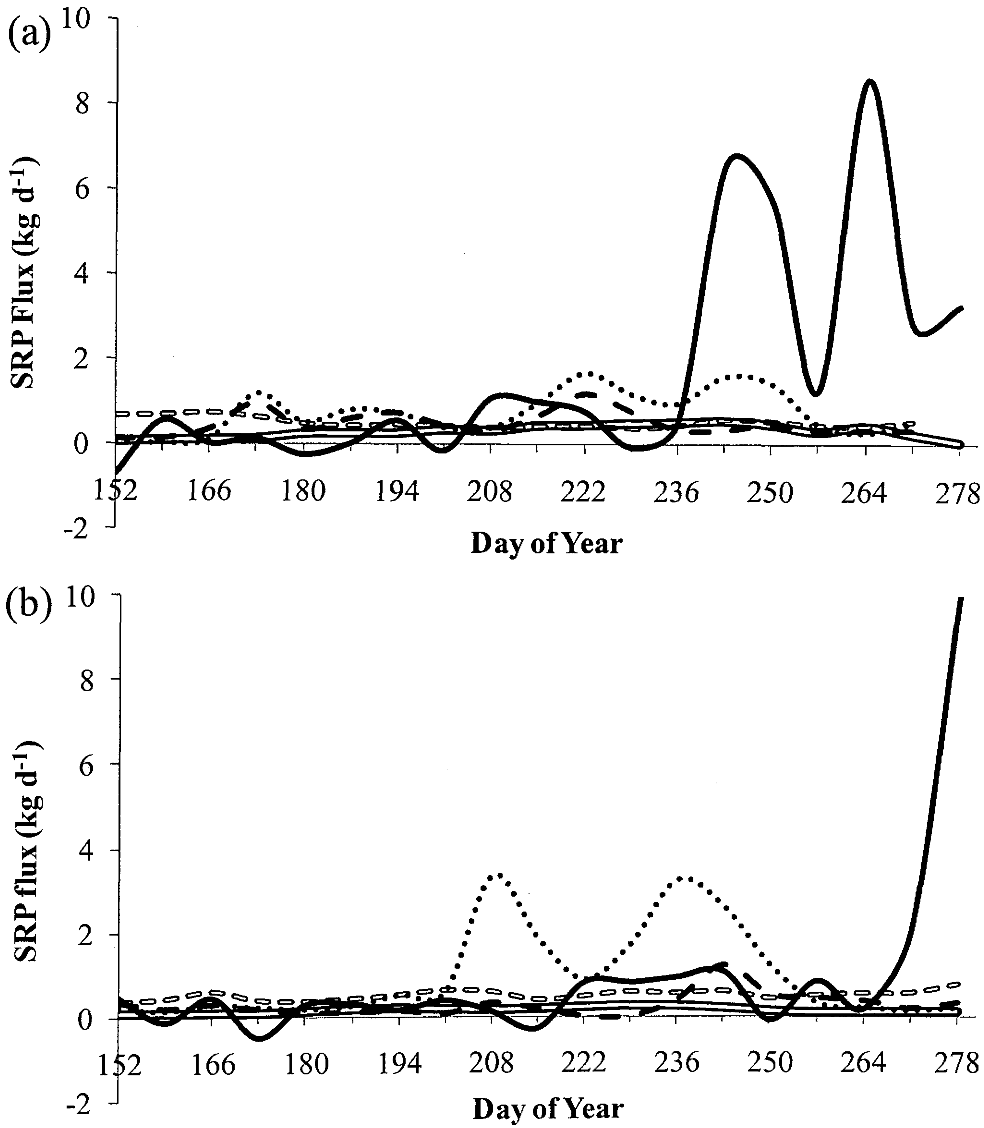

Figure 6.5 Weekly average SRP fluxes (kg d^{-1}) for Esthwaite Water over the study period from external point (solid dashed lines), external diffuse (dotted lines), vertical entrainment (solid lines), vertical diffuse loading using the average value of K_Z (8.6×10^{-7}) (hollow lines) and epilimnetic sediment release using Drake and Heaney (1987) (hollow dashed lines) for **a)** 2008 and **b)** 2009.

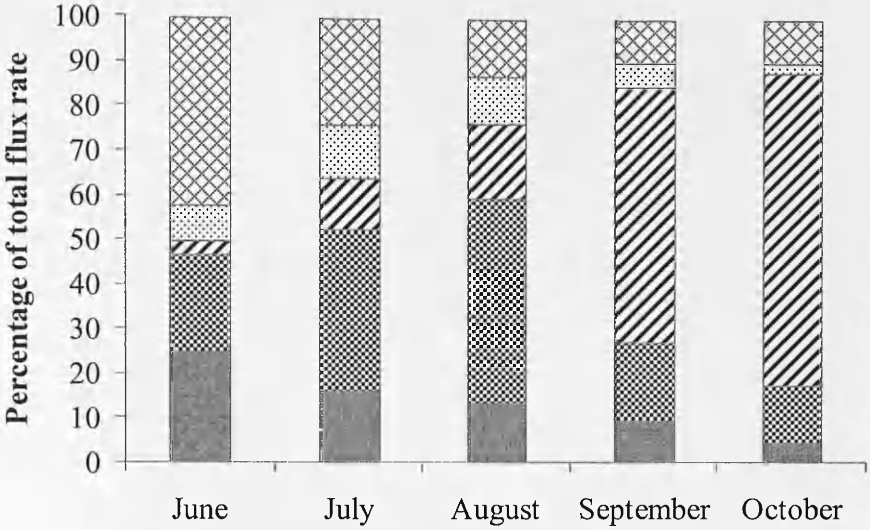

Figure 6.6 Average daily SRP flux (kg d^{-1}) expressed as a percentage of the total by month. The different shading represents the following: ■ Point source, ▦ Diffuse sources, ▨ Vertical entrainment, ░ Vertical diffusion and ⊠ Epilimnetic sediment release.

