

**Carbon fixation, flux and burial efficiency in two contrasting
eutrophic lakes in the UK (Rostherne Mere & Tatton Mere)**

by
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THE ROSTHERNE BELL

By D. Watts Russell

Merrily, merrily, over the Mere,
The echoes rose and fell;
Rose on the breeze, fell on the ear,
Dingdong the Rostherne bell.

On buttress old, and crumbling stone,
The masons plied their trade,
Repaired the courses overthrown,
The rents that time had made.

When, lo! from battlement to base
A shivering shakes the steeple;
Down drops the big bell from its place,
Right in among the people!

Down the steep bank that crowns the lake
It crashed, and leapt, and rolled,
Through birch-wood copse, and briar, and brake,
And 'mid the Lindens old.

Till on the margin of the Mere,
'Tis fain at length to settle,
Exhausted by its mad career,
That ponderous mass of metal.

But oh the sweat, and oh the toil,
The strain of the muscles' power,
The bursting sob, the weary coil
To try it back to the Tower!

Quoth one in wrath: 'Thou senseless lump,
I would the devil had you!'
When at the word, with a spring and a thump,
Back towards the lake it flew.

First, in its headlong course, it crushed
Th' unlucky wight who swore,
Then down the bank it madly rushed
They never saw it more.

In depths unfathomable drowned,
No more that tuneful tongue
Shall greet the ear with cheerful sound
At morn or even song.

And now whenever peal the bells
From Rostherne's tower so hoary,
The wailing sound too plainly tells
Of its departed glory.

ABSTRACT

Much of the current research into the processing and storage of carbon (C) in small lakes has focused on arctic and boreal lake systems, due to their global abundance. However this has led to an imbalance in the interpretation of lake functioning. Oligotrophic lakes are prevalent in the arctic and boreal zone, but are typically net heterotrophic due to loading of catchment-derived dissolved organic carbon (DOC) which alters their metabolic balance. In comparison, temperate lake systems tend to be more nutrient rich, typically due to anthropogenic activity, and would therefore be expected to exhibit the signs of net autotrophy, as a result of higher rates of gross primary production (GPP) and lower rates of catchment-derived DOC potentially subsidising respiration (R).

In order to test the hypothesis that temperate, eutrophic lakes are net autotrophic ($GPP > R$) on an annual basis the C-dynamics of Rostherne Mere (maximum depth, z_m , 31 m) and Tatton Mere ($z_m = 11$ m), two monomictic Cheshire-Shropshire meres, were quantified over an 18 months period from 2010 – 2012. This monitoring study used high-resolution (hourly) oxygen (O_2) sonde measurements, combined with high-resolution data from an automated on-lake monitoring buoy at Rostherne Mere (as part of the national UKLEON lake network) to calculate rates of epilimnion C-fixation. For both lakes, sediment traps were also used to determine water column C-flux and sediment core data to establish C-burial efficiency of these strongly stratifying lakes. Water column profiles of dissolved O_2 and CO_2 was also measured at 2 – 4 weekly intervals across both lakes. Particular attention was focused on: i) the long term C-storage of eutrophic, monomictic lakes; ii) up-scaling C-accumulation estimates from these two meres to the Cheshire-Shropshire meres region and all UK eutrophic waters; and iii) methodological sensitivity for estimating C-fixation, flux and burial efficiency and upscaling C-accumulation estimates. The results show that both lakes are net autotrophic on an annual basis, on average fixing 121 ± 2 g C $m^{-2} yr^{-1}$ and sequestering 68 ± 4 g C $m^{-2} yr^{-1}$, a C-burial efficiency of ~60%.

If up-scaled to the Cheshire-Shropshire meres region, annual C-accumulation was estimated to be 506 ± 32 t C yr^{-1} or 0.05 ± 0.001 Mt C since 1900. From this, it was estimated that UK eutrophic waters could be sequestering 0.12 ± 0.01 Mt C yr^{-1} or 13.3 ± 0.2 Mt C since 1900. Annual UK CO_2 emissions are ~ 128.85 Mt C yr^{-1} , therefore UK eutrophic waters currently offset 0.09% of yearly UK CO_2 emissions.

Despite the finding that eutrophic, stratifying lakes have high C-fixation and sequestration values, lakes in other areas of the globe such as the arctic and boreal zones are typically a more important long term C-sink as they are far more abundant within the landscape and local soils are typically very poor within low C retention rates. Further investigation is needed into how lakes function on a regional and national scale, the importance of lake type and number when up-scaling C accumulation estimates and the potential impact on future C accumulation as a result of a changing environment and supra-regional policies in areas such as Europe.

Keywords: limnology, carbon cycle, lake metabolism, autotrophy, heterotrophy, eutrophication, lake sediments, temperate, high-resolution monitoring, Rostherne Mere, Tatton Mere.

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1.1 RESEARCH IN CONTEXT

The Earth's climate is regulated by complex chemical, physical and biological interactions between the atmosphere, terrestrial biosphere and hydrosphere. These processes are extremely sensitive to change, particularly within the atmosphere, through either natural or anthropogenic emissions of gases and aerosols and can produce feedbacks to the climate system (Denman et al., 2007). The global carbon cycle has a vital role within the climate system as it incorporates terrestrial, aquatic and atmospheric processes.

The natural carbon cycle is driven through the continuous exchange of large volumes of carbon, particularly in gaseous forms CO_2 and CH_4 , between the atmosphere, terrestrial biosphere and hydrosphere. For the last ~10,000 years this natural system has largely maintained stable concentrations of atmospheric gases, however since ~1750, anthropogenic burden of this system has led to the natural cycle being perturbed by human activities such as increases in fossil fuel emissions and land cover change, which releases previously captured carbon back into the atmosphere, see Figure 1.1 (Denman et al., 2007; Prentice et al., 2001). Currently, the rate of anthropogenic CO_2 emissions are outpacing the storage potential of the natural carbon cycle, leading to global levels of atmospheric CO_2 to rise steadily from around $275 \mu\text{mol mol}^{-1}$ in 1750 to approximately $390 \mu\text{mol mol}^{-1}$ in 2011 (NOAA, 2013). There is currently an upward trend of around $1.9 \mu\text{mol mol}^{-1}$ a year, the largest growth rate observed since continuous direct atmospheric measurement began. Prior to industrialisation decadal and centennial changes in atmospheric CO_2 variations were less than $10 \mu\text{mol mol}^{-1}$ and most likely due to natural processes (Figure 1.2).

The rate of global atmospheric CO_2 change is however not stable as short-term, interannual variations in the rate of atmospheric CO_2 concentration change are primarily controlled by changes in the flux of CO_2 between the atmosphere and the terrestrial biosphere, with a smaller but significant fraction due to buffering on the oceans. The variability in the terrestrial flux with the atmosphere is driven in

response to climatic fluctuations in temperature, precipitation, CO₂ and nutrient availability. If the climate was to become more favourable for growth, the likelihood is that productivity increases and carbon uptake from the atmosphere is enhanced through the uptake of CO₂ by plants and the return of CO₂ to the atmosphere by the decay of organic material. El Niño-Southern Oscillation (ENSO) events are also a major source of interannual variability in atmospheric CO₂ concentration, as they affect the interaction between biospheres through changes to land and sea surface temperatures, precipitation and the increased incidence of fires (Denman et al., 2007; Prentice et al., 2001).

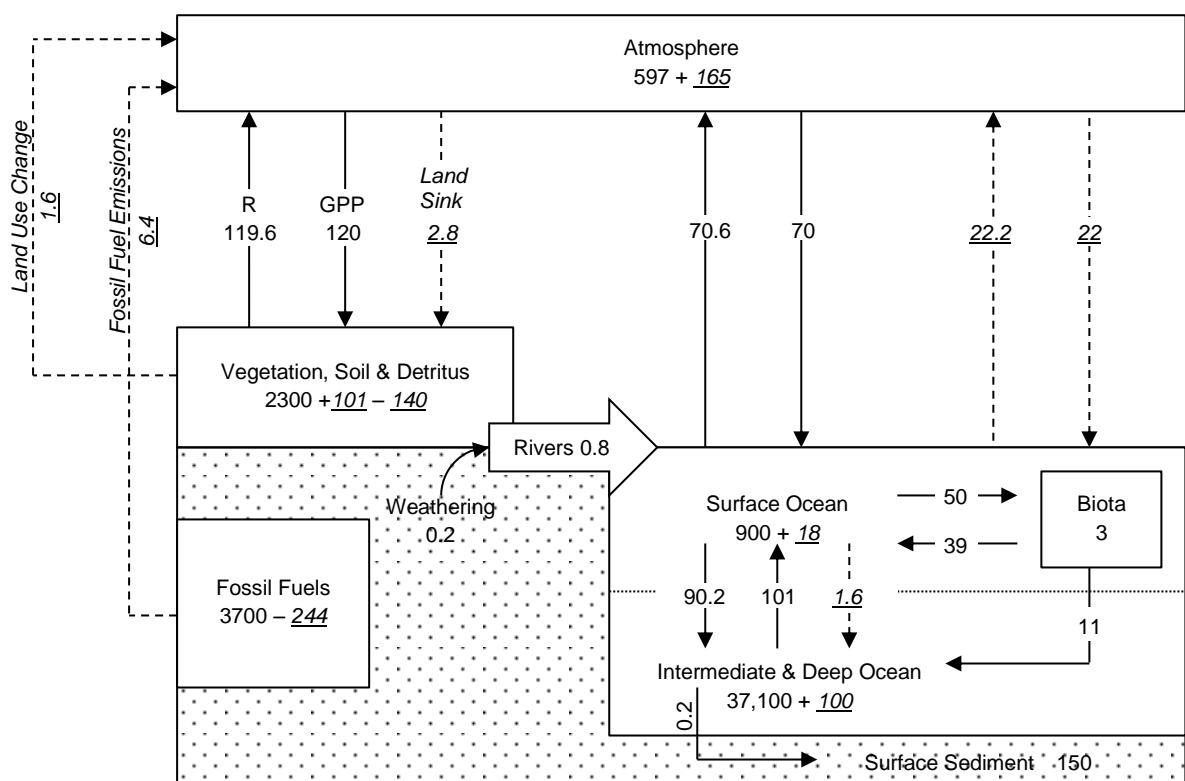


Figure 1.1 The global C cycle for the 1990s, showing the main annual fluxes in GtC yr⁻¹. Pre-industrial ‘natural’ fluxes are solid lines and ‘anthropogenic’ modifications and fluxes are dashed lines, italics and underlined (modified from Denman et al., 2007)

After entering the atmosphere about 50% of anthropogenic CO₂ remains trapped here, whilst about 30% is taken up by the oceans and the remainder utilised in the terrestrial biosphere. The majority of the anthropogenic CO₂ pulse retained in the atmosphere is removed within 30 years; a further 30% is removed within a few

centuries; and the remaining 20% will typically stay in the atmosphere for many thousands of years (Denman et al., 2007). Increasing levels of CO₂ within the atmosphere can have a negative feedback effect on the climate as a consequence of enhancing the natural greenhouse effect within the earth's atmosphere where water vapour and CO₂ trap surface reflected, long wave radiation within the atmosphere which is then re-radiated either into space or back toward the earth's surface (Lockwood, 2005). Carbon uptake and storage in the terrestrial biosphere arises from the net difference between carbon uptake by vegetation growth, reforestation and soil sequestration, and carbon loss due to heterotrophic respiration, deforestation, fire, pollution and other disturbance factors affecting biomass and soils (Solomon et al., 2007).

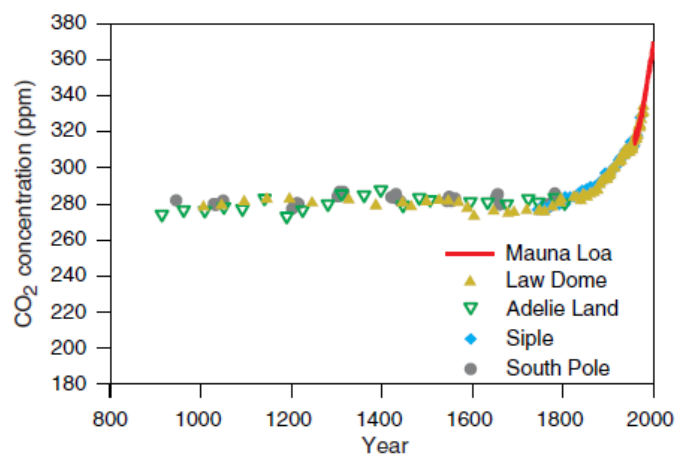


Figure 1.2 Atmospheric concentrations of CO₂ over the past 1,000 years. Ice core and firn data for several sites in Antarctica (shown by different symbols) are supplemented with the data from direct atmospheric measurements at Mauna Loa (red line) over the past few decades (Prentice et al., 2001).

Similarly to increases in atmospheric CO₂ concentrations global average surface temperatures have increased significantly during the 20th Century, especially since 1950, see Figure 1.3. The rate of warming over the last 50 years (0.13°C ± 0.03°C per decade) is nearly twice that for the last 100 years trend with most of the observed increase in global average temperatures since the mid-20th century being very likely due to the observed increase in anthropogenic greenhouse gas concentrations (Solomon et al., 2007). The most prominent effects of increasing temperatures are reduced terrestrial and ocean uptake of atmospheric CO₂, increasing the fraction of anthropogenic emissions remaining in the atmosphere.

This positive carbon cycle feedback leads to larger atmospheric CO₂ increases and greater climate change with increased emissions, but the strength of this feedback effect varies markedly among current climate models (Denman et al., 2007; Solomon et al., 2007).

Warming over the last few decades is widespread across the globe and has been faster over land regions than the oceans, but due to the distribution of continental landmass is greatest at higher northern latitudes. There is evidence to suggest long term changes in large scale atmospheric circulation, such as strengthening westerly winds and modification of the North Atlantic Oscillation (NAO), influencing regional climate trends and weather patterns where there are strong interactions with the atmosphere, oceans and other components of the climate system (Trenberth & Jones, 2007).