6.4.4 Drivers of flux variability

The interpolated SRP concentrations at 11.7 m show differences between the patterns of hypolimnetic accumulation of phosphorus for the two years (Fig. 6.7). In 2008, the SRP concentrations show a linear growth for most of the study period, peaking after day 243 with a rapid drop during lake overturn in October. The peak in SRP in 2009 occurs earlier (~ day 236) and at a much lower concentration.

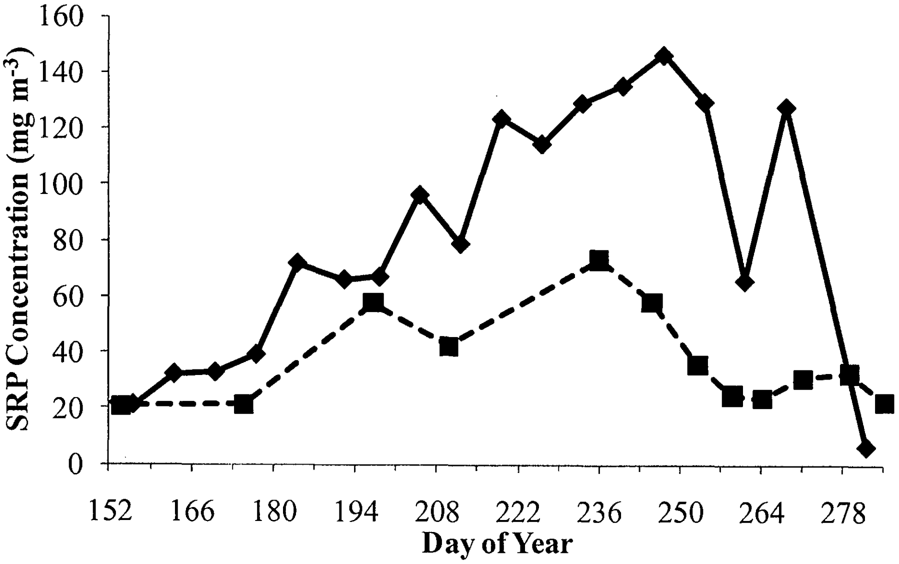

Figure 6.7 SRP concentrations in Esthwaite Water at 11.7 m over the study period in 2008 (solid lines) and 2009 (dashed lines).

Average hydrographic and meteorological conditions were similar in the two years (Table 6.2). However, in 2009, both the Schmidt stability and the mixed layer depth were more variable (higher standard deviation), particularly during the summer (June, July, August) compared to 2008. Mixed layer depths in 2009 had a negative trend between day 152 and 233 (June to late-August), while in 2008 there was no trend (Fig. 6.8). There were also more deepening and fewer shoaling events in summer 2009 than in 2008 (Table 6.2).

Table 6.2 Mean and standard deviation of meteorological and lake hydrographical data for Esthwaite Water in 2008 and 2009

		Wind speed (m s^{-1})		**Air temperature (°C)**		**Rainfall (mm)**		**Schmidt Stabilty (J m^{-2})**		**Mixed layer depth (m)**		**Mixing events (no.)**	
		$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	**deepen**	**shallow**
2008	Whole period	2.2	1.0	13.9	2.2	6.6	11.6	80.5	35.9	-5.4	1.8	27	24
	June	2.3	1.0	13.3	1.5	6.1	14.1	97.3	23.5	-4.8	0.9	4	4
	July	2.1	0.7	15.2	2.0	4.9	6.5	104.1	26.4	-4.2	0.7	3	4
	Aug	2.1	0.8	15.3	1.4	7.8	8.8	93.0	22.2	-4.6	0.7	6	6
	Sept	1.9	1.4	12.8	1.4	5.2	10.1	39.5	12.6	-7.2	1.5	12	8
	Oct	2.9	0.8	9.6	2.1	16.1	24.3	14.8	6.7	-10.3	1.0	2	2
2009	Whole period	2.3	1.0	14.4	2.5	5.7	8.9	82.4	45.6	-5.4	2.2	34	19
	June	1.9	0.8	14.5	3.4	2.6	8.0	106.4	31.6	-3.6	1.1	5	3
	July	2.7	0.9	15.6	2.0	7.5	10.6	126.0	35.9	-4.4	1.1	6	3
	Aug	2.6	0.9	15.2	1.1	8.5	8.6	77.2	18.1	-5.4	1.4	8	6
	Sept	2.2	1.2	13.3	1.3	3.5	6.6	29.9	5.5	-7.2	2.1	11	7
	Oct	2.2	1.4	10.0	1.7	7.1	9.8	13.9	7.5	-10.7	1.3	4	0

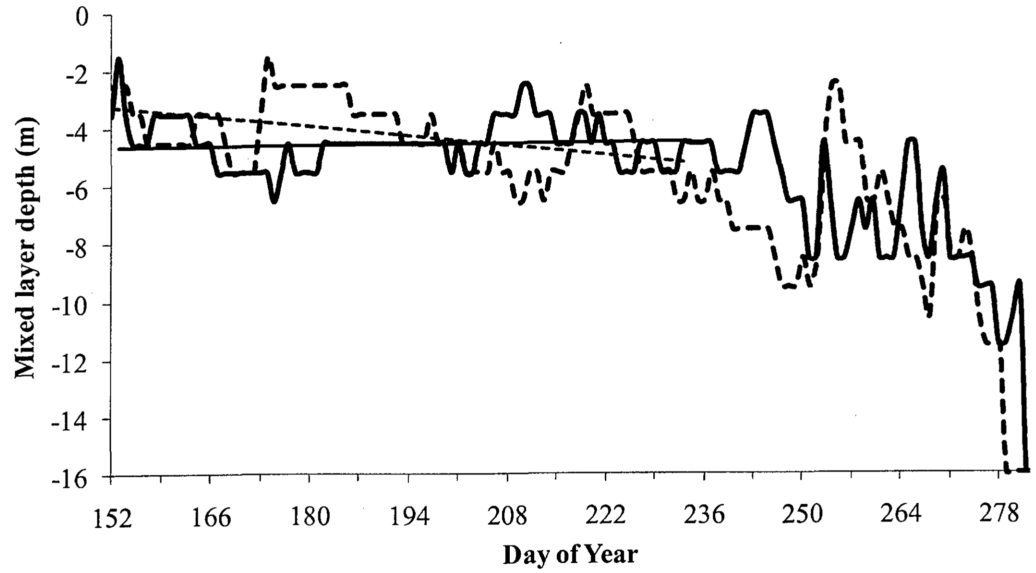

Figure 6.8 Changes in the mixed layer depth in Esthwaite Water over the study period in 2008 (solid lines) and 2009 (dashed lines). Trend lines for 2008 are shown as thin solid lines and in 2009 as thin dashed lines.

6.5 Discussion

6.5.1 Interannual variability

The total SRP loading and the relative contribution of different sources varied between years (Table 6.1, Figs 6.5a and b). This was despite the fact that average forcing conditions for the two study periods were very similar (Table 6.2). Many previous budget or flux studies rely on estimates for single years or are based on assumptions of steady states (Wodka et al. 1983, Stauffer 1987, Marsden 1989, Heinz et al. 1990, Brett and Benjamin 2008), implicitly assuming that loading from different sources is consistent. In addition, many previous studies have only considered the different phosphorus fluxes in terms of total phosphorus (e.g. Larsen et al. 1981, Soranno et al. 1997) and thus may be overestimating the fraction that is bioavailable. It is also interesting that two years with relatively similar average forcing conditions resulted in very different overall SRP loads, emphasising the complexity in the connection between these conditions and the resulting phosphorus supply.

Most of the overall variation in the total SRP load was a result of the differences in the internal anoxic loading in each year, which contrasts with the consistency of the external sources. Interannual variability in this source has also been identified in previous studies of the entrainment pathway and has been qualitatively linked to differences in physical forcing conditions (Effler et al. 1986, Soranno et al. 1997). Year-to-year variation in the loading caused by entrainment of TP from the hypolimnion in Lake Mendota was linked to the frequency of storm events and water column stability (Soranno et al. 1997), where a year with almost twice as many entrainment events led to anoxic supply increasing by a third in the lake. In the present study, the occurrence of more mixing events in 2009 had the opposite effect, with lower overall loading from anoxic sources during that year. The findings of this study suggest that the entrainment of hypolimnetic phosphorus as a dominant supply mechanism is unlikely to be solely dependent on the number of mixing events and maybe more related to the timing of these events during stratification.

This study found that for both 2008 and 2009 where discharges were above the long-term average, internal loading either exceeded or was equal to the external load of SRP in this small lake. It was characterised by distinct high flow event-dominated deliveries in both years, with diffuse sources forming the larger source type (Figs 6.5a and 6.5b). This is unsurprising as diffuse sources are considered to be flow-dependent and are therefore enhanced under higher flow conditions (Bowes et al. 2008). Calculating the loading using the 30-year average discharge levels resulted in external loads being 25% lower than either study year, thus emphasising the likely importance of internal loading during the stratified period in an average year. It might also be expected that the point source supply would usually represent a larger proportion of the external supply. Future climate change scenarios predict that discharge levels are likely to be lower in the summer (Fowler and Kilsby 2007) which will increase the importance of flow independent phosphorus sources such as external point sources or internal loading (Jones et al. 2011).

6.5.2 Variability and uncertainty in flux estimates

The range of estimates for the diffusive flux provides some indication of the potential variation in the contribution of the vertical diffusive supply. Diffusive fluxes of phosphorus in Esthwaite Water ranged from 0.03 – 4.0 mg P m^{-2} d^{-1} across the study years and are similar to those estimated in Lake Constance (0.7 ±0.4 mg P m^{-2} d^{-1}) which assumed a K_z of 4×10^{-6} m^2 s^{-1} (Heinz et al. 1990). In the hypereutrophic

Onondaga Lake the flux was much larger ~4.6 – 4.9 mg P m^{-2} d^{-1}, with similar values of K_z (2×10^{-7} - 6.5×10^{-6} m^2 s^{-1}) (Wodka et al. 1983). Instantaneous values of hypolimnetic K_z have also been found to range over two orders of magnitude (10^{-7} – 10^{-5} m^{-2} s^{-1}) in Esthwaite Water (Miller 2008). In lakes with larger surface areas, where fetch lengths and thus wind energy input will be greater, vertical diffusive mixing may be expected intuitively to be stronger. This implies that the vertical diffusive flux of phosphorus may be relatively more important in such lakes. Understanding the variation in the range of vertical diffusivity is clearly very important in addition to understanding the gradient in phosphorus concentration when calculating the potential SRP load. This study suggests that only doubling or halving the value of K_z may be anticipated to result in a large variation in the SRP load from this source. Vertical eddy diffusion in the hypolimnion is most suppressed during periods of strong stratification and low wind forcing, while it is most enhanced when stratification is weak (Imberger and Patterson 1990). This relates to the inverse relationship between the buoyancy frequency N^2, a measure of stratification and K_z found by Jassby and Powell (1975) in Castle Lake. Examining the Schmidt stability during the two summers in this study suggests that mixing was likely to be more enhanced in 2009 when the stratification was less stable, while lower levels of diffusion would be anticipated in the mid-summer (June, July). This suggests that there is likely to be a trade-off in SRP loading through this mechanism, between high stability – low K_z conditions in lakes where hypolimnetic phosphorus concentrations increase but diffusion is slow and low stability – high K_z conditions where vertical diffusion is relatively fast but hypolimnetic phosphorus concentrations are lower.