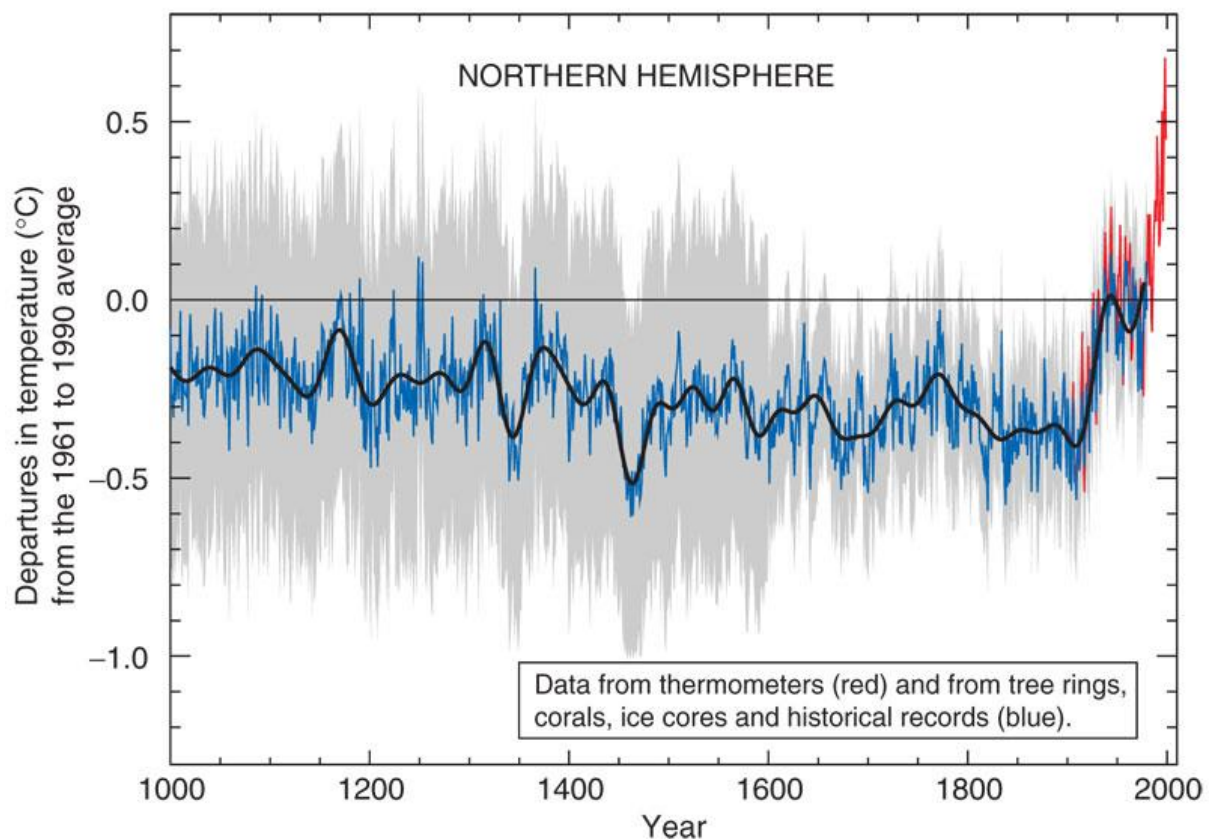


Figure 1.3 Millennial Northern Hemisphere (NH) temperature reconstruction (blue) and instrumental data (red) from AD 1000 to 1999. Smoother version of NH series (black), and two standard error limits (gray shaded) are shown (Houghton et al., 2001).

The increase in global atmospheric CO₂ levels leads to both positive and negative feedbacks to the carbon and climate system as a result of biogeophysical and biogeochemical processes in terrestrial and aquatic systems. Changes in the rate of terrestrial photosynthesis and plant productivity respond to variations in temperature, precipitation and nutrient availability. If climate conditions become more favourable for growth, productivity increases, and carbon uptake from the atmosphere and storage in the terrestrial system is enhanced. Land-use changes however, such as deforestation, lead to loss of carbon from vegetation and soils. Even so, the current global balance in terrestrial systems is a net uptake of CO₂ (Cole et al., 2007; Prentice et al., 2001; Dean & Gorham, 1998). Changes to productivity in aquatic systems are more complex however, as CO₂ does not significantly limit photosynthesis in the oceans. Other physical and biological factors such as light availability, temperature, nutrient availability and competition have much greater influence on organisms, meaning anthropogenic carbon is not directly taken up and stored. However, considerable volumes of CO₂ can be buffered within the water column through the dissolution of calcium carbonate (CaCO₃) from the deep ocean (Denman et al., 2007).

Table 1.1 The organic carbon burial rates in lakes and oceans gathered from a range of sources. Lake types studied denoted by o = oligotrophic, m = mesotrophic, e = eutrophic and r = reservoir.

	Source	Lake types studied	Burial rate (g C m ⁻² yr ⁻¹)	Total burial (Tg C yr ⁻¹)
Oceans	Dean & Gorham (1998)	-	-	97
~71% Surface	Denman et al. (2007)	-	-	100
	Dean & Gorham (1998)	o m r	14	42
All Lakes	Stallard (1998)	o m r	4.5	-
~0.6% Surface	Einsele et al. (2001)	o m e r	-	69
	Cole et al. (2007)	o m e r	-	50
Small Lakes (< 500 km²)	Mulholland & Elwood (1982)	o	27	-
	Dean & Gorham (1998)	o m	72	23
~0.2% Surface	Einsele et al. (2001)	o m e	40	48

Despite the importance of terrestrial and atmospheric carbon cycling most of the research investigating the response of natural systems to projected anthropogenic CO₂ rises has been focused on the oceans because they provide the largest

potential global carbon sink (Cole et al., 2007; Downing et al., 2006; Einsele et al., 2001; Dean & Gorham, 1998). More recently a number of authors have begun to explore the huge potential of lakes for carbon storage. However, there are significant variations in the estimates given for lake C-dynamics from these studies, largely due to the variability of lake productivity. This variability is typically as a result of lake type and trophic status, lake size, the number of lakes within different studies and an incomplete understanding of lake metabolism (Table 1.1).

1.2 THE CARBON CYCLE IN LAKES

Compared to the world's oceans, small lakes (typically < 500 km²) only cover approximately 0.2% of the earth's surface yet are estimated to sequester anywhere between 23 Tg (x10¹² g) and 48 Tg of organic carbon each year, the equivalent to 1/3 of annual ocean carbon burial (Table 1.1). This disproportionate processing of carbon in small lakes makes them a potentially meaningful component of the global carbon cycle.

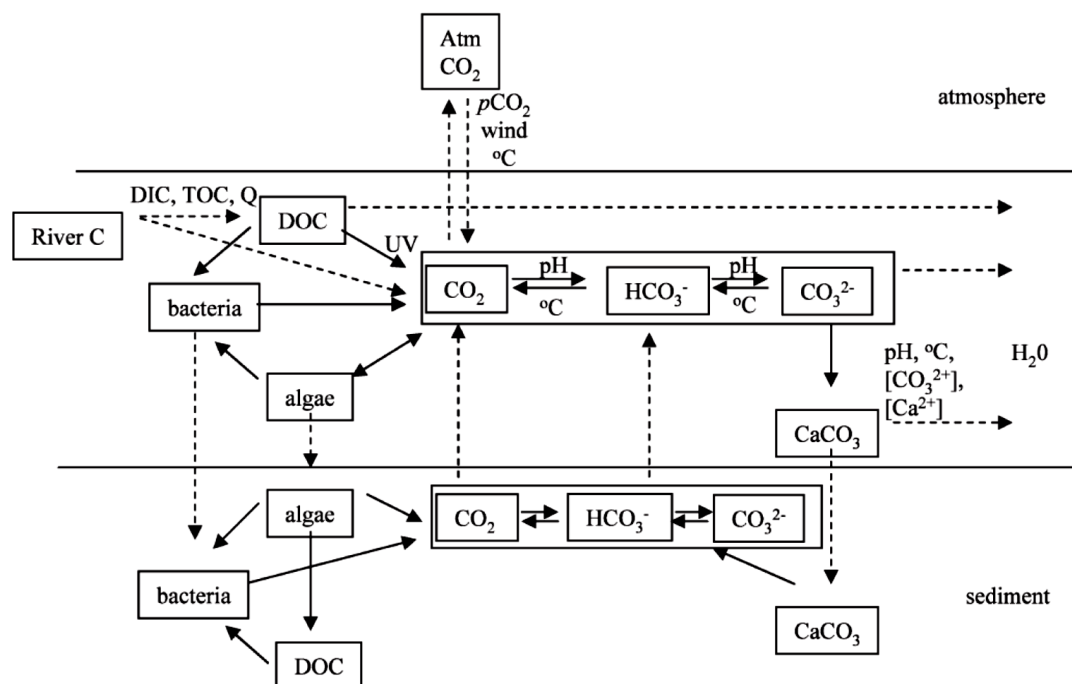


Figure 1.4 A simplified conceptual diagram of carbon flux in lakes. Carbon pools (boxes); exchanges (dashed arrows); conversions (solid arrows); processes (labelled on solid arrows) (Finlay et al., 2009).

Figure 1.4 shows a typical open-basin lake system which has interactions with the terrestrial system and atmosphere. Until recently, however, this view of lakes was not widely held as inland waters were considered passive transporters of organic and inorganic carbon from the land to the ocean. This attitude has been challenged by a number of authors (Tranvik et al., 2009; Cole et al., 1994, 2007; Downing et al., 2006) and it is now widely accepted that inland waters, especially lakes, are active components of the global carbon cycle that processes terrestrially derived carbon for storage in sediments, emission to the atmosphere or export to the oceans (Figure 1.4).

1.2.1 Organic Carbon

Organic carbon available in lakes and rivers is generally composed of either dissolved or particulate matter. The most abundant fraction of the organic pool is DOC and plays an important role in the aquatic carbon cycle and energy balance. DOC is a primary food source in the aquatic food web and an essential part of the acid-base chemistry of many low-alkalinity freshwater systems forming water-soluble complexes with trace metals, aiding their mobility and transport from terrestrial systems to the ocean (Pace & Prairie, 2004; McKnight et al., 2003; Wetzel, 2001). DOC is arbitrarily defined from POC, for the purpose of scientific study, as any fraction below 0.45 μm , typically as the result of filtration.

Typically aquatic systems contain a combination of allochthonous (terrestrially derived) and autochthonous (photosynthetically produced) organic carbon. Carbon sourcing is known to have significant impact on lake functioning and can impact pH, metal binding and subsequent availability of organic compounds (Scott et al., 1998; McKnight et al., 1992). The instantaneous measurement of DOC and POC has been found to be highly biased towards recalcitrant compounds that are resistant to microbial decay. These compounds persist in inland waters for longer periods than more labile components which are utilised more rapidly because they are typically more biologically available (Bass et al., 2010; Wetzel, 2001).

1.2.1.1 Allochthonous Organic Carbon

Characteristically, the majority of allochthonous organic carbon that enters the aquatic environment is plant matter. In general this plant matter enters rivers and

lakes as decomposed dissolved organic compounds, which has been broken down in-situ or the upper horizons of the soil, that it is resistant to further rapid microbial degradation (Wetzel, 2001; Del Giorgio & Cole, 1998). On entering the lake, either from a river channel, through run-off or groundwater flow, DOC is gradually broken down by photochemical or biological processes to DIC and POC (Wetzel, 2001; Stumm & Morgan, 1981), with the resulting CO₂ and CH₄ typically being released to the atmosphere and the particulate matter transferred to the sediments. Further degradation of DOC also releases bound nutrients such as P and N, increasing their bioavailability (Porcal et al., 2009; Wang et al., 2000). It has been well documented that detrital DOC and POC constitutes a much greater percentage of organic matter within a lake than living matter because the decomposition of organic matter releases carbon, energy and nutrients into the ecosystem (Hanson et al., 2003; Houser et al., 2003; Cole, 1999; Tranvik, 1992; Wetzel, 1992).

1.2.1.2 Autochthonous Organic Carbon

Autochthonous DOC has several origins including photosynthetic inputs of the littoral and pelagic flora through secretion and autolysis of cellular contents, the excretion of DOC by zooplankton and other higher animals and the bacterial chemosynthesis of organic matter with a subsequent release of DOC (Wetzel, 1983). Phytoplanktonic DOC is typically colourless and composed of carbohydrates and amino acids that can be rapidly metabolised by bacteria (Søndergaard et al., 1995; Wright, 1970). Aquatic macrophytes in the littoral zone also release DOC in amounts comparable to that released by phytoplankton (Wetzel, 1990; Wetzel & Manny, 1972). However, decomposition of these labile compounds is often very rapid meaning they constitute only a small proportion of DOC in natural waters (Gergel et al., 1999).

1.2.1.3 Distribution of Organic Carbon

Levels of DOC and POC within a lake system are often extremely stable from year to year (Fukushima et al., 1996), aside from small seasonal fluctuations observed in the surface waters. For DOC this is most often attributed to the highly recalcitrant compounds that are slow to decompose and are typically balanced by inputs of similar compounds into the lake. Highly labile organic matter, usually produced by phytoplankton, is difficult to monitor as its breakdown is extremely rapid and would

not be revealed by a standard sampling frequency such as weekly or monthly (Wetzel, 2001).

Observed levels of POC equally follow a seasonal pattern of distribution, mostly following the productivity of phytoplankton during periods of stratification. In more productive or eutrophic lakes large spikes in POC build in the hypolimnion during summer months as large inputs from the epilimnion renders it anoxic and intensified bacterial productivity causes increases in POC.

The ratio of DOC:POC has been observed to be consistent at around 10:1 in oligotrophic to mesotrophic lakes (Sobek et al., 2006; Hanson et al., 2004), however, this figure is more variable in eutrophic lakes as the DOC:POC ratio fluctuates with season and depth and can be anything from 1:1 during high productivity months to 10:1 in winter (Wetzel, 2001; Hanson et al., 2004).

1.2.2 Lake Metabolism

Traditionally, lake monitoring and research has explored nutrient cycling, chiefly phosphorus and nitrogen enrichment (Kalf, 2001; Wetzel, 2001). Such enrichment is responsible for modifying the productivity regime within lakes, shifting them from unproductive or oligotrophic towards productive or eutrophic systems. More recently, quantifying rates of primary production and respiration, and the relative dominance between the two, has become critical to understanding energy flows and nutrient cycling (Figure 1.5). These developments have led to a growing literature on the metabolism of small lakes (Tranvik et al., 2009; Sobek & Tranvik, 2005; Hanson et al., 2003; Prairie et al., 2002).

Primary production and respiration are the major metabolic pathways by which organic matter is produced and transformed within lake systems. GPP is the total fixation of inorganic carbon by any organism photosynthesising within a system and R is the remineralisation of any system organic carbon to CO₂. Net ecosystem production (NEP) is the difference between GPP and ecosystem R and can be used to represent the overall metabolic balance of an ecosystem (Equations 1.1 and 1.2).

$$\text{NEP} = C_{\text{storage}} + C_{\text{export}} - C_{\text{import}} \quad (1.1)$$

$$= \text{GPP} - R \quad (1.2)$$

When NEP is positive, GPP exceeds R, the system becomes net autotrophic as significantly more organic material is produced than degraded, with a majority of this material being stored in the system (Staehr et al., 2010; Cole et al., 2000). When NEP is negative, R exceeds GPP and the system becomes net heterotrophic, as it respire more organic carbon than was fixed by primary productivity within the lake. Sustained negative values of NEP suggest that ecosystem respiration within a lake is being subsidised by organic matter that was imported from the terrestrial catchment (Sobek et al., 2005; Hanson et al., 2003).