The epilimnetic sediment flux result also generates uncertainty, indicated by the near order-of-magnitude range in its estimated values (Table 6.1). This variation implies that the flux can range from being a negligible contribution to the phosphorus budget to an important source. The values of the phosphorus release rate used in these estimates were taken from the literature and all are based on phosphorus release experiments performed under laboratory conditions. This implies that they are likely to be maximum values achieved under near perfect conditions for release and not subject to pH buffering near the sediment in real lakes (Drake and Heaney 1987, Olila and Reddy 1995) or other natural perturbations such as uptake and release cycles by macrophytes or other biota which has been suggested as a highly efficient closed nutrient recycling loop with little external leakage (Carpenter and Lodge 1986). The size of the epilimnetic sediment area in a lake will also be an important determinant of the importance of this process, highlighting the role of lake morphometry. These results emphasise the need for a better understanding of the short term variability in vertical diffusion and epilimnetic oxic sediment release in order to provide a more accurate phosphorus budget.

6.5.3 Importance of fluxes during the study period

As a proportion of the total flux rate, the anoxic loading became more important towards the end of summer and into autumn, when the entrainment flux rate dominated, as the lake began to mix deeply and overturn. This phosphorus source had the largest variability over time, driven by its dependence on the build-up of phosphorus in the hypolimnion and the frequency and occurrence of mixed layer deepening or shoaling. This combination of factors resulted in a relatively small contribution to the total flux between June and August and a dominance in September and October (Fig. 6.7). Clearly, entrainment supply requires a lake to be stratified with associated anoxic release of phosphorus but also for the stratification to be weak enough (or external wind mixing strong enough) to allow mixed layer deepening and entrainment to occur. This process is therefore unlikely to be important in shallow lakes lacking stratification where wind-induced resuspension often dominates (e.g. Søndergaard et al. 1992) or those with oxic hypolimnia. It may however be more significant in large eutrophic systems where hypolimnetic accumulation of phosphorus occurs and stronger wind forcing due to longer fetches results in a weaker stratification.

Conversely, epilimnetic sediment release appears to be relatively more important during the early summer. In lakes with large littoral areas, the release of epilimnetic SRP due to the senescence of macrophytes has been identified as an important additional source during autumn (Landers 1982, Pettersson et al. 2003) this study has not taken this into account. However, as the end of stratification in Esthwaite Water occurs in the early autumn, it is unlikely that the decomposition of macrophytes in the lake will have been far advanced, and therefore we do not consider it to be an important mechanism during the stratified period. The importance of phosphorus supply from macrophyte release will clearly depend on whether it occurs before or after a lake's overturn. Lakes which tend to be stratified into the late autumn and early winter period may result in this release forming an important source for algae which can utilise the higher nutrient concentrations. In lakes where overturn happens before this release occurs, lower light levels and deeper mixing may offset the access that the algae have to these additional nutrients.

6.5.4 Drivers of flux variability

The main cause of the between-year difference in the anoxic load appears to be related to the differences in the build-up of SRP concentrations in the hypolimnion (Fig. 6.7). Although the initial build up was similar in both years, in 2009 the eventual maximum hypolimnetic SRP concentration was less than half that in 2008. Phosphorus has been found to accumulate in the lower hypolimnia of stratified lakes following the onset of anoxia, which has been assumed to occur at dissolved oxygen concentrations <1 mg l^{-1} (Nürnberg 1987) but has also been observed at higher concentrations (Larsen et al. 1981). At the start of the study period in both years, bottom waters were anoxic and SRP followed an approximately linear pattern of accumulation, similar to the patterns observed in other lakes (e.g. Larsen et al. 1981, Wodka et al. 1983, Soranno et al. 1997). In 2009 this increase was not maintained after day 197, after which there was a decline in the mixed layer depth (Fig. 6.8).

The higher number of mixing events during the summer in 2009 compared to 2008 are likely not only to introduce oxygen into the hypolimnion but also to remove some of the accumulated SRP (Nürnberg 1987). This may have prevented the large build-up of hypolimnetic SRP which was seen in 2008 where the mixed layer was more stable. This implies that the timing of mixing events may have a strong control on the importance of anoxic internal loading. Variability in mixing energy have been related to external forcing conditions and the passage of weather fronts in Toolik Lake, Alaska (MacIntyre et al. 2006, MacIntyre et al. 2009). Low stability and greater mixing caused by this pattern of weather in the early summer may prevent large SRP accumulation in the hypolimnion, while a more stable thermal structure will allow the build-up of high SRP concentrations, with the potential for much larger loading in the autumn. Changes to these external forcing conditions due to the effect of climate change such as an increase in drier summers may favour the latter case with potentially significant consequences to the level of phosphorus supply in the late summer and autumn. Similar to the phosphorus release from senescent macrophytes, the importance of SRP loading in the autumn is dependent upon whether the loading associated with mixing at the time of the overturn can be accessed by the phytoplankton prior to the light limitation imposed by the increase in mixed layer depth. Few studies provide direct evidence for the interaction of these opposing influences, however, the increase in late summer phytoplankton biomass was qualitatively linked to the entrainment of hypolimnetic water in Lake Erken (Pettersson et al. 2003). Deeper mixing resulted in no overall reduction in phytoplankton biomass during autumn when the community was dominated by nitrogen-fixing buoyant species in a modelling study of Blelham Tarn (Bernhardt et al. 2008). The relative importance of deeper mixing or nutrient release on phytoplankton growth may be anticipated both to influence and be influenced by the algal community present in the lake.

In this study we have examined a number of the mechanisms and pathways for the supply of SRP to the pelagic, epilimnetic water in a small, temperate lake. Inter-annual variability had an important effect on the total SRP load in the lake each year and much of this was driven by the internal anoxic supply. An important factor in the variation of the anoxic load between years was the level of build-up of SRP in the hypolimnion. The lower SRP build-up in 2009 was related to more mixing events in the early summer, which in contrast to a previous study, did not result in higher loading through entrainment. This illustrates the importance of timing of the physical processes which control anoxic loading. Alterations to these physical processes for example through climatic changes would therefore be expected to have important effects on the potential impact of internal SRP loading in small lakes such as Esthwaite Water.