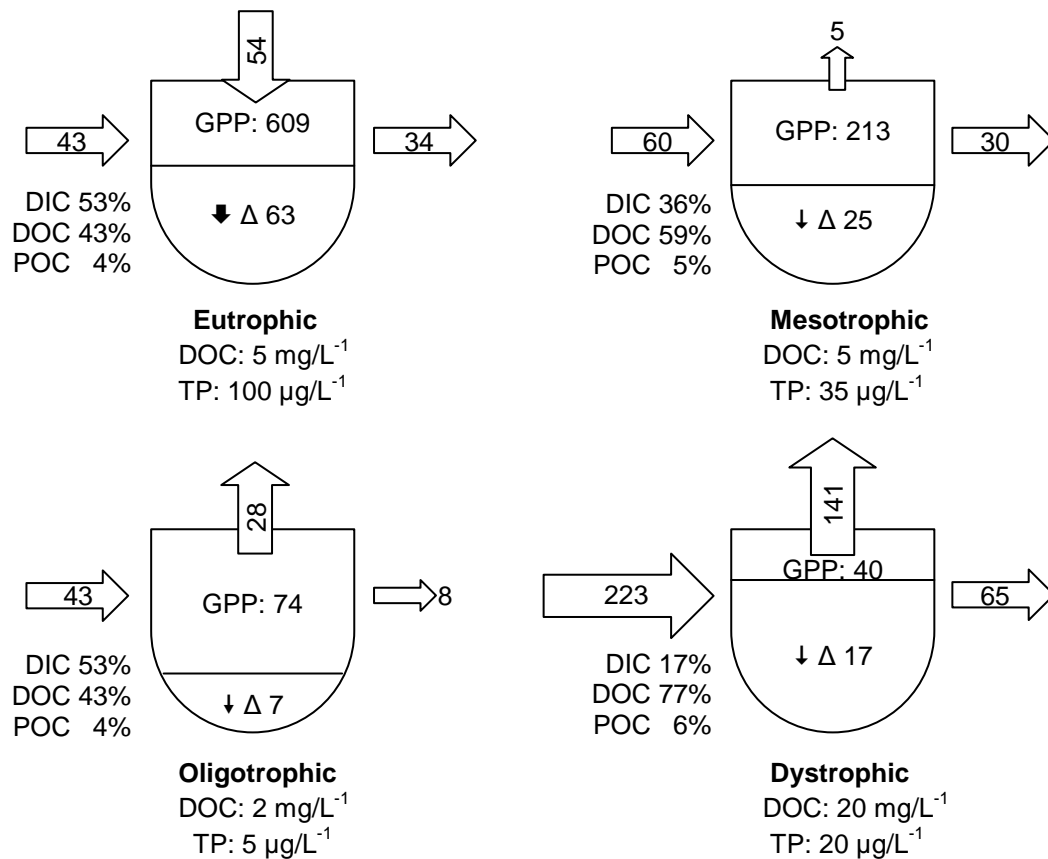


Figure 1.5 Carbon input, storage (Δ), net atmospheric flux and output from four lakes representing the classical categories of lake trophic status. Units for the values in the arrows are $\text{g cm}^2 \text{ yr}^{-1}$. DOC and TP concentrations are mean annual values (adapted from Hanson et al., 2004).

Due to its increasing abundance within aquatic systems, terrestrial DOC has been found to have a strong influence on the metabolic functioning of aquatic ecosystems (Lennon et al., 2006; Hanson et al., 2003; Hudson et al., 2003; Gergel et al., 1999). The majority of studies into carbon budgets of lakes indicate external loading often dominates over internal production (Bass et al., 2010; Canham et al., 2004; Cole & Caraco, 2001; Carignan et al., 2000). Prairie et al. (2002) proposed a productivity threshold within lakes controlled by DOC concentration, at levels up to 4 – 6 mg/L systems would most likely be autotrophic and $GPP > R$ whereas at levels over 6 mg/L $R > GPP$ and net heterotrophy would be prevalent. Hanson et al. (2003) developed this threshold further by suggesting DOC concentrations below 10 mg/L would support a balanced metabolism but lakes with concentrations greater than 10 mg/L would have a negative metabolism.

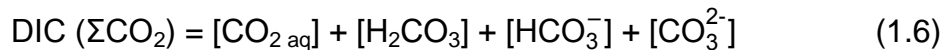
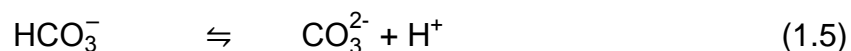
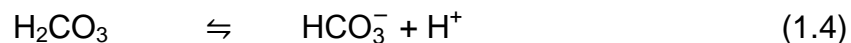
Levels of DOC in freshwater systems have been observed to be increasing globally, especially within the last few decades (Evans et al., 2005). The potential mechanisms responsible for recent changes in aquatic DOC concentrations include increasing atmospheric CO_2 concentrations, climate warming, N deposition, and hydrological changes. Any change in DOC concentrations and properties in lakes and streams will also impact the interactions between DOC, nutrients, and trace metals. Terrestrial DOC is known to impart colour into lakes, which reduces both visible and UV light within the water column, thus acting as a sunscreen for aquatic micro-organisms. As discussed earlier DOC, through its constituent acids, has an effect on the pH of aquatic systems, binds metals and affects their toxicity and the bioaccumulation of nutrients such as N, P and Fe, controlling their bioavailability and mobility. Clearly, changes in DOC quality and quantity are likely to have ecological repercussions.

There is potential for the DOC cycle to be modified as a result of climate change, since one of the sinks for aquatic DOC is its degradation to CO_2 and CH_4 . If the balance between DOC losses to the atmosphere versus transfer to the sediments of lakes is altered, greenhouse gas production and release to the atmosphere can increase or decrease, affecting the severity of climate change. In addition, if lake water levels fall, previously protected organic sediments may be exposed to greater

aeration which would lead to greater CO₂ and CH₄ evasion to the atmosphere (Benoy et al., 2007; Mortsch & Quinn, 1996).

1.2.3 Inorganic Carbon & pH

Inorganic carbon is the primary source of carbon for photosynthesis. These organic compounds are produced by a variety of organisms including algae, cyanobacteria and higher plants both within lakes or the catchment and imported into the aquatic system. The majority of inorganic carbon exists as DIC in a number of forms (Equations 1.3 to 1.6). CO₂ is extremely soluble in water and when it dissolves is hydrated to form carbonic acid (H₂CO₃), a weak acid which dissociates quickly to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions.



For convenience dissolved CO₂ and H₂CO₃ added together is termed "free CO₂" because the amount of H₂CO₃ is usually extremely low. The effect of pH on the proportions of free CO₂, bicarbonate, and carbonate is illustrated in Figure 1.6. Free CO₂ is present in significant proportions between pH 4 and 7, decreasing rapidly by pH 8, and only accounts for 0.003 % by pH 9; between pH 7 and 10 bicarbonate predominates; above pH 9.5 carbonate is significant.

Lakes offset anthropogenic CO₂ rises because they act as a buffer to atmospheric CO₂ increases and can regulate atmospheric CO₂ concentration through a number of mechanisms (Volk & Hoffert, 1985). The uptake of anthropogenic CO₂ is dominated by inorganic carbon uptake at the surface and physical transport of anthropogenic carbon from the surface to deeper water layers. Figure 1.7 outlines the main carbon pumps that regulate natural atmospheric CO₂ changes within lakes.

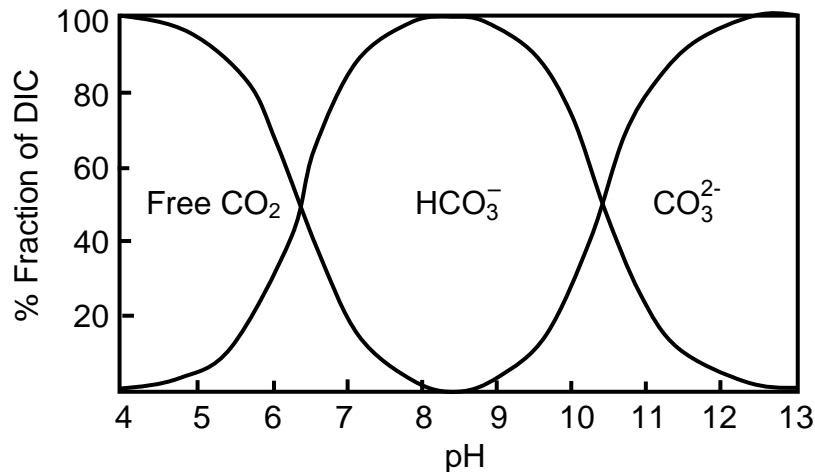


Figure 1.6 Relationship between pH and relative proportions of inorganic carbon species in solution (reproduced from Wetzel, 1975).

The solubility pump in water is driven by a difference in the partial pressure of CO_2 which results in a flux of carbon from a higher concentration to a lower concentration. Because of its solubility and chemical reactivity, CO_2 is easily taken up by lakes and dissolved CO_2 can be exchanged with the atmosphere until the partial pressure in surface water and air are equal. As atmospheric CO_2 increases, the dissolved CO_2 content of water in the lake surface increases at a similar rate, most of which reacts with water to form bicarbonate (HCO_3^-). Meanwhile, the carbonate (CO_3^{2-}) content decreases, since the net effect of adding CO_2 to water is a reaction with CO_3^{2-} to form HCO_3^- . There is therefore less available CO_3^{2-} to react with further CO_2 additions, causing an increasing proportion of the added CO_2 to remain in its dissolved form or free CO_2 . This increase in CO_2 concentration restricts further uptake, so that the overall ability of surface lake water to take up CO_2 decreases at higher atmospheric CO_2 levels.

The uptake capacity for CO_2 also varies significantly due to additional factors, most importantly water temperature, salinity and alkalinity (Wetzel & Likens, 2000; Stumm & Morgan, 1981). In freshwater systems, however, lake salinity varies very little over a yearly cycle and is not as important as temperature and alkalinity for altering the uptake of CO_2 . Alkalinity is the acid buffering capacity of a water body; without which any acid added would immediately change lake water pH. The higher the alkalinity, the greater the ability of the water body to neutralise added acids.

Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. The pH of water determines the solubility and biological availability of chemical constituents such as nutrients like P, N, and C (Wetzel & Likens, 2000; Stumm & Morgan, 1981).

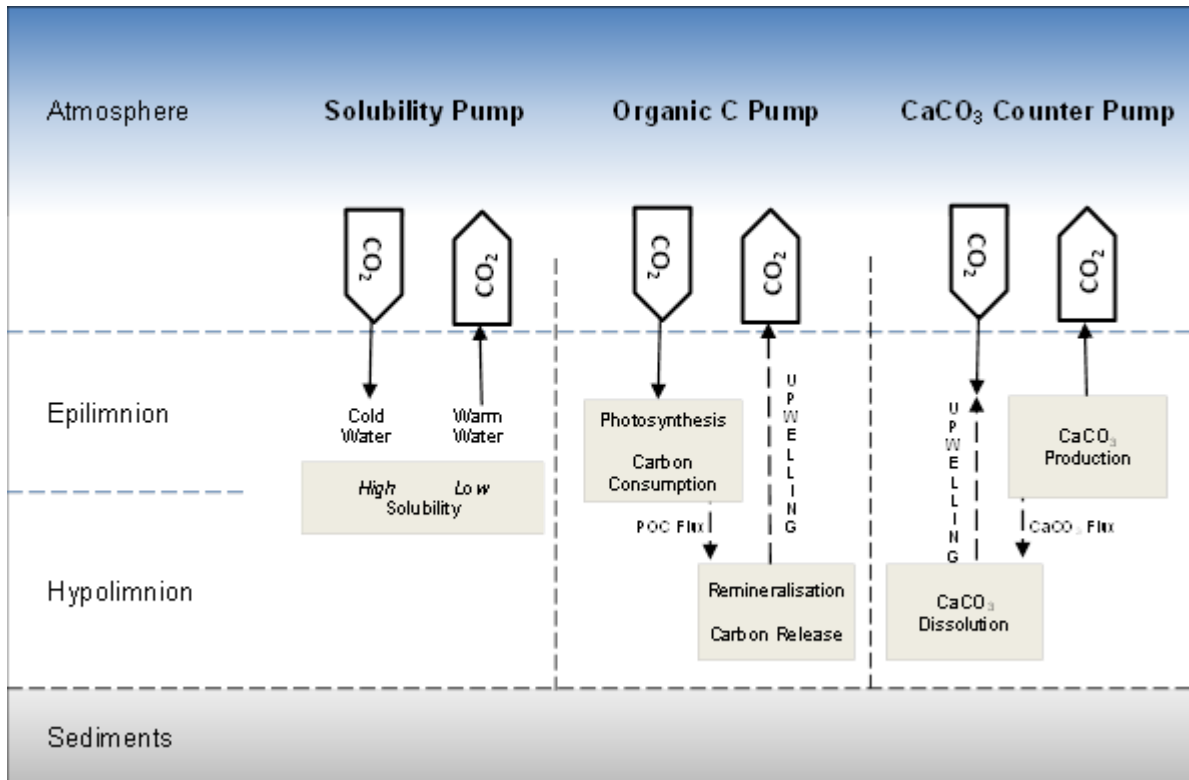


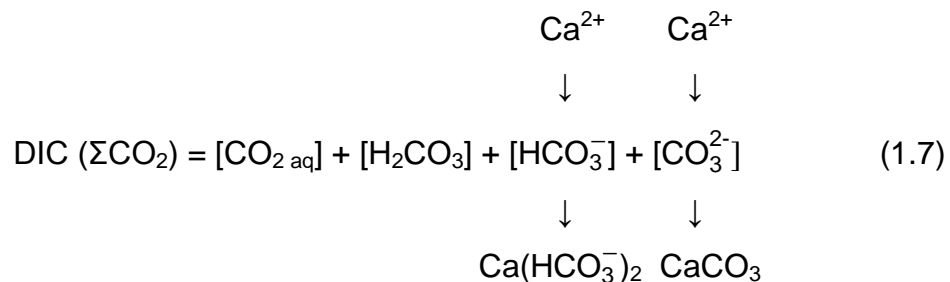
Figure 1.7 Three main carbon pumps govern the regulation of natural atmospheric CO₂ changes by lakes (adapted from Denham et al., 2007).

The sum of CO₂, HCO₃⁻ and CO₃²⁻ constitutes the dissolved inorganic carbon (DIC) fraction within a water body and is utilised in the production of particulate organic carbon (POC) which leads to the transfer of organic carbon vertically, in a downward flux, from the surface of a lake to the deeper water of a lake creating an organic carbon pump within lake circulation (Denham et al., 2007; Prentice et al., 2001). Organic particles are then re-mineralized, oxidized to DIC and other inorganic compounds such as CO₂ through the action of bacteria, with an accompanying decrease in dissolved oxygen. The gradient of CO₂ between the lake surface water (low) and deeper lake water (high) is maintained by the solubility and organic carbon pumps and regulates the exchange of CO₂ between lakes and atmosphere (Denham et al., 2007; Prentice et al., 2001).

Current empirical data, from mainly oligotrophic to mesotrophic lakes, suggest that spatial and temporal differences in partial pressure of CO₂ ($p\text{CO}_2$) arise mainly from changes in primary production, ecosystem respiration and mixing regime, factors that are strongly influenced by subsidies of inorganic nutrients and organic material from the catchment (Hanson et al., 2003; Prairie et al., 2002; Cole et al., 1994).

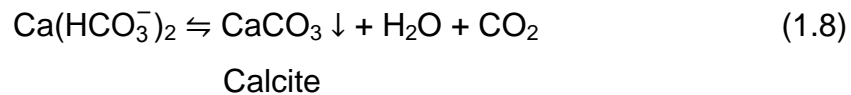
1.2.4 Calcium Carbonate (CaCO₃)

Typically Ca²⁺ influences growth in aquatic environments as it is a micro-nutrient required for metabolism in higher plants. The concentration of Ca²⁺ has a seasonal dynamic linked to the stratification cycle in most lake, with a typically uniform concentration during the mixed phase and spatial variability within the water column associated with rapid increases in the rate of photosynthesis during the summer months (Otsuki & Wetzel, 1974). When combined with inorganic carbon Ca²⁺ forms compounds including CaCO₃ and Ca(HCO₃⁻)₂ which are controlled by the availability of CO₂ (Equation 1.7).



The calcium carbonate counter pump in Figure 1.7 highlights that there are changes in the release of CO₂ within surface waters during the formation of CaCO₃ by organisms and photosynthesis. This disturbs the equilibrium, allowing new CO₂ to diffuse into the water, resulting in greater than expected amounts of dissolved CO₂. A large amount of “free CO₂” remains in solution to maintain an equilibrium with Ca²⁺, HCO₃⁻, CO₃²⁻ and CaCO₃. This is because Ca(HCO₃⁻)₂ can only exist in solution and the amount of free CO₂ required to maintain the stability of this compound increases rapidly with an increase in the HCO₃⁻ content. However, if CO₂ is lost from a solution of Ca(HCO₃⁻)₂ in equilibrium with ([CO₂_{aq}] + [H₂CO₃]) and CO₃²⁻, CaCO₃ will precipitate until the equilibrium is re-established as shown in Equation 1.8. In

alkaline, hard water lakes CaCO_3 can also start precipitating when pH is increased sufficiently to promote the above reaction to occur. Excess CO_2 can be lost through a number of processes including photosynthetic utilisation and inflows of CO_2 enriched groundwater, promoting the release of CO_2 to the atmosphere from the surface waters (Wetzel, 2001).



The calcium ion and CaCO_3 equilibrium are especially important in fresh water. This equilibrium requires that a small amount of carbonic acid is always present. If it is removed, by photosynthesis for example, then the bicarbonate changes to carbonate, which precipitates because of its low solubility. Insoluble CaCO_3 precipitates when CO_2 is removed during periods of high photosynthesis. If CO_2 is added to the system, by respiration, then the carbonate changes to bicarbonate until the excess CO_2 has been used up (Lampert & Sommer, 2007). Organic matter coated with CaCO_3 in the surface sediments reduces the rate of dissolution of sedimenting CaCO_3 and can form a major sink for inorganic carbon and organic carbon matter, especially in alkaline, hard water ecosystems (Wetzel, 1970; 1972).

1.2.5 Lake Sediments

Compared to other fluxes in the global carbon cycle, organic carbon burial constitutes a small flux of about 100 Tg C yr^{-1} in marine sediments (Denman et al., 2007), and this has led to the accumulation of vast stocks of carbon, removed from the active carbon cycle. The rate of sequestration of organic carbon in the sediments of lakes is comparable to or even higher than in marine sediments and soils (Downing et al., 2009; Cole et al., 2007; Einsele et al., 2001). Lakes not only bury organic carbon, but are also active sites for the mineralisation of organic carbon, originating from autochthonous or allochthonous sources. The organic carbon that reaches the lake sediment surface will partly be mineralised to CO_2 or CH_4 by heterotrophic micro-organisms, and partly be buried in the sediments. The proportion that is buried is termed the organic carbon burial efficiency, while the fraction of the sediment organic carbon that is lost through microbial processing is termed organic carbon mineralisation. As a consequence, the amount of organic

carbon that is eventually buried is a direct function of the burial efficiency. The burial efficiency in lake sediments is related to oxygen exposure, but the effect of temperature on organic carbon mineralisation and burial remains unclear (Cole et al., 2007). Relationships between lake sediment mineralisation and temperature are subject to a number of interdependent factors such as lake depth and mixing regime, organic carbon source and lake trophic status. With the current focus on anthropogenically driven global warming and the substantial amount of carbon buried by lakes in their sediments, it is critical to gain understanding of how temperature affects burial efficiency rates within lakes, and clarify the future role of lakes as carbon sinks.

However, the reasons for the high efficiency of organic carbon burial in lake sediments are still poorly understood. Extensive studies on marine sediments have identified a wide array of different factors that may contribute to the preservation of organic carbon in sediments such as primary production rate, chemical composition of organic matter, sediment accumulation rate and bottom water oxygen concentration (Hedges et al., 1999). Many of these factors are interdependent, and their relative importance is likely to shift with any predicted changes to the climate.

Bacteria are the major decomposers of organic matter in aquatic systems (Fenchel & Blackburn, 1979). Temperature is an important factor determining microbial activity in both the water column and sediment (White et al., 1991; Graneli, 1978). In stratified, temperate lakes, water in the epilimnion overlying the littoral sediments can be 10 – 15°C warmer than water in the hypolimnion, and this should result in significantly higher rates of activity. Yet, the activity of microbial communities may also be dependent on the quality and quantity of organic matter reaching the sediments, highlighting the potential differences in externally derived to internally derived carbon (den Heyer & Kalff, 1998).

Eutrophication increases the input of autochthonous carbon to the sediment, which compared to allochthonous carbon is more labile, i.e. easier to decompose than the complex organic matter from the catchment, and therefore mineralised to a far greater extent than buried in the sediments (Sobek et al., 2009; Cole et al., 2007). Oxygen consumption during carbon mineralisation leads to anoxic bottom waters,

which is typically observed in eutrophic stratified lakes. Cornett & Rigler (1980) estimated that as much as 85% of oxygen consumption in the hypolimnion of lakes occurs in the sediments. As anoxic conditions do not impede the degradation of autochthonous carbon, eutrophication thereby promotes the production of inorganic carbon (CO₂ and CH₄) in hypolimnetic sediments. The inorganic carbon can, dependent on water column depth, result in the emission of CO₂ and CH₄ from the lake to the atmosphere (McGinnis et al., 2006). This means that if a lake is subject to eutrophication, the carbon burial efficiency is likely to be lower than a lake subject to high levels of allochthonous carbon loading but overall volume of primary production will promote an increased burial rate. Inorganic carbon production is also likely to increase in eutrophic lakes and be emitted to the atmosphere (Sobek et al., 2009).

Changes to the climate have the capacity to modify the export of carbon from catchments to lakes. There have been recorded increases in the export of terrestrial carbon from the catchment in some regions, e.g. DOC in northern Europe, and this has resulted in an observed increase in the sedimentation of allochthonous carbon in lakes (von Wachenfeldt & Tranvik, 2008). Increased allochthonous carbon input to the sediments has probably resulted in a higher carbon burial efficiency in these lakes as allochthonous carbon is more likely to be buried in the sediments than mineralised (Figure 1.8).

Climate change could also modify the thermal properties of lakes. Surface waters are expected to experience substantial heating, while hypolimnetic waters will warm at a much slower but measureable rate (De Stasio et al., 2006). This has two implications with respect to the fate of sediment carbon. Firstly, higher epilimnetic temperatures will promote carbon mineralisation, as the bacteria involved in mineralisation are more efficient in warmer temperatures, and thereby reduce the burial efficiency in epilimnetic sediments. Secondly, an increased temperature difference between epilimnetic and hypolimnetic waters implies prolonged periods of stratification, which have the potential to greatly increase the oxygen deficiency and inorganic carbon production in bottom waters (Jankowski et al., 2006). The strong relationship between carbon burial efficiency and oxygen exposure time, i.e. the less time sediments are exposed to oxygen the more efficient they are at burying carbon, suggests that increasing hypolimnetic oxygen deficiency would result in a small

increase in the burial efficiency of hypolimnetic sediments in the future (Sobek et al., 2009). However, the relationship is strongest between carbon from allochthonous and oxygen exposure time (Gudasz et al., 2010; Sobek et al., 2009).

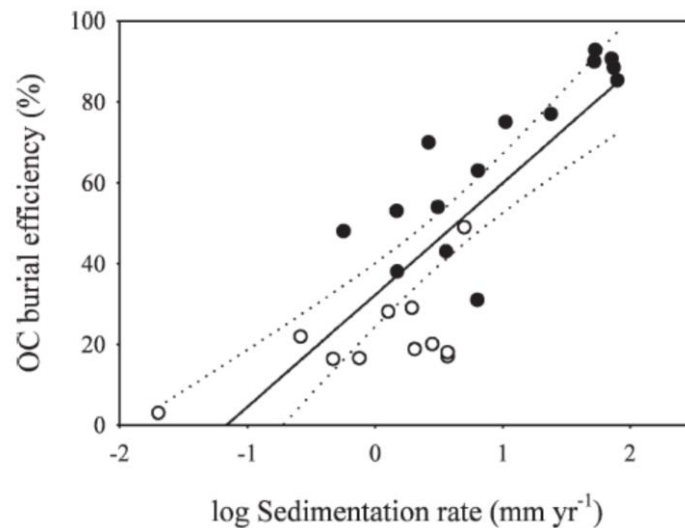


Figure 1.8 The relationship between the organic carbon burial efficiency and the sedimentation rate. Open circles represent sites receiving sediment from mainly autochthonous sources; closed circles represent sites receiving sediment from mainly allochthonous sources. The dashed lines show the 95% confidence bands (Sobek et al., 2009).

The high burial efficiency in lake sediments illustrates the importance of lakes as modifiers of carbon. In both research by Sobek et al. (2009) and Cole et al. (2007), the mean burial efficiency for allochthonous lake sediments was 66% with the remainder being mineralised to CO₂ and CH₄, which may eventually reach the atmosphere. The efficiency of lake sediments at transforming terrestrial carbon suggests that they could not only act as carbon sinks, but also as transformers of terrestrial organic carbon to atmospheric CO₂ and CH₄. The efficiency of autotrophic systems was much lower, with a mean burial efficiency of 22% and higher levels of mineralisation and inorganic carbon production. This could possibly be attributable to the very large differences between the studied sediments in terms of organic matter sources, degradation pathways and microbial decomposers (Sobek et al., 2009; Cole et al., 2007).

1.3 PROJECT AIMS

The aim of this project is to determine the carbon dynamics of eutrophic lakes in the UK. The project will focus on the Cheshire-Shropshire Meres, specifically Rostherne Mere and Tatton Mere, testing the following overarching hypothesis:

H1: The eutrophic lakes of the Cheshire-Shropshire Meres are (A) autotrophic systems, therefore (B) a net carbon sink in the UK's carbon budget.

A: Establishing autotrophy/heterotrophy for Rostherne Mere and Tatton Mere.

Objectives: Use high-resolution O₂ measurements to define daily NEP and calculate daily, monthly and seasonal C-fixation estimates using the metabolic equation $\delta O_2/\delta t = NEP + F + A$, first established by Odum (1956).

Specific questions to address **A**:

- What is the level of autotrophy/heterotrophy for each lake?
- How does autotrophy/heterotrophy change seasonally?
- How variable are C-dynamics between years?
- What is the spatial variability in C-dynamics at each lake?

B: Establish the importance of eutrophic lakes as a C-source/sink (B1) over time and (B2) space.

B1: Examine the long C-storage of Rostherne Mere and Tatton Mere.

Objectives: Measure the flux of C through the water column into the sediments using sediment traps and sediment core analysis.

Specific questions to address **B1**:

- How efficient are the lakes at transferring C to the sediment surface?
- What is the burial efficiency?
- Can a reliable lake-basin C-accumulation rate be estimated?

B2: Up-scale C-accumulation estimates from Rostherne Mere and Tatton Mere to the Cheshire-Shropshire meres region and all UK eutrophic waters.

Objectives: Calculate and compare C-storage potential for all the Cheshire-Shropshire meres and UK eutrophic waters, based on average areal values for Rostherne Mere and Tatton Mere.

Specific questions to address **B2:**

- How representative are these two lakes of the Cheshire-Shropshire meres?
- How representative are these two lakes of UK eutrophic standing waters?
- What is the role of eutrophic lakes in the UK C-cycle?
- How do C-dynamics, burial and storage of these temperate, eutrophic lakes compare to other lake systems globally?

C: Review the analytical techniques and methods used during this project in addressing the overarching hypothesis H1 (parts A and B).

Objectives: Examine key analytical variables within equations used to calculate NEP, CO₂ flux and converting O₂ production to C-assimilation; and examine the process of up-scaling from individual lakes, to regional and national scales.

Specific questions to address **C:**

- What affect does varying these key measurements/constants have in the final estimates?
- What impact does a single-site sonde deployment have on metabolism estimates?
- Is a full C-balance needed or are metabolic estimates representative?
- What are the errors and assumptions associated with up-scaling within the project at each scale?

2.1 UK INLAND WATER DISTRIBUTION

The United Kingdom has a total inland water area of approximately 3504 km² (~1.4% of total area) comprising 675 km² in England, 125 km² in Wales, 1604 km² in Scotland and 1100 km² in Northern Ireland. Current estimates suggest that about 50% of this total inland water area could be eutrophic, though there is a significant disparity between nations, as over 80% of inland water in England is thought likely to be eutrophic, compared to some 40% in Wales, 15% in Scotland and 85% in Northern Ireland. The total UK area of eutrophic standing waters is therefore likely to be around 1785 km² (JNCC, 2008).

2.2 THE CHESHIRE & SHROPSHIRE MERES

The Cheshire & Shropshire meres are a group of more than 60 productive lakes (total lake area approximately 7.5 km²) with a distinct nutrient status that lie on the glacial geology of the Cheshire-Shropshire plain that offer a unique study opportunity due to their varied size, morphometry and nutrient status. Their distribution is neither uniform nor random, with most of the sites occurring in distinct local groupings (Figure 2.2). A comprehensive review of the meres by Reynolds (1979) determined that the mean maximum depth and total area of the largest 45 meres was 6.3 m and 0.11 km² respectively (Figure 2.1).

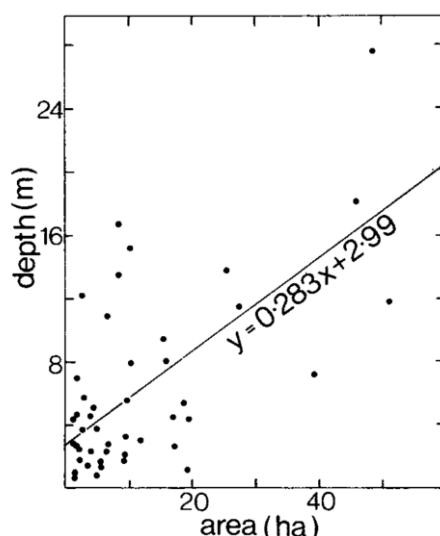


Figure 2.1 The relationship between maximum known depth and present surface area of the 45 largest meres (Reynolds, 1979).

Through long term data records and sediment cores, that have been extracted from a number of the meres, it is believed that the eutrophic condition of these lakes is long established (Grimshaw & Hudson, 1970; Gorham, 1957; Tattersall & Coward, 1914). Their distinct status results from receiving large concentrations of nutrients from their managed, surrounding catchments which flow into the meres either via surface inflow or groundwater that has percolated through the glacial deposits rich in minerals and salts. Consequently the meres are rich in major ions, with an abundance of bicarbonate causing the waters to become alkaline and essentially well buffered against acidification. The groundwater flow maintains extremely stable water levels, long water retention times and high nutrient concentrations within the meres. The combination of long retention times and high nutrient concentrations contributes to efficient utilisation of nutrients available. The open water planktonic communities in the meres are typical of temperate eutrophic lakes with a prevalence of diatoms, *Dinoflagellates* and blue-green algae. These populations are on average large and fast growing, with algal populations often exceeding 20 g m⁻² dry weight, and approaching the theoretical upper limit on population size determined by the underwater light climate rather than the lack of nutrient availability (Reynolds, 1979).

Nitrogen has been suggested as being an important limiting nutrient in many of the Shropshire & Cheshire meres (Moss et al., 1992). There may also be internal sources of nutrients, such as nitrogen fixation by cyanobacteria and the release of phosphate and ammonium from the sediment during anoxic conditions (Mortimer, 1941). Nearly all of the meres are also rich in DOM and deep enough to allow stable thermal stratification and anoxia of the lower water layers to occur during the summer, often 6 – 8 months per year. These long periods of stratification allow for high accumulation rates, excellent levels of organic preservation and enable detailed analysis of sediments to be carried out with high temporal resolution.

However despite the relative stability of the meres over the last ~150 years, there are a number of potential threats to their unique characteristics including climate change, further enrichment, reduced water levels due to natural and anthropogenic sediment infilling, and habitat change or fragmentation including invasive species.