Chapter 7 Discussion

The overall aim of the work presented in this thesis was to investigate the contribution of heterogeneity within surface waters and sediments to internal phosphorus fluxes and budgets in a small lake (Fig. 7.1). This discussion chapter provides a synthesis of the findings of the research, drawing together the linkages between each of the stand-alone papers under the three general themes of the thesis: heterogeneity, phosphorus sources and physical forcing.

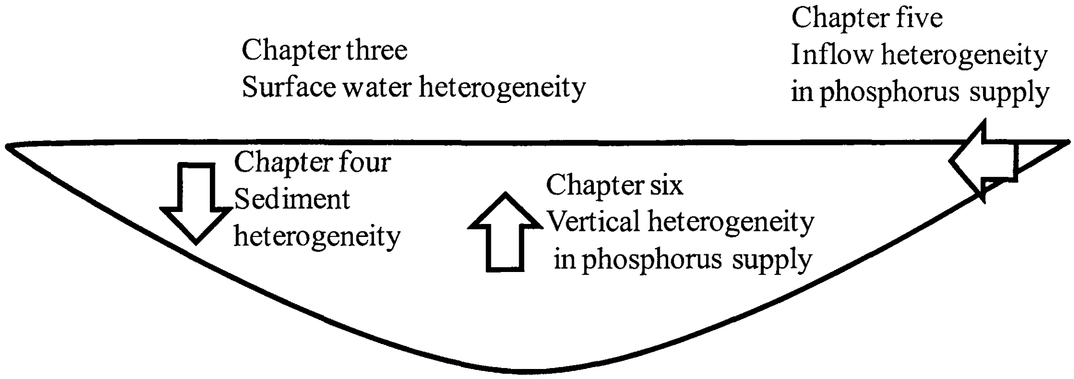

Figure 7.1 Diagram of a lake reflecting the structure of the thesis.

7.1 Heterogeneity

A key characteristic of spatial heterogeneity in lakes are the different scales of pattern which can exist at all levels in the lake (Kratz et al. 2005, Pinel-Alloul and Ghadouani 2007). In the surface waters of Esthwaite Water, small-scale patchiness was present across physical, chemical and biological variables. At the lake basin scale, water depth was found to influence water temperature and fetch influenced chlorophyll *a* concentrations (Chapter 3). In addition, the transition from stream to lake at the main inflow illustrated the dynamic nature of the spatial heterogeneity present, over time (Chapter 5). In the lake surface sediments, different sediment variables were found to have different spatial distributions with overlying water depth. The difference in distribution patterns was related to the particle size and density with which the variable was associated and thus its propensity to be resuspended (Chapter 4). Spatial heterogeneity within this small lake is therefore a distinct characteristic of the lake structure.

These results are likely to be applicable to other small, temperate lakes, as they are largely governed by physical processes. Small lakes have short fetches and are usually subject to relatively weak wind forcing conditions, found to influence the surface water and sediment heterogeneity in this study. In addition, small temperate zone lakes, like Esthwaite Water, are also likely to be subject to moderate heat fluxes resulting in only small temperature differentials between shallow and deep water, restricting the occurrence of convective motions and limiting the influence of these processes on spatial organisation of the chemistry or biology. It may also be anticipated that lakes with shallow water transition zones, frequently a feature of small lakes, are likely to show similar heterogeneity around their inflows as that found in Esthwaite Water. Finally, the temporal variability in the vertical supply of phosphorus, generated as a result of vertical diffusion and mixed layer depth deepening is also likely to be applicable to other lakes which stratify and have anoxic hypolimnia and phosphorus release from the sediment.

In the surface waters, this heterogeneity is much more systematic over the study period than may be implied from previous studies which focus on single events or atypical forcing conditions (Pinel-Alloul et al. 1999, Rinke et al. 2009). This more 'systematic' heterogeneity clearly has implications for our approach in characterising water bodies as part of our efforts to manage and improve lake water quality. This indicates that an appreciation of the physical processes which drive basin-scale patterns should be incorporated into this process. In addition, relatively little is reported about the heterogeneity in phosphorus gradients in the transition zones of lakes or how it might influence whole-lake concentration estimates in a small lake. This study found that the length scale for the transition zone was short and therefore the inflow only had a small influence on the wider lake. However, for soluble reactive phosphorus, this influence became important during the growing season. This suggests that these areas, even within small lakes, should be considered as distinct zones when characterising a lake basin.

Our understanding of the spatial location of processes in the lake environment can provide information on the relative importance of different processes in different types of lakes; this understanding can be used to inform strategies to better manage water quality. An example of this is that embayments around inflows have been found to be periodic sources of algal blooms for the wider lake due to the combination of high nutrient concentrations and sheltered, warm, relatively shallow water (Izydorczyk et al. 2008, Hart and Wragg 2009). Efforts to remove influent nutrient sources which supply these algal blooms and the wider lake have been attempted by the entire diversion of river inflows in an attempt to cut off this nutrient source, however the overall success of such schemes is debated (Welch et al. 1992, Robertson et al. 2000, von Westernhagen 2010).

Spatial heterogeneity in surface sediment distribution has been previously described as zones of erosion/ resuspension, transport and accumulation, defined by the distribution of single, bulk variables, which are then assumed to represent the distribution of all variables (Håkanson and Jansson 1983, Rowan et al. 1992). The use of sediment water content of 50% to represent the transition from erosion/transport to accumulation is based on the study of large lakes. This implies that the whole of Esthwaite Water should be considered an accumulation area, even though the distribution of sediment variables in the lake did not reflect this. The calculation of the accumulation area based on the basin slope of Blais and Kalf (1995), is derived from the empirical regression of the depth of the transition zone against lake depth for a subset of lakes. The transition zone depth was again taken from the distribution with depth of a single variable assumed to represent all other variables. The prediction from this model was also a poor match to the distribution of the different sediment variables measured in Esthwaite Water, implying that it's transferability beyond the lakes used in their study is questionable. Similarly, the equations used to calculate the wave mixed depth and the mud energy boundary depth were originally developed from the study of large reservoirs and lakes (e.g. Beach Erosion Board 1972), which develop much larger waves because they are exposed to much stronger wind forcing due to their large fetches. The expectation from these studies is that the sediment distribution in Esthwaite Water will be a product solely of wave mixing, however the differing distributions of different sediment variables found in this study, suggest that this assumption is incorrect in Esthwaite Water and therefore may also be questionable in other lakes with a similar morphology. These findings also highlight the importance in understanding the distribution of the individual variable of interest, which at a broader level, links to the consideration of heterogeneity for individual variables throughout a lake environment both in the water and sediment.