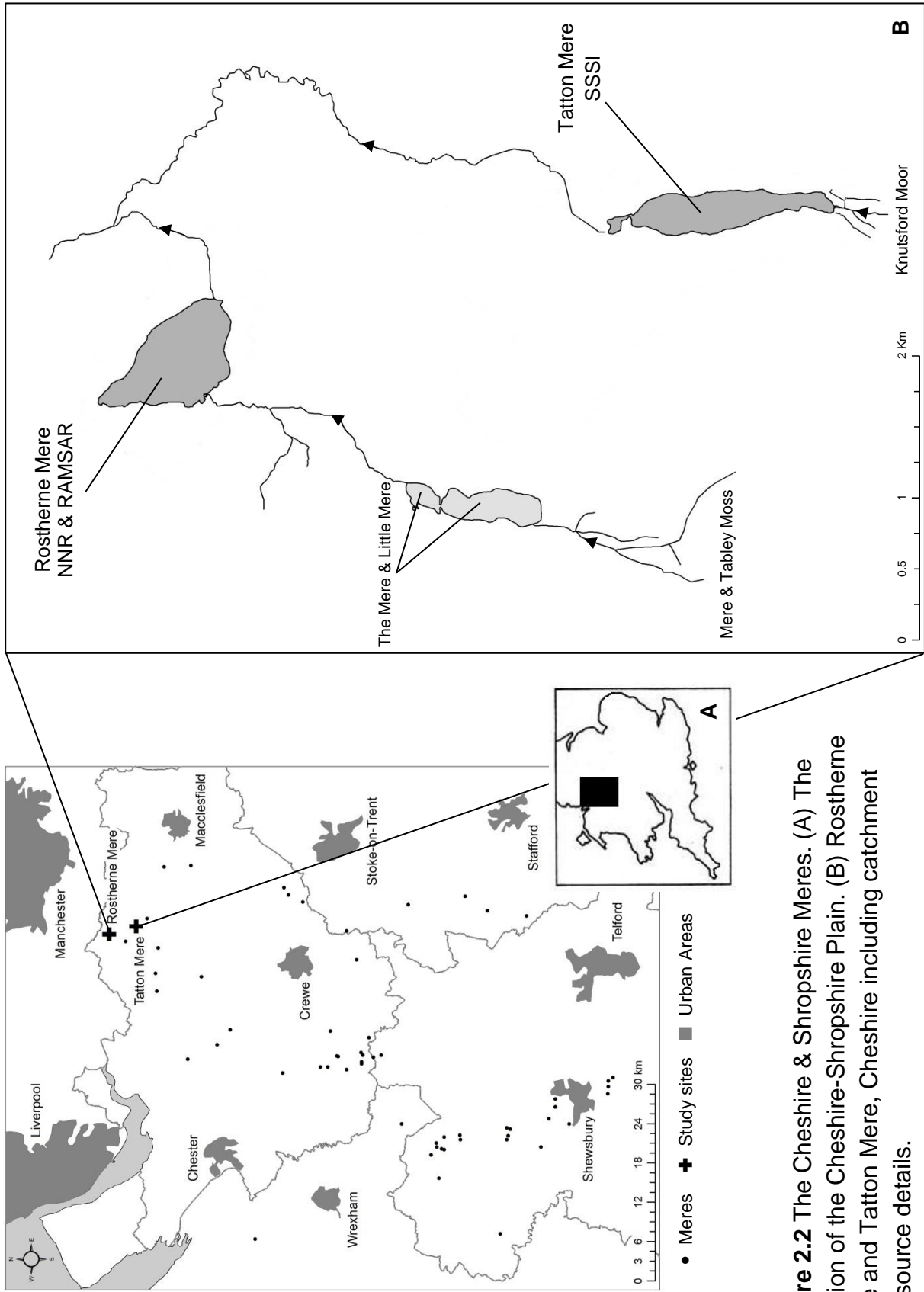


Figure 2.2 The Cheshire & Shropshire Meres. (A) The location of the Cheshire-Shropshire Plain. (B) Rostherne Mere and Tatton Mere, Cheshire including catchment and source details.

2.2.1 Rostherne Mere, Cheshire

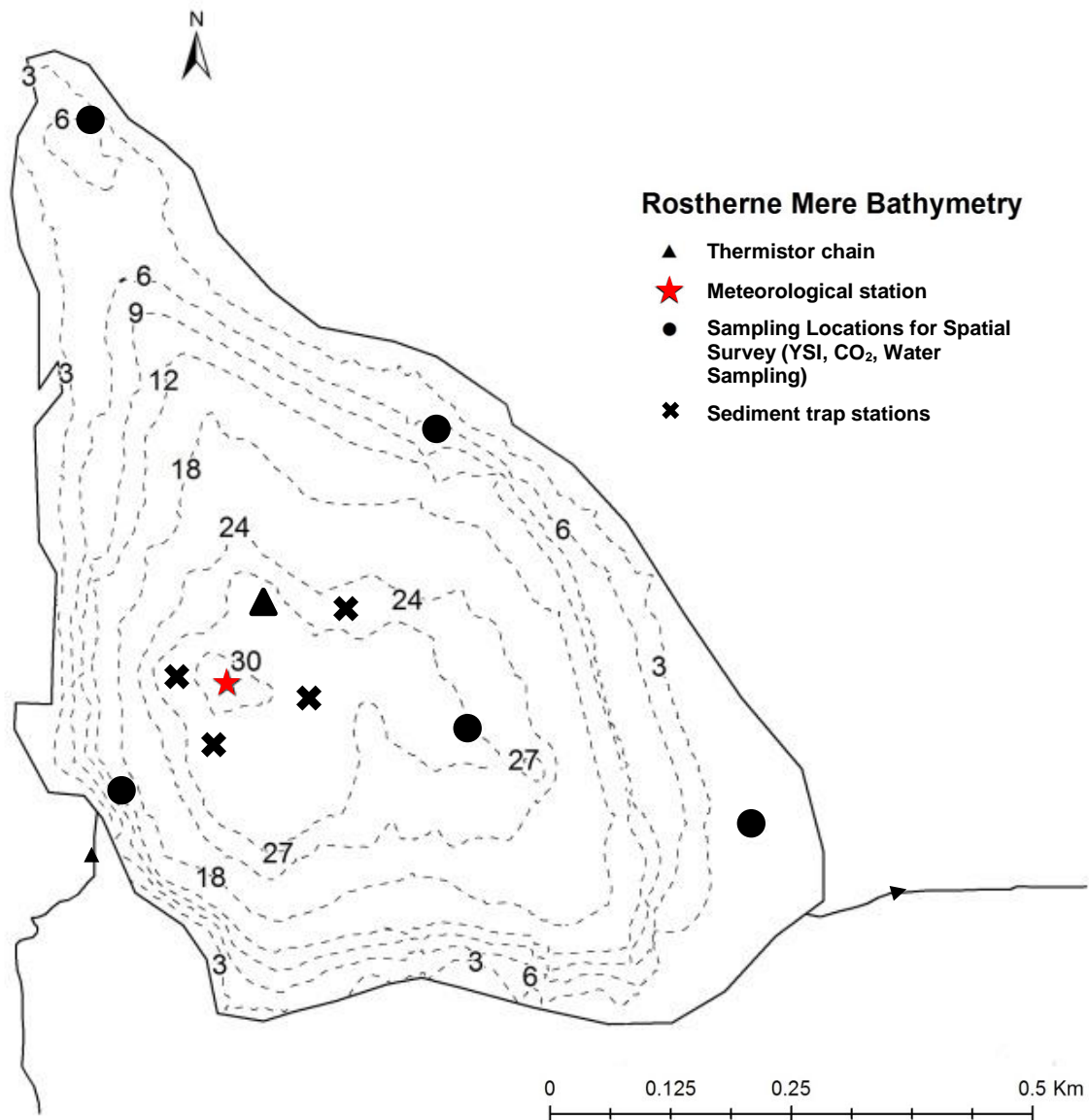


Figure 2.3 Bathymetry of Rostherne Mere (surveyed May 2010). Depths shown are in metres.

Rostherne Mere, the deepest and one of the largest of the Cheshire & Shropshire meres, is designated a SSSI, RAMSAR site and became a National Nature Reserve in 1961 (Figure 2.3). The lake has an area of 0.49 km² and a catchment area of more than 9 km²; its maximum depth is 31 m, with a mean depth of 13.6 m (Livingstone & Reynolds, 1981). There is limited surface drainage within the catchment, with the only surface inflow into Rostherne Mere of any significance

being Rostherne Brook which drains from another smaller lake, The Mere at Mere, about 1.5 km to the south. The main surface outflow from Rostherne Mere is to the east through Blackburn's Brook. The balance of the supply is assumed to be mainly through deep-percolating ground water. The lake is eutrophic, with a high bicarbonate alkalinity (1.9 meq L^{-1}) and high concentrations of available phosphorus ($216 \mu\text{g L}^{-1}$), nitrogen ($1217 \mu\text{g L}^{-1}$) and silicon (This study; Grimshaw & Hudson, 1970; Gorham, 1957; Tattersall & Coward, 1914). The water column stratifies thermally in the summer months; the benthic oxygen demand is such to render the entire hypolimnion anoxic within only a few months.

It is believed that the creation of the lake depression was caused by the gradual dissolution of the rock-salt layers contained within the deeper geological strata (Tattersall & Coward, 1914). The eutrophic status of the lake is a result of anthropogenic nutrient enrichment notably runoff from the surrounding farmland and, between 1935 and 1991, by effluent discharge from a since diverted nearby sewage treatment works (Carvalho, 1993) and is maintained to date by efficient nutrient recycling within the sediments and water column. The degree of nutrient enrichment together with morphological and hydrological characteristics of the lake and its water catchment result in summer stratification and regular development of algal blooms well documented since the beginning of the century (Pearsall, 1932; Tattersall & Coward, 1914).

Chemical analyses of the water of Rostherne Mere have previously been carried out by Tattersall & Coward (1914), Gorham (1957), Grimshaw & Hudson (1970), and Carvalho (1993). Most of these data, however, only gives detail on the available concentrations of nitrogen and phosphorus. A number of previous studies have considered various aspects of Rostherne Mere nutrient budgeting (Moriera, 1996; Walker, 1987; Rogers, 1975; Brinkhurst & Walsh, 1967), but to date no study has focused on the carbon cycle and the impact eutrophication has upon the lakes mass-balance. This interaction is important to consider, especially since the introduction of European Commission's Water Framework Directive (WFD) in the early 2000s, as significant reductions in nitrogen and phosphorus loading into rivers and lakes across UK has led to a steady decline in the concentrations of these nutrients being recorded in the water column (Moss et al., 2005; Krivtsov et al., 2001, 2002).

Rostherne Mere's current hypertrophic status is unlikely to continue indefinitely, meaning we might expect a very long continuing reduction in TP concentrations in Rostherne Mere, perhaps over several decades before it achieves P limitation and the expected progressive oligotrophication (Moss et al., 2005).

The lake and its catchment have attracted the attention of the scientific community for nearly a century due to its unusual over-deep basin and fully stratifying nature, with a valuable monitoring record being developed over this period. For these reasons it is considered an important site for research in freshwater biology, water chemistry, and lake sediments (e.g. Krivtsov et al., 2001, 2002; Moss et al., 1994, 1997; Carvalho & Moss, 1995; Reynolds & Bellinger, 1992; Reynolds & Sinker, 1976; Pearsall, 1932; Tattersall & Coward, 1914). More recently Rostherne Mere has formed part of the United Kingdom Lake Ecological Observatory Network (UKLEON) project, which monitors key freshwater sites at high resolution in an attempt to model aquatic biogeochemistry and the level of regional coherence in lake response to a changing climate. The lake makes an ideal research candidate due to the ease of site access, existing research infrastructure and the security of being able leave monitoring equipment.

2.2.2 Tatton Mere, Cheshire

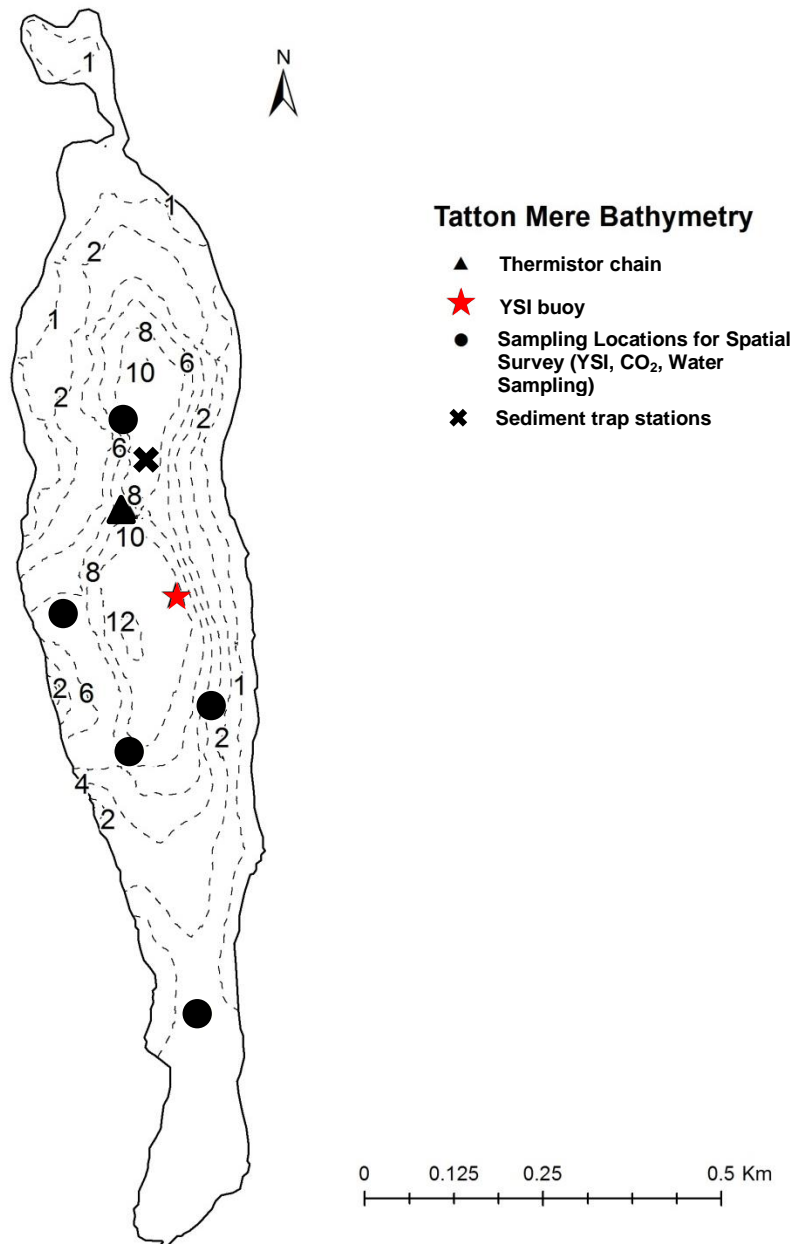


Figure 2.4 Bathymetry of Tatton Mere (surveyed May 2010). Depths shown are in metres.

Part of the larger Tatton Park Estate, Tatton Mere sits in 8.1 km² of landscaped deer park and is currently owned and managed by the National Trust (Figure 2.4). Like many of the meres on the Shropshire-Cheshire plain it is designated as a SSSI and is included in the recently designated Midland Meres & Mosses (Phase 1) RAMSAR site, which protects wetlands of international importance. To date Tatton has mainly

only been included in a number of studies of the larger Shropshire-Cheshire meres system with basic surface water chemistry being recorded (Bennion & Simpson, 2011; Carvalho & Moss, 1995; Moss et al., 1994). With an area of 0.32 km² and a maximum depth of 11 m it is smaller and shallower than neighbouring Rostherne Mere, but closer to the average max depth/total area for the meres calculated by Reynolds (1979) in Figure 2.1. Subsequently, due to its shallower depth the mere only supports weak stratification during the summer months. It is fed through both surface and groundwater flow from Knutsford Moor. Like many of the surrounding meres Tatton Mere has elevated levels of nitrogen (826 µg L⁻¹) and phosphorus (442 µg L⁻¹), and a history of anthropogenic disturbance dating back many centuries (This Study; Moss et al., 1994).

Table 2.1 A comparison of the physical and chemical characteristics of Rostherne Mere and Tatton Mere, Cheshire, where ^(a) this study, ^(b) Woof & Wall (1984), ^(c) Moss et al. (1994) and ^(d) Carvalho (1993).

	Rostherne Mere	Tatton Mere
Surface Area (km ²)	0.49 ^(b)	0.32 ^(c)
Maximum Depth (m)	31 ^(a)	12 ^(a)
Volume (m ³)	6.9 x 10 ⁶ ^(a)	1.3 x 10 ⁶ ^(a)
Catchment Area (km ²)	9.4	5.1
Retention Time (days)	600 ^(d)	120 ^(a)
Mixing Regime	Monomictic ^(a)	Monomictic ^(a)
TP Annual Average (µg L ⁻¹)	216 ^(a)	442 ^(a)
TN Annual Average (µg L ⁻¹)	1217 ^(a)	826 ^(a)
DOC Annual Average (mg L ⁻¹)	7.30 ^(a)	4.40 ^(a)
Alkalinity (meq L ⁻¹)	2.26 ^(a)	2.06 ^(a)

2.3 THE CLIMATE OF NORTH WEST ENGLAND

The North West of England has a very varied landscape from dramatic upland areas such as the Pennines and Lake District to lowland plains surrounding Liverpool and Manchester. The Cheshire plain lies at the southernmost point of North West England between north Wales, the Mersey estuary and the Pennines. The UK Met Office station at Manchester Airport, less than 7 km from the area of study, provides a detailed record of the regions climate (Table 2.1).

Table 2.2 Summary of 1981 – 2010 averages at Manchester Airport Met Station (adapted from UK Met Office, 2012).

	Mean Max Temp (°C)	Mean Min Temp (°C)	Sunshine (hours)	Rainfall (mm)	Days of Rainfall ≥ 1mm	Wind at 10m (m s ⁻¹)
Jan	7.3	1.7	52.5	72.3	13.1	4.7
Feb	7.6	1.6	73.9	51.4	9.7	4.6
Mar	10	3.3	99	61.2	12.3	4.7
Apr	12.6	4.9	146.9	54	11.2	4.1
May	16.1	7.7	188.3	56.8	10.4	4.1
Jun	18.6	10.5	172.5	66.1	11.1	3.6
Jul	20.6	12.6	179.7	63.9	10.9	3.5
Aug	20.3	12.4	166.3	77	12	3.5
Sept	17.6	10.3	131.2	71.5	11.1	3.7
Oct	13.9	7.4	99.3	92.5	13.6	4.1
Nov	10	4.2	59.5	81.5	14.1	4.1
Dec	7.4	1.8	47.1	80.7	13.5	4.2
Year	10.1		1416.2	828.8	142.9	4.1

The climate of Cheshire is dominated by exposure to westerly maritime air masses, but protection given by the Pennines and north Welsh mountains means the area is sheltered from some of the extremes experienced in other parts of North West England. For example, rainfall is generally well distributed throughout the year, but there is seasonality within the data. Spring is the driest season in the region with

maximum rainfall occurring during autumn/winter. Being on a low-lying plain, temperatures in Cheshire can be on average between 0.5°C and 1°C warmer than more exposed areas of North West England. Lowest temperatures usually occur in January with peak temperatures typically during July.

The wind rose for Rostherne Mere, generated from data collected at the Rostherne Mere on-site automatic meteorological station, reflects typical wind conditions for North West England (Figure 2.5), with a prevailing south-westerly wind direction through the year, but a high frequency of north to north-east winds in spring. The climate of Cheshire and Greater Manchester is modified by the channelling of winds between the Pennines and hills of north Wales, giving the winds a southerly bias.

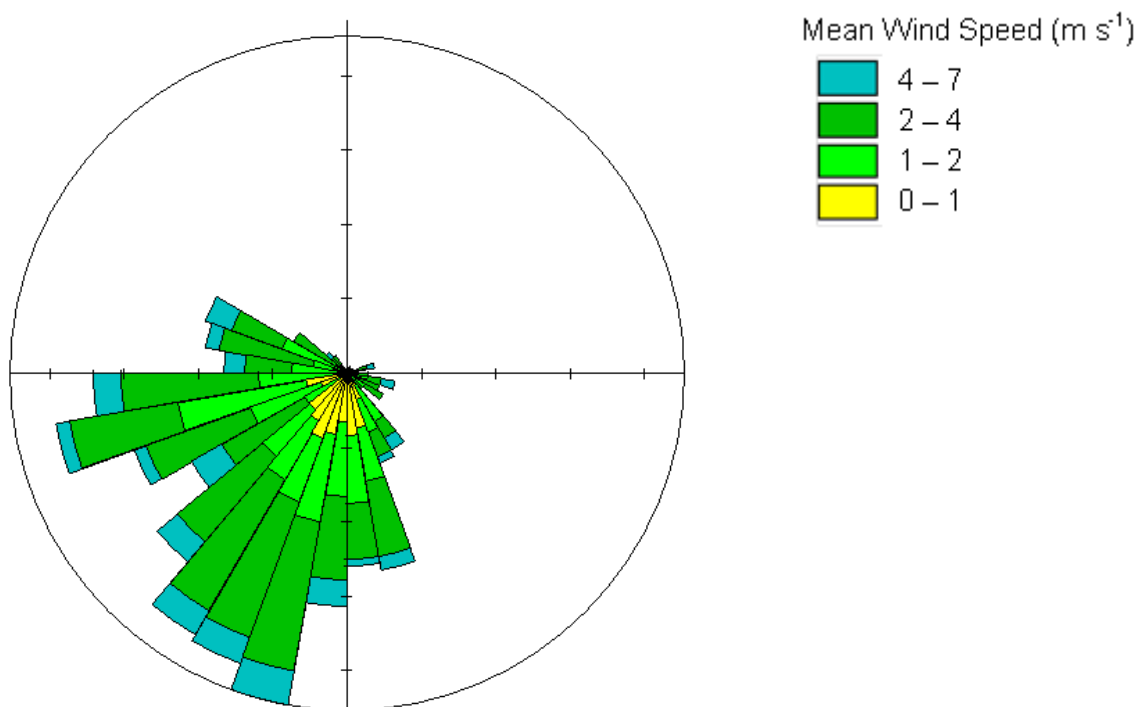


Figure 2.5 Wind rose data for Rostherne Mere Oct 2010 – Apr 2012. Data collected from the on-lake automatic weather station.

The temperature data recorded by the automatic weather station situated on Rostherne Mere, Cheshire (Figure 2.6) show the mean air temperature during 2011 was 10.9°C (30 year average for Manchester – 10.1°C; UK Met Office, 2012). A mean maximum of 20.4°C and a mean minimum of -1.5°C were recorded in 2011,

the mean maximum was very close to the 30 year average of 20.6°C but the mean minimum was significantly below the 30 year average of 1.6°C (~3°C cooler). During the 2010 stratification period (stratification periods highlighted by grey bars/dashed lines) mean air temperature was 13.8°C, a slightly higher mean air temperature of 14.1°C was recorded during the same period in 2011. However, the winter of 2010/2011 was extremely cold as temperatures dropped well below freezing during December 2010, something not experienced during the winter of 2011/2012. December 2010 was exceptionally cold with the monthly average air temperature being ~4.5°C cooler than expected (Dec 2010 -0.09°C; 30Av 4.5°C); similarly monthly average air temperature in April 2011 was in excess of 2.5°C warmer than would be expected (Apr 2011 11.6°C; 30Av 8.75°C). Warmer than average mean air temperatures in April 2011 could potentially have led to a more rapid onset of stratification in Rostherne Mere and Tatton Mere than in previous years. The mean air temperature recorded at the beginning of 2012 was very close to the 30 year average (2012 6.4°C; 30Av 6.2°C).

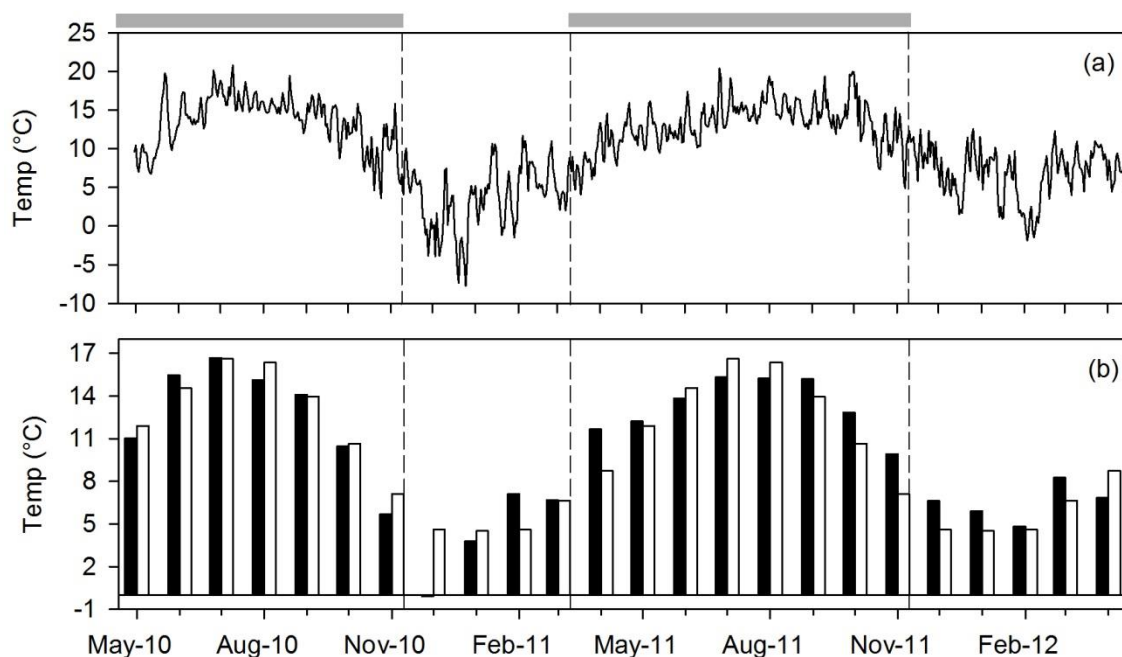


Figure 2.6 Mean temperature data for Rostherne Mere, Cheshire. (a) Daily mean temperature (°C) for study period and (b) monthly mean temperature (black bars) compared with 30 year mean (white bars).

The rainfall patterns recorded in Knutsford, Cheshire (Figure 2.7) show that in 2011 total rainfall was 916.2 mm (30 year average for Manchester – 828.8 mm; UK Met Office, 2012). During the 2010 stratification period rainfall totalled 502.7 mm, a slightly higher total of 561.8 mm fell during the same period in 2011. However, the winter of 2010/2011 was extremely dry only 191.5 mm of rainfall was recorded; 78% of total rainfall expected during this period. December 2010 was exceptionally dry with only 11% of the expected rainfall; similarly April 2011 was very dry with only 20% of the 30 year average rainfall recorded during the month. The wettest month was April 2012 when 125.4 mm of rainfall was recorded, the equivalent of 225% of average. Lower than average rainfall levels in 2010, especially during the winter, means that groundwater levels are unlikely to have been fully recharged in the Rostherne Mere and Tatton Mere catchments.

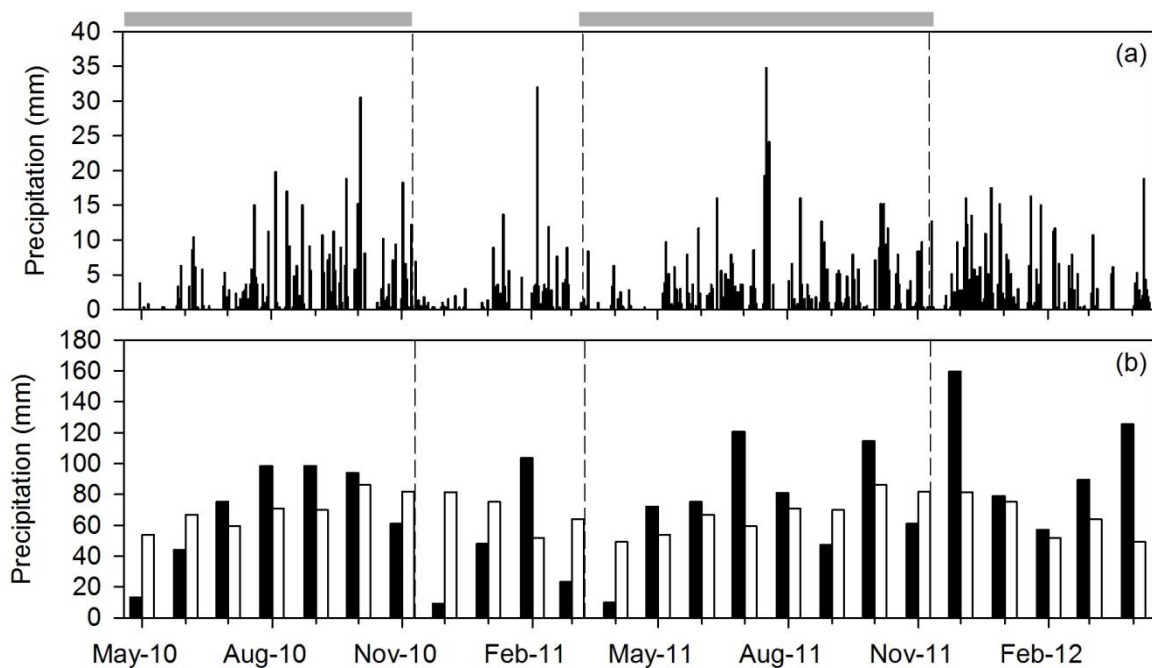


Figure 2.7 Precipitation data for Knutsford, Cheshire (6 km from Rostherne Mere and 1 km from Tatton Mere). (a) Daily mean precipitation (mm) for study period and (b) total monthly precipitation (black bars) compared with 30 year mean (white bars).

2.3 METHODS

Initial surveys began at Rostherne Mere in spring 2010 and Tatton Mere in winter 2010, both concluding in April 2012 at the beginning of a new stratification cycle. An identical procedure was followed when sampling at Rostherne Mere and Tatton Mere.

2.3.1 Meteorological Data

A range of meteorological variables were collected using an automatic weather and water quality monitoring station situated on Rostherne Mere (Figure 2.8) to determine the climate of the study area and used in the calculation of lake metabolism data. The stations meteorological sensors, mounted approximately 2m from the surface of the lake, included:

- Air Temperature ($^{\circ}\text{C}$)
- Solar Radiation (W m^{-2})
- Barometric Pressure (mB)
- Wind Speed (m s^{-1})
- Wind Direction ($^{\circ}$)



Figure 2.8 Automatic weather and water quality monitoring station on Rostherne Mere, Cheshire.

Data were collected for each variable every 1 minute, stored on local data-loggers and transmitted over-the-air every 24 hours to be stored at the UK Environmental Change Network data centre. The station forms part of the UK Lake Ecological Observatory Network (UKLEON) led by CEH Lancaster, who also manages the data within the UK Environmental Change Network. The station is, however, owned and maintained by Loughborough University. A YSI 600R water quality sonde was also deployed in the surface of the lake from the station between May 2010 and April 2012, with data managed locally (see Section 2.3.3).