This principle for surface sediment distribution is demonstrated by the quantification of burial and annual flux-to-bed rates for total phosphorus and organic carbon. An accurate estimate of the total phosphorus flux to the lake bed in Esthwaite Water validated the amount of phosphorus retained in the lake assumed by the steady state phosphorus budget. Taking account of heterogeneity therefore provides us with a clearer understanding of lake processes. Quantifying the amount of phosphorus retained in the lake sediment also has implications for the short-term restoration potential of the lake, relevant to the WFD targets, as internal loading from the sediment can extend the time required for improving lake condition.

Understanding within-lake spatial heterogeneity in organic carbon burial is also important from the perspective of calculating the contribution of lakes to regional or global carbon burial (Downing et al. 2008, Buffam et al. 2011). Our results provide an important context for such studies which typically estimate whole lake burial on the basis of single sites subject to maximum burial rates. This study shows that use of a single site can result in large inaccuracies in the burial rate calculation in a single lake. Extrapolating these results to the global level implies that lake organic carbon burial could be overestimated by 50%.

The implications of this study can also be related to improving our understanding of the ecological sensitivity. A greater awareness of the spatial heterogeneity in sediments and surface waters and the processes which generate this heterogeneity can inform the likely location of biodiversity 'hot spots', around nutrient rich inflow transition zones or in wind sheltered parts of the lake (e.g. Feldmann and Nõges 2007, Léonard et al. 2008). Understanding the impact of wind forcing on the surface waters and sediments may also inform where efforts to restore lakes through macrophyte planting may be expected to be more successful (e.g. Amano et al. 2008), choosing wind sheltered locations and areas with suitable sediment substrates. This study also provides an improved understanding of the dynamic nature of the internal vertical phosphorus supply, which is likely to provide an important source of nutrients to the epilimnetic phytoplankton during the summer growing season. This supply route and the physical structure of the stratification which influences it, is therefore likely to have an important effect on the algal community composition in the surface waters (e.g. Huisman et al. 2004, Berger et al. 2006).

7.2 Phosphorus sources

This thesis has considered both spatial and temporal heterogeneity in the examination and calculation of a number of different source pathways in the supply part of a soluble reactive phosphorus (SRP) budget during the growing season. This is a novel approach, as frequently lake phosphorus budgets are calculated as a mass balance approach using total phosphorus (Vollenweider and Kerekes 1980, Welch and Jacoby 2001). This can provide an annual load but does not provide detail about the bioavailability of the phosphorus or the temporal variability in the different sources and their relative importance during the growing season when they can be utilised by the lake algae. Information on the dynamics of phosphorus sources over time are important for providing a more accurate picture of lake processes which can be used to provide more accurate data for modelling the lake system or understanding which sources to target for remediation.

Gaining insights into temporal-spatial dynamics of external inflow sources of phosphorus provides an important context for understanding how phosphorus from catchment streams meets the lake. The transition zone between catchment streams and lake waters represents the interface for most external phosphorus supply in catchments drained by surface runoff. Few previous studies have considered the transition zone in the supply and dispersal of phosphorus in lakes. In this study, the strong gradient observed across this zone in SRP suggests that it is rapidly dispersed in the lake and available for use by the lake biota. In addition to purely physical mixing processes which are implicitly reported to dominate in this region (e.g. Fischer et al. 1979, Rueda et al. 2007), the results suggested that seasonal biological uptake of SRP by phytoplankton in the transition zone, with potential for their subsequent advection, was an alternative route for dispersal of this source. The seasonality of these processes, relating to discharge levels and the growing season for phytoplankton, highlight that neither phosphorus sources nor the processes acting on them are likely to be static in time.

Internal sources have often previously been ignored or treated as the residual of external sources, however they can often represent a large proportion of the total load (Søndergaard et al. 1993, Soranno et al. 1997). In addition, measured sediment phosphorus release rates (Lee et al. 1977, Nürnberg 1984, Penn et al. 2000), frequently used as an implicit proxy for internal supply, do not account for the isolation of deepwater sediments by lake stratification which can restrict the ability of phytoplankton to access the phosphorus released, as it must be transported into the epilimnetic water. This study has shown that internal sources can represent an important component of the total supply during the growing season. While this may only be confirming the findings of previous studies (Larsen et al. 1981, Soranno et al. 1997), it is an important result from the perspective of lake managers and policy makers who are attempting to achieve real improvements in lake water quality, very little attention in the policy literature has been given to lake internal phosphorus sources and the focus of effort remains in the catchment.

Improving our understanding of inter-annual and sub-seasonal variability in different phosphorus sources provides an important illustration of how dynamic these sources can be over time, calling into question the previous focus on total phosphorus, steady states and single year studies for characterising phosphorus budgets (Wodka et al. 1983, Heinz et al. 1990, Brett and Benjamin 2008). It is clear that while some sources are relatively continuous over the growing season, such as the external sources, others such as anoxic supply are more temporally discrete in their relative importance. In lake systems where phosphorus may be limiting phytoplankton growth, understanding the temporal variability in different phosphorus sources could improve our understanding of phytoplankton population dynamics. Understanding how the importance of different phosphorus sources varies during the growing season, such as the dominance of the internal anoxic supply in the late summer and autumn, and due to differing forcing conditions, has implications for predicting how lakes might respond to a changing climate. Under a warmer climate, it is predicted that summer rainfall will be less in the UK, which is likely to reduce the importance of external diffuse phosphorus sources during the summer time (Jones et al. 2011), whilst stratification is predicted to start earlier and last for a longer period of time (Hondzo and Stefan 1993), which may enhance oxygen depletion and hypolimnetic anoxia therefore potentially resulting in more phosphorus release from sediments (Malmaeus et al. 2006, Jeppesen et al. 2009). Whether and how this phosphorus might reach the epilimnion before lake overturn is far from clear given the trade-off between mixing and stratification.