2.3.2 Physical Characteristics & Water Chemistry

A range of standard limnological techniques and water samples were taken at typically 3 week intervals during stratification, increasing to monthly visits during the mixed period. A consistent method of survey was used at the meres which included a vertical profile at the deepest point of each lake (Figure 2.9; 2.10) and a spatial surface survey covering both littoral and pelagic areas (Figures 2.3 & 2.4). These points did not vary during the project and were established from an initial bathymetric survey across the meres.

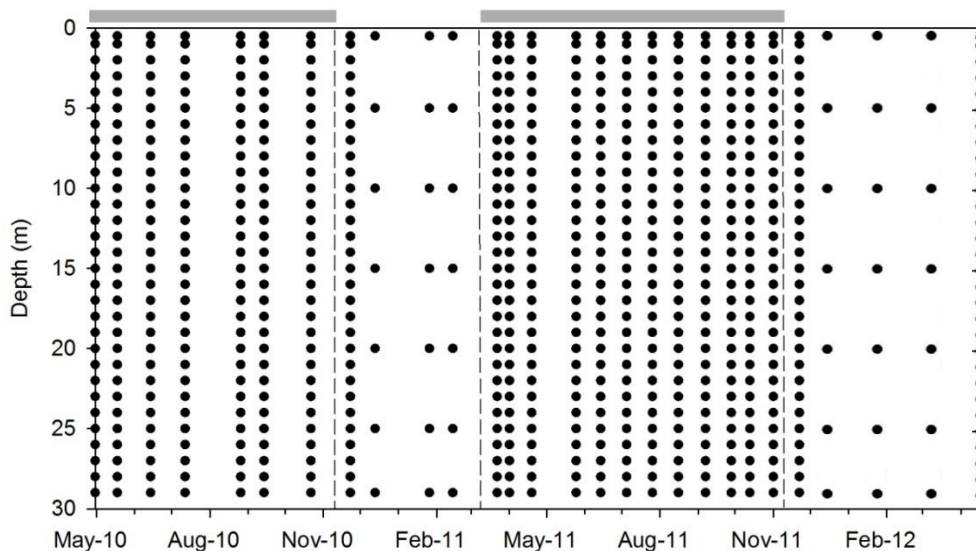


Figure 2.9 Water column survey depths and dates at Rostherne Mere.

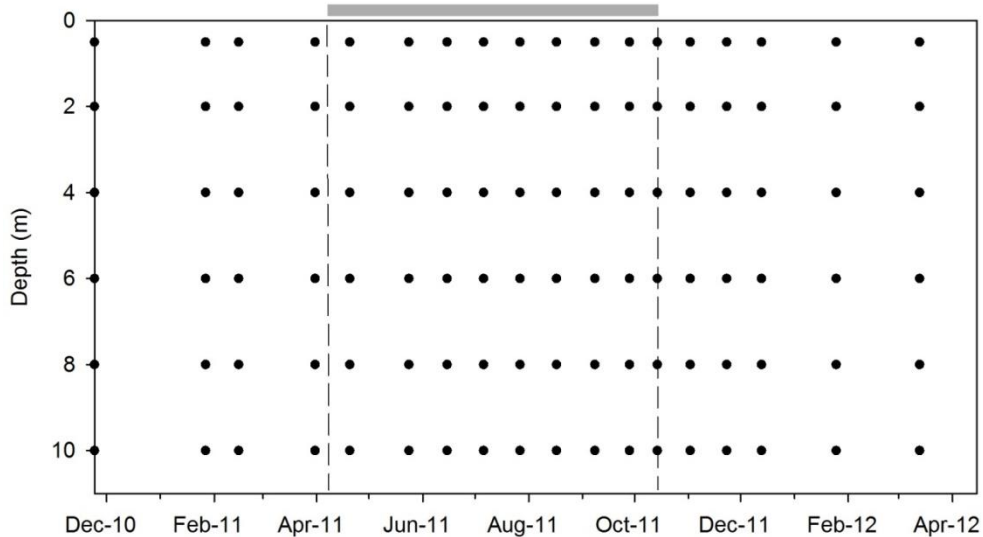


Figure 2.8 Water column survey depths and dates at Tatton Mere.

2.3.2.1 Lake Bathymetry

Detailed bathymetric surveys were carried out at both Rostherne Mere and Tatton Mere in May 2010 using a Garmin GPSMAP 431s sonar with dual-beam transducer. The unit is designed to transmit a sound pulse from the transducer in the water surface and record that same signal when it bounces back from the bed of the lake. An echo-sounder attached to the transducer filters and records the travel time of the pulse. At the same time that the pulse occurs, the in-built GPS unit records the location of the reading. The unit and transducer were attached to the boat transom and following a systematic grid pattern across the lake, depth data points were generated (approximately 2700 data points for Rostherne Mere and 1000 data points for Tatton Mere). The individual data points were then mapped in ArcGIS v10.1.

2.3.2.3 YSI Sonde and CO₂ Gas Analyser

Oxygen concentration, temperature, pH and conductivity were measured at 1 m intervals in the vertical profile and within the surface 0.5 m for the spatial surveys using a YSI 6600 V2 multi-parameter sonde. The sonde was regularly laboratory calibrated using standard solutions. $p\text{CO}_2$ was measured at the same intervals as the YSI survey using a PP Systems EGM-4 Gas Analyser with a Cole-Palmer peristaltic pump. An atmospheric reading was taken at the lake side during each visit. Whilst the lake was mixed (isothermal) the Rostherne Mere sampling interval was increased as the water column was assumed homogenous. Data were plotted

using Surfer 8.0 and the data between surveys interpolated using programme defaults for Ordinary Kriging, a statistical technique that estimates the value at locations not sampled from weighted average values of nearby locations.

2.3.2.4 Water Sampling

Water samples were collected for DOC, POC and alkalinity analysis at 3 m intervals in the vertical profile and within the surface 0.5 m for the spatial survey in 500 ml polypropylene bottles. The bottles were rinsed out twice with lake water prior to filling and every effort was made to ensure no air bubbles were trapped in the samples. Within 24 hours of collection the samples were filtered through pre-washed Whatmann GF/F glass-fibre filters (0.45 μm) using a hand pump. These filters were pre-combusted prior to fieldwork by heating to 550°C for 2 hours and weighed before use. POC was measured from the GF/F filters by drying overnight at 105°C, weighing then combusting at 550°C for 2 hours and weighing again. Samples for DOC were transferred into a 60 ml HDPE Nalgene bottle, taking care not to trap air bubbles in the sample. The samples were labelled, sealed with Nescofilm, a laboratory self-sealing film designed to resist air and gas diffusion, and stored at $\sim 4^\circ\text{C}$ overnight in the refrigerator before analysis at Loughborough University on a Shimadzu TOC analyser (TOC-VCSN) with an ASI-V auto sampler. The standards (50 ppm to 100 ppm) were automatically calibrated using the TOC analyser.

A small amount of each water sample was left unfiltered for determining alkalinity by titration to two end points with colour indicator solutions. The method, adapted from Wetzel & Likens (2000), is described below:

1. Place 0.01 M HCl into a burette
2. Pipette 10 ml unfiltered water sample into a 100 ml conical flask
3. Add 5 drops phenolphthalein indicator to conical flask
4. If pale pink, titrate to colourless (usually a few drops) and record volume of acid used in ml (y_1)
5. Add 5 drops BDH indicator
6. Titrate to grey colour and record total volume of acid used in ml (y_2)

Both phenolphthalein alkalinity and total alkalinity were determined using Equation 2.1:

$$\text{Alkalinity (meq/L)} = 10y/x \quad (2.1)$$

where 10 represents the volume of standard acid used i.e. 0.01 M, x is volume of water sample, here 10 ml, with y_1 used for phenolphthalein alkalinity and y_2 for total alkalinity. The relationships between various forms of alkalinity are expressed as follows:

- a. $y_1 = 0$. All alkalinity is bicarbonate.
- b. $y_1 < \frac{1}{2}y_2$. Bicarbonate and carbonate alkalinity both exist.
- c. $y_1 = \frac{1}{2}y_2$. All alkalinity is carbonate.

Classification of the principle forms of alkalinity was obtained from Equations 2.2 to 2.3:

$$\text{Bicarbonate Alkalinity} = y_2 - y_1 \quad (2.2)$$

$$\text{Carbonate Alkalinity} = y_1 \quad (2.3)$$

Separate water samples were collected every 4 months for nutrient analysis, they included:

- Total Phosphorus (TP) – all forms of P in the water column.
- Soluble Reactive Phosphorus (SRP) – P immediately available for growth.
- Total Nitrogen (TN) – all forms of N in the water column.
- Nitrate-N – N immediately available for growth ($\text{NO}_3\text{-N}$).

A single 500 ml sample was taken at 0.5 m, 12 m and 24 m at Rostherne Mere and 0.5 m, 5 m and 10 m at Tatton Mere in polypropylene bottles rinsed twice with lake water prior to filling. Within 24 hours of collection the samples were prepared for analysis at the Lancaster Environment Centre, a 60 ml sample filtered through pre-washed Whatmann GF/F glass-fibre filters (0.45 μm) (for SRP and Nitrate-N) and another 60 ml unfiltered sample (for TP and TN). Field blanks of filtered de-ionised and unfiltered de-ionised water were also provided.

2.3.3 Lake Metabolism

The metabolism of the meres was determined from the ‘free-water’ approach (Odum, 1956) using in-situ measurements of dissolved oxygen diel fluctuations, a period of 24 hours day and night, as a proxy for rates of GPP and R. Identical YSI 600R sondes were deployed in the surface, mixed layer of both lakes and programmed to record oxygen concentration, temperature, pH and conductivity every 15 minutes. The YSI sondes were regularly cleaned and calibrated to minimise drift in readings, especially during periods of high productivity. A mean sampling interval of 1 hour was used to calculate NEP daily estimates, with meteorological data such as wind speed, air temperature and barometric pressure from the automatic weather station on Rostherne Mere. Epilimnion or mixed layer depth (z_{mix} in Table 2.3) was inferred from a permanent thermistor or temperature sensor chain deployed in each lake and determined as the depth where water temperature starts to decrease at a rate of 1°C m^{-1} or more. The metabolism of a system is calculated from an equation first established by Odum (1956) and is typically written as:

$$\delta\text{O}_2/\delta t = \text{NEP} + F + A \quad (2.4)$$

$$\text{NEP} = \text{GPP} - R \quad (2.5)$$

where GPP is photosynthesis, R is respiration, $\delta\text{O}_2/\delta t$ is the observed change in dissolved oxygen through time, F is atmospheric flux of oxygen and A represents other processes that cause changes in dissolved oxygen concentration at the sampling site. $\delta\text{O}_2/\delta t$ can be directly measured, F is modelled as a function of the oxygen concentration gradient between water and atmosphere with a wind-driven exchange coefficient, and A is assumed to be negligible and typically removed from the calculation. The equations used to calculate lake metabolism are shown in Table 2.3, and their use is visualised in Figure 2.11.

The physical exchange of oxygen with the atmosphere (F; Eq. 2.13) is the product of the difference in measured dissolved oxygen concentration ($\text{O}_{2\text{ aq}}$) from dissolved oxygen saturation ($\text{O}_{2\text{ sat}}$), piston velocity ($k\text{O}_2$) and the depth of the mixed layer (z_{mix}). Oxygen saturation is the oxygen concentration in water in equilibrium with the atmosphere and is calculated as a function of ambient temperature (Eq. 2.6), but must also be corrected for barometric pressure (Eq. 2.7, 2.8). The piston velocity

drives the rate of exchange between the lake and the atmosphere (Eq. 2.12). It is dependent upon the gas transfer coefficient (k_{600} ; Eq. 2.11), estimated as a function of wind speed at 10 m above the lake surface (U_{10} ; Eq. 2.10), and the Schmidt number (sO_2). The Schmidt number represents the ratio of diffusion of momentum to the diffusion of mass in a fluid; the diffusion coefficient is temperature dependent and is therefore calculated as a function of temperature (Eq. 2.9).

Table 2.3 Equations used to calculate lake metabolism.

Parameter	Equation	Source	Eq.
The governing equation	$\delta O_2 / \delta t = NEP + F + A$	Odum (1956)	2.4
Oxygen saturation as a function of temperature (T, Celsius)	$O_{2\text{ sat}} \text{ (mg L}^{-1}\text{)} = -0.00006 T^3 + 0.0069 T^2 - 0.3906 T + 14.578$		2.6
Correction of $O_{2\text{ sat}}$ for barometric pressure (BP, millibars)	Correction factor = (BP 0.0987 – 0.0112) / 100	Staehr et al. (2010)	2.7
	$O_{2\text{ sat}} \text{ (mg L}^{-1}\text{) BP Correction} = O_{2\text{ sat}} \text{ (mg L}^{-1}\text{)} \cdot \text{correction factor}$		2.8
Schmidt number, from water temperature (T, Celsius)	$sO_2 = 1800.6 - 120.10 T + 3.7818 T^2 - 0.047608 T^3$	Wanninkhof (1992)	2.9
Wind speed correction at 10 metres height (U_{10}) from measured wind speed height (U_z)	$U_{10} = U_z \cdot 1.22$	Wanninkhof (1992)	2.10
Piston velocity (converted from cm/h to m/d)	$k_{600} \text{ (m d}^{-1}\text{)} = ((2.07 + (0.215 \cdot U_{10})^{1.7}) / 100) \cdot 24$	Cole & Caraco (1998)	2.11
	$kO_2 \text{ (m d}^{-1}\text{)} = k_{600} (sO_2 / 600)^{0.5}$	Jähne et al. (1987)	2.12
Gas Flux (Z_{mix} = mix layer depth)	$F \text{ (mg O}_2 \text{ L}^{-1} \text{ d}^{-1}\text{)} = kO_2 (O_{2\text{ sat}} - O_{2\text{ aq}}) / Z_{\text{mix}}$		2.13
Day fraction and daylight determination	Day fraction = Actual Date – (Last Day of Previous Year)		2.14
D_i = Current time; S_R = Sunrise; S_S = Sunset	Daylight “Day (1) or Night (2)” = IF(AND((D_i – FLOOR($D_{i-1}, 1$)) > S_R , (D_i – FLOOR($D_{i-1}, 1$)) < S_S), 1, 2)		2.15
R	$R \text{ (mg O}_2 \text{ L}^{-1} \text{ d}^{-1}\text{)} = F - \delta O_2 / \delta t$		2.16
GPP	$GPP \text{ (mg O}_2 \text{ L}^{-1} \text{ d}^{-1}\text{)} = \delta O_2 / \delta t - F + R$		2.17
NEP	$NEP \text{ (mg O}_2 \text{ L}^{-1} \text{ d}^{-1}\text{)} = GPP - R$		2.18
NEP to C Flux Conversion	$\text{mmol CO}_2 \text{ L}^{-1} = ((\text{SUM mg O}_2 \text{ L}^{-1} \text{ d}^{-1}) / (16 \cdot 2)) / PQ$ $\text{mg C L}^{-1} = (\text{mmol CO}_2 \text{ L}^{-1} \cdot 44) \cdot (12 / 44)$ $\text{g C m}^{-2} \text{ d}^{-1} = \text{mg C L}^{-1} \cdot Z_{\text{mix}} / \text{DAYS}$		2.19
PQ = 1.25 DAYS = no. of days in dataset			

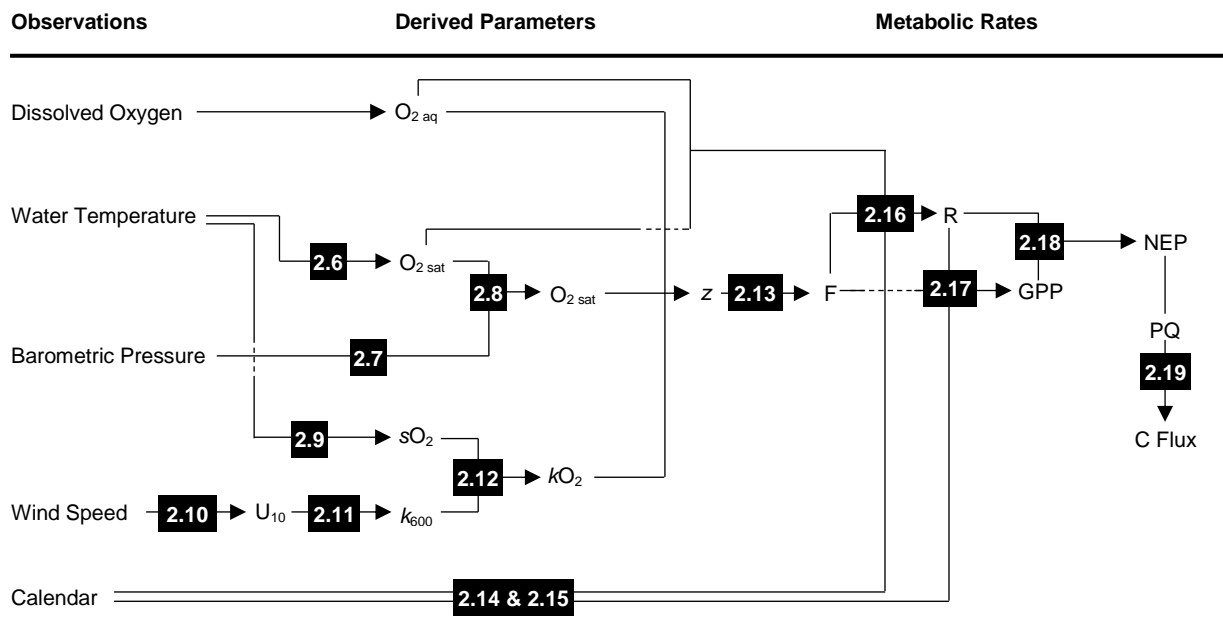


Figure 2.11 Converting measured data to metabolic process. Numbers refer to equations explained in Table 2.3.