Understanding phosphorus dynamics between the water and sediment at different temporal and spatial scales is particularly important during the summer growing season because soluble phosphorus tends to be limiting algal growth in the epilimnion. Therefore the sources and timing of phosphorus supply from the inflows, via the transition zones and hypolimnion can enhance algal productivity. The research in this thesis shows that areas such as the transition zones and the hypolimnion can act as 'hot spots' of phosphorus supply and the supply from these sources is controlled by temporally variable physical mechanisms of hydrological dilution, vertical diffusion and entrainment.

The overall significance of the research in this thesis for catchment and lake managers is that restoration efforts on small lakes like Esthwaite Water require an understanding of the internal dynamics of the lake system. The catchment and lake need to be viewed holistically, in that we not only need to appreciate the delivery of nutrients and sediments from the catchment but also appreciate their fate and likely impact once they have entered the lake. The spatial and temporal heterogeneity found within the surface waters and vertical phosphorus supply processes suggested by this study could have implications for the sighting of water intakes and the timing and depth of water abstraction in a reservoir context or the location of monitoring sites. Small lakes are important sites for biogeochemical processing of material; focusing and burial rates of sediment have important implications not only in these sites but also in reservoir systems where sedimentation can have serious impacts on the viability of the water supply (e.g. Morris and Jiahua 1998, Mau and Christensen 2001). Phosphorus once stored in the sediments, presents a legacy effect for lake restoration. Release under anoxic conditions and the diffusion and entrainment pathways can maintain phosphorus concentrations potentially well above the concentrations required by the phytoplankton.

7.3 Physical forcing conditions

Many of the previous studies in lakes of abiotic, physical drivers of spatial heterogeneity in surface waters have tended to focus on intense and episodic physical events or large scales in large lakes (Pinel-Alloul et al. 1999, Thackeray et al. 2004, Rinke et al. 2009). Similarly, much of the previous work to elucidate the processes contributing to surface sediment heterogeneity have been carried out in large or shallow lakes where wave-driven resuspension and downslope gravitational transport has been found to dominate (Håkanson 1977, Carper and Bachmann 1984, Blais and Kalff 1995). In addition, much of our understanding of transition zone dynamics comes from the study of large, deep river-lake interfaces where physical processes resulting in vertical flow structuring are considered to dominate (Carmack et al. 1979, Fischer et al. 1979, Stevens et al. 1995, Vidal 2006). The results from this study on a small lake suggest that even the relatively weak forcing conditions were sufficient to generate horizontal spatial heterogeneity in the surface waters. However, the predicted sediment focusing processes from large or shallow lakes were not significant in this small, moderately deep lake and the transition zone in a shallow water embayment, often common in small lakes, was not subject to the same physical processes as that of large deep transitions and mixing by dilution was considered to be more important.

The key difference between the processes observed in small and large lakes, for the surface water and sediment heterogeneity appears to relate to the strength of the wind forcing conditions experienced by lakes of different sizes. On large lakes, the larger fetches result in higher wind speeds and the development of larger waves, which have a greater influence on the distribution of sediment. On a small, relatively deep lake, like Esthwaite Water, the wave influenced zone is small compared to the overall depth of the lake due to the small fetch. In a similar way, the lower wind speeds recorded over the lake did not result in the thermocline tilting and up- and downwelling effects observed for larger lakes but did cause some surface advection of buoyant phytoplankton. These findings suggest that the forcing conditions experienced by small, temperate lakes such as Esthwaite Water are likely to influence the lake in a different way to the effects seen in large lakes, and thus assumptions made about how these processes scale should be re-examined.

For example, while the lake heat flux resulted in the differential heating of shallow waters in this lake, it did not impact on the other variables in Esthwaite Water. However, convective motions generated by differential heating are frequently observed in lakes at lower latitudes where they can have a much larger influence on lake function (Monismith et al. 1990, Verberg et al. 2011). Similarly, fetch-related organisation of chlorophyll is reported in large lakes or under stronger forcing conditions to relate to an epilimentic 'conveyer' resulting in up- and downwelling of the thermocline, resulting in a strong horizontal temperature gradient (Blukacz et al. 2009, Rinke et al. 2009). In this study, the high Wedderburn numbers indicated that the thermocline was stable and there was no temperature gradient, thus the resulting pattern was due simply to the downwind advection of buoyant plankton.

Although the established sediment focusing processes of slopes and wave mixing were not important in Esthwaite Water, we found that small particles could be resuspended at all depths in the lake and calculated that wind-induced current speeds were sufficient to do this. This mechanism has previously been neglected in studies of sediment focusing and yet our study suggests that it may represent an important focusing mechanism in small lakes. Small lakes typically have small fetches and as a result waves are small and predicted wave mixed depths are shallow even when predicted using maximum wind speeds. The hydrological dilution in the shallow stream-lake transition zone of this study, also illustrates how physical forcing processes may vary between large inflows in deep water, and those in shallow water, characteristic of small lakes. These differences are likely to affect the area of influence that a transition zone might have on the wider heterogeneity of the lake. Large lakes are higher energy environments than small lakes (Fee et al. 1996) and therefore it is probably unsurprising that the physical processes occurring in small lakes are weaker and result in different effects on the lake environment. The findings of this thesis emphasize the importance of basin morphometry in small lakes, as a determinant of fetch, in the influence of physical mixing processes in both typical conditions and as a maximum wave mixed depth. These mixing processes in turn then go on to affect the heterogeneity of both the surface waters and sediments.

In addition to spatial heterogeneity, physical forcing processes also influence temporal patterns in phosphorus supply. Both external and internal phosphorus sources show strong variability over time, determined by the influence of discharge, stratification and mixing events (Effler et al. 1986, Soranno et al. 1997). The results of this thesis suggest that the evolution and overall importance of internal phosphorus loading from the anoxic hypolimnion may be strongly dependant on the strength of stratification and the number of mixing events which occur during the early summer period. This implies that understanding the balance of buoyancy and mixing forcing over the course of the summer is important for interpreting variations in phosphorus supply at an inter-annual level. Previous research suggests inter-annual variability in mixed layer depth is greater in large than small lakes (Fee et al. 1996), however, although large lakes are also subject to higher levels of turbulence than small lakes, it is unclear how this size dependence of mixing affects vertical fluxes of phosphorus on an inter-annual level (Fee et al. 1994). The findings of this thesis, at a higher temporal resolution to these previous studies, show that mixing events are highly temporally variable over the summer in the small study lake. This has a consequent effect on the inter-annual variability in phosphorus supply and it is therefore likely that similar variability in mixing processes in other small lakes will influence variability in their phosphorus budgets.

Chapter 8 Conclusions

The four research papers presented in this thesis have demonstrated the importance of considering spatial and temporal heterogeneity in surface waters and sediments when calculating phosphorus fluxes and budgets in a small lake. The main conclusions and implications of the work are detailed below.

Heterogeneity, and in particular spatial heterogeneity, was found to be a distinct characteristic of the small lake both in the surface waters and sediments. Heterogeneity was present from small scale patchiness to basin scale patterns relating to physical processes in the lake. The spatial heterogeneity was also found to be subject to different temporal dynamics, with 'systematic' patterns in sediments and surface waters and seasonal effects detected in phosphorus patterns at the inflow transition zone and in internal lake sources of phosphorus. Understanding this heterogeneity is important as it affects our understanding of the spatial location of processes, how we estimate lake-wide concentrations of phosphorus and other variables and how we estimate annual sediment burial which has potential implications for estimates of global fluxes of material.

Phosphorus sources are both temporally and spatially variable, particular sources have distinctly different patterns of variability, both on seasonal and inter-annual timescales. External sources of phosphorus from the catchment inflows on a seasonal scale were driven by short-term variations in discharge, however at an inter-annual scale, overall fluxes for the stratified period were similar. In comparison, anoxic sources from sediments in deep water showed a similar seasonal trend in phosphorus supply, being low in the early summer and peaking in the late summer and autumn but large inter-annual variability in overall flux. This variability has implications for improving our understanding of the processes responsible for phosphorus supply and the assumptions made when calculating phosphorus budgets.

The influence of physical drivers on the internal anoxic phosphorus supply appears to relate to the timing of mixing events across the thermocline and the strength of stratification. Unfortunately, it was not possible in this study to fully resolve how these effects directly influence deep water oxygen concentrations, redox conditions and phosphorus concentrations. Physical forcing within a small lake can be expected to be relatively weak; however this forcing is still likely to influence spatial heterogeneity in different regions such as the sediments, inflow transition zones, shallow and deep water and up- and downwind areas of the lake. The importance of particular physical processes may differ between large and small lakes owing to the influence of basin morphometry on fetch and water depth. Wave mixing has a smaller effect in small, relatively deep lakes because their fetch is short relative to the water depth, therefore the established explanation for sediment focusing as being a wave driven process may not hold in all lakes.

8.1 Prospects for future work

A number of suggestions for possible future research have developed from the insights gained by this thesis. These suggestions extend the work done in this thesis by increasing the range of trophic levels, variables and seasons considered, increasing the resolution of measurement to better resolve processes and making more linkages between the physical, chemical and biological processes in the context of a changing environment. The following section details these suggestions.

This thesis found evidence for a ‘systematic’ heterogeneity within surface water during the study period among physical, chemical and biological variables. This work could be further extended to examine whether this heterogeneity persists over other seasons or periods of physical change such as the spring during the development of stratification or autumn as stratification begins to breakdown. It would also be interesting to examine heterogeneity within higher trophic levels such as zooplankton and fish in relation to the patterns of physical forcing and the effects of heterogeneity found within the chlorophyll *a* and this too may necessitate the consideration of other time periods such as the spring zooplankton population peak or night time surveys.

The findings of this thesis suggest that theoretical wind-induced currents are capable of the resuspension of small particles at all depths in the lake. The logical test of this theoretical finding is the in-situ measurement of both water currents and sediment resuspension in a small lake. Most studies of this kind are carried out in large lakes and few direct current measurements or the quantification of their effect on sediment are available for small lakes.

To get a better understanding of the biological influence on phosphorus in the inflow transition zone, additional data is needed to develop a phosphorus and chlorophyll *a* gradient to discharge relationship. In addition, direct measures of biological productivity and phosphorus uptake and species composition both in the water and on the sediment surface across space would provide an indication of how active an area the transition zone is for phosphorus cycling.

In order to resolve some of the uncertainties which exist in the contribution of epilimnetic phosphorus release and cycling, high resolution measurements of phosphorus and water currents are required in order to develop relationships with measured hydrodynamic processes occurring over the diel cycle. Improving our understanding of the variability of hypolimnetic phosphorus supplies also requires the measurement of high resolution phosphorus and dissolved oxygen concentrations in order to link the vertical mixing processes to the response in the deep water of the lake.

Very few studies have been able to directly link the phosphorus flux in the late summer and autumn to changes in phytoplankton biomass and community composition, even though it is often implicitly assumed to be the mechanism for a late summer phytoplankton peak in eutrophic lakes with anoxic hypolimnia. It is unclear whether this mechanism is important for all such lakes or whether the breakdown of stratification and deeper mixing cancel its effect in some lakes and that the timing of overturn is important. This area warrants more attention because often the dominant species of phytoplankton at this time of year are the potentially harmful cyanobacteria. The final recommendation for further research is understanding what the effect of prolonged stratification, which develops earlier and persists later into the autumn, predicted to occur with climate change, is likely to have on the anoxic supply of phosphorus given the potential trade-offs between mixing and stability found in this thesis.

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