Respiration (R ; Eq. 2.16) is determined from the physical exchange of oxygen and the observed change in dissolved oxygen through time; in this case 1 hour intervals. Gross Primary Productivity (GPP ; Eq. 2.17) is the product of the physical exchange of oxygen, the observed change in dissolved oxygen and respiration. The main assumptions within the equation are that GPP is zero at night, and therefore R is estimated directly from night time changes in dissolved oxygen concentration, and daytime R is equal to night time R . Daylight is determined by inputting sunrise and sunset times for each month then performing a logical test (IF) asking, is the current time interval before or after sunrise/sunset?

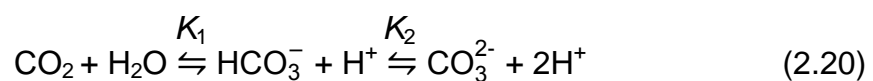
The calculated NEP value (Eq. 2.18) is the observed changes in dissolved oxygen after accounting for the atmospheric exchange and is used to infer the productivity of the meres, i.e. a positive figure infers net autotrophy and a negative figure infers net heterotrophy. The oxygen derived NEP figure was converted to carbon units using a photosynthetic quotient (PQ), the molar ratio of the rate of oxygen production to that of carbon assimilation, of 1.25 (Hanson et al., 2003; Williams & Robertson, 1991; Grande et al., 1989). Equation 2.19 shows how the volumetric rates of carbon assimilation ($\text{mmol CO}_2 \text{ L}^{-1}$) can be turned into areal rates (g C m^{-2}) by multiplying by mixing depth (z_{mix}). These rates represent the average carbon assimilation per

square metre of the entire lake, which when multiplied by the lake area, gives an estimate of whole lake carbon assimilation flux.

To evaluate the reliability of the metabolic rates to errors associated with the modelling previously described (Table 2.3; Figure 2.9) a simple sensitivity analysis was performed, where several parameters in the model were modified by $\pm 10\%$ to investigate their influence on daily NEP estimates (Staehr et al., 2010; Dubois et al., 2009; Bade et al., 2004). Two key assumptions central to the method of calculating metabolism were tested. First, was testing the sensitivity of metabolism to uncertainty in estimating the oxygen saturation concentration (Table 2.3; Eq. 2.6). Incorrect values of $O_{2 \text{ sat}}$ could originate due to errors in temperature, barometric pressure measurements, or poor calibration. Errors of this sort would cause inaccuracies in the oxygen flux term (F) of the governing equation for oxygen dynamics. Second, was testing the sensitivity of metabolism to uncertainty in k , the piston velocity (Table 2.3; Eq. 2.12). This error would also influence the O_2 flux term (F), but in a different manner than error in $O_{2 \text{ sat}}$.

2.3.4 Dissolved Inorganic Carbon

The components of the carbonate system within the meres were calculated from the direct measurement of two quantities (CO_2 and pH). Inorganic carbon is the primary source of carbon for photosynthesis and forms the acidity buffer within the lake, which can help to regulate against increases in CO_2 . The carbonate species are related by the following equilibria (Equation 2.20):



where K_1 and K_2 are equilibrium constants, often referred to as the first and second dissociation constants of carbonic acid, respectively. The equations used to estimate of the relative importance of the DIC species are presented in Table 2.4. Equilibrium constants presented are suitable for low salinity and freshwater ecosystems and from temperatures 0 - 50°C.

Table 2.4 Equations used to calculate lake DIC fractions.

Parameter	Equation	Source	Eq.
Henry's Constant	$K_H = 10^{(2385.73 / \text{Temp (K)} - 14.0184 + 0.01526 \text{Temp (K)})}$	Maberly (1996), refit from Harned & Davis (1943)	2.21
K_1	$K_1 = \text{EXP}(290.9097 - 14554.21 / \text{Temp (K)} - 45.0575 \ln \text{Temp (K)})$	Millero (1979), refit from Harned & Davis (1943)	2.22
K_2	$K_2 = \text{EXP}(207.6548 - 11843.79 / \text{Temp (K)} - 33.6485 \ln \text{Temp (K)})$	Millero (1979), refit from Harned & Scholes (1941)	2.23
$[\text{H}^+]$	$[\text{H}^+] = 10^{-\text{pH}}$		2.24
DIC	$\text{DIC } (\mu\text{mol L}^{-1}) = \text{CO}_2 (1 + K_1 / [\text{H}^+] + K_1 K_2 / [\text{H}^+]^2)$	Zeebe & Wolf-Gladrow (2001)	2.25
CO_2	$\text{CO}_2 (\mu\text{mol L}^{-1}) = f\text{CO}_2 \cdot K_H$	Zeebe & Wolf-Gladrow (2001)	2.26
HCO_3^-	$\text{HCO}_3^- (\mu\text{mol L}^{-1}) = \text{DIC} / (1 + [\text{H}^+] / K_1 + K_2 / [\text{H}^+])$	Zeebe & Wolf-Gladrow (2001)	2.27
CO_3^{2-}	$\text{CO}_3^{2-} (\mu\text{mol L}^{-1}) = \text{DIC} / (1 + [\text{H}^+] / K_2 + [\text{H}^+]^2 / K_1 K_2)$	Zeebe & Wolf-Gladrow (2001)	2.28

2.3.4.1 Carbon Dioxide Flux

Surface partial pressure CO_2 flux, equation 2.29, was calculated at monthly intervals from the $p\text{CO}_2$ data collected during the water chemistry surveys at the meres to determine the fate of CO_2 .

$$f\text{CO}_2 = k\text{CO}_2 \cdot K_H (p\text{CO}_{2 \text{ aq}} - p\text{CO}_{2 \text{ sat}}) \quad (2.29)$$

where $f\text{CO}_2$ is the flux of a CO_2 gas across the air–water interface, $k\text{CO}_2$ is the gas transfer velocity at a given temperature, K_H is Henry's Constant for CO_2 solubility in freshwater, and $p\text{CO}_{2 \text{ aq}}$ and $p\text{CO}_{2 \text{ sat}}$ are the measured gas partial pressures in freshwater and air, respectively. The equations used to calculate CO_2 flux are shown in Table 2.5, and their use is visualised in Figure 2.12. Equilibrium constants presented are suitable for low salinity and freshwater ecosystems and from temperatures 0 - 50°C.

The initial $p\text{CO}_2$ values collected represent its mole fraction measured in dry air, so a correction has to be applied that assumes the air at the air-water interface to be saturated with water vapour ($p\text{H}_2\text{O}$; Eq. 2.30). In dry air and at 1 atm the value of the mole fraction is equal to the value of the partial pressure. Henry's Constant (K_H)

is the concentration of a CO₂ gas in solution at a given temperature and is directly proportional to the partial pressure of that gas above the solution (Eq. 2.33). The piston velocity ($k\text{CO}_2$) drives the rate of exchange between the lake and the atmosphere (Eqs. 2.36; 2.37). It is estimated as a function of wind speed at 10 m above the lake surface (U_{10} ; Eq. 2.35), and the Schmidt number ($s\text{CO}_2$) when wind speeds are $\geq 3\text{ m s}^{-1}$. The Schmidt number represents the ratio of diffusion of momentum to the diffusion of mass in a fluid; the diffusion coefficient is temperature dependent and is therefore calculated as a function of temperature (Eq. 2.34).

Table 2.5 Equations used to calculate CO₂ lake-atmosphere exchange fluxes.

Parameter	Equation	Source	Eq.
Water vapour pressure (T, Kelvin)	$p_{\text{H}_2\text{O}} = \text{EXP}(24.4543 - (6745.09/T) - 4.8489 \ln(T/100) - 0.000544)$	Zeebe & Wolf-Gladrow (2001)	2.30
$p\text{CO}_2$ aq (T, Kelvin)	$p\text{CO}_2 \text{ aq } (\mu\text{atm}^{-1}) = \text{CO}_2 (\mu\text{mol mol}^{-1}) \cdot (\text{BP (atm)} - p_{\text{H}_2\text{O}})$	Zeebe & Wolf-Gladrow (2001)	2.31
$p\text{CO}_2$ sat	$p\text{CO}_2 \text{ sat } (\mu\text{atm}^{-1}) = \text{CO}_2 (\mu\text{mol mol}^{-1}) \cdot (\text{BP (atm)} - p_{\text{H}_2\text{O}})$	Zeebe & Wolf-Gladrow (2001)	2.32
Henry's Constant	$K_{\text{H}} = 10^{(2385.73 / \text{Temp (K)} - 14.0184 + 0.01526 \text{ Temp (K)})}$	Maberly (1996), refit from Harned & Davis (1943)	2.33
Schmidt number, from water temperature (T, Celsius)	$s\text{CO}_2 (\text{m d}^{-1}) = 1911.1 - 118.11 T + 3.4527 T^2 - 0.04132 T^3$	Wanninkhof (1992)	2.34
Wind speed correction at 10 metres height (U_{10}) from measured wind speed height (U_z)	$U_{10} = U_z \cdot 1.22$	Wanninkhof (1992)	2.35
Piston velocity (converted from cm/h to m/d)	$k\text{CO}_2 (\text{m d}^{-1}) = ((2.07 + (0.215 U_{10})^{1.7}) / 100) \cdot 24$ $U_{10} < 3\text{ m s}^{-1}$	Cole & Caraco (1998)	2.36
	$k\text{CO}_2 (\text{m d}^{-1}) = 0.31 \cdot U_{10} \cdot (s\text{CO}_2 / 600)^{-0.5}$ $U_{10} \geq 3\text{ m s}^{-1}$	Wanninkhof (1996)	2.37
Gas Flux	$f\text{CO}_2 (\text{mmol m}^{-2} \text{ d}^{-1}) = k\text{CO}_2 \cdot K_{\text{H}} (p\text{CO}_2 \text{ sat} - p\text{CO}_2 \text{ aq})$	Vachon et al. (2010)	2.29
Carbon flux (converted from $\text{m}^{-2} \text{ d}^{-1}$ to $\text{m}^{-2} \text{ y}^{-1}$)	$\text{mg CO}_2 \text{ m}^{-2} \text{ y}^{-1} = (f\text{CO}_2 \cdot 44) / 1000$ $\text{mg C m}^{-2} \text{ y}^{-1} = (\text{g CO}_2 \text{ m}^{-2} \text{ y}^{-1}) \cdot (12 / 44)$		2.38

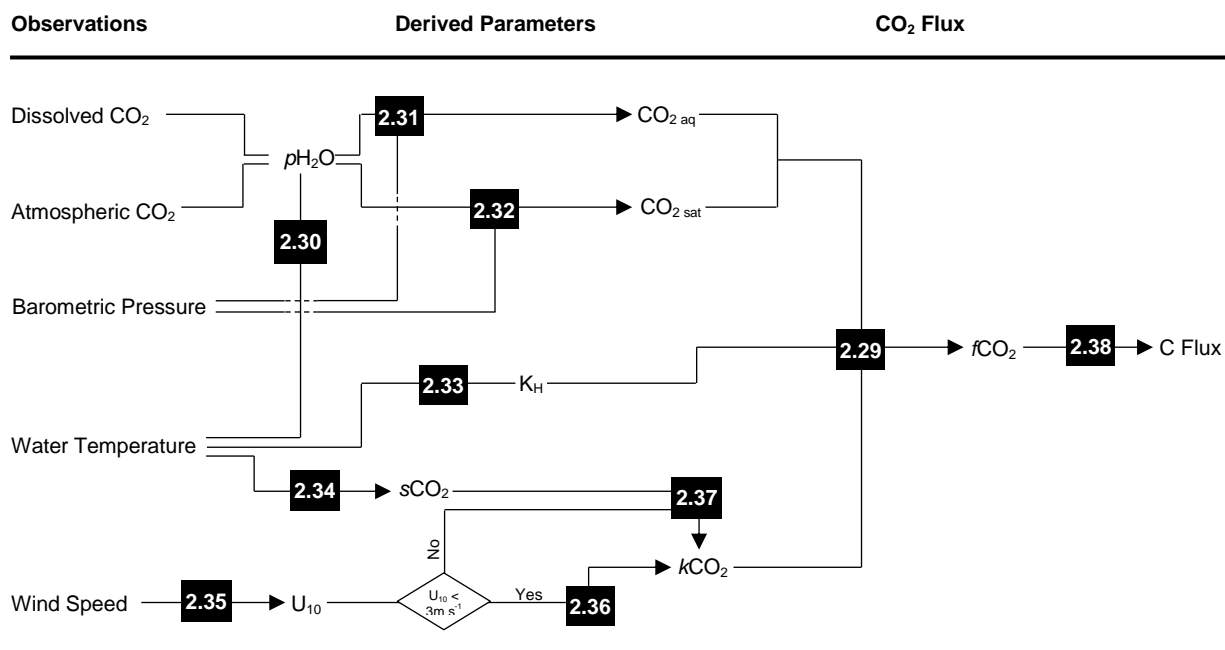


Figure 2.12 Converting measured data to CO₂ flux. Numbers refer to equations explained in Table 2.5.

2.3.4.2 Calcium Carbonate

The formation and dissolution of CaCO₃ can provide an insight into the buffering capabilities of a lake system as the equilibrium is sensitive to concentration of dissolved CO₂ in the water column. Sudden changes in the concentration of CO₂ can occur through a number of processes including losses as a result of photosynthetic utilisation and inflows of excess CO₂ from enriched groundwater, promoting the release of CO₂ to the atmosphere from the surface waters (Wetzel, 2001). This equilibrium can be estimated using the Saturation Index (SI) in Equation 2.39:

$$SI = pH - pH_s \quad (2.39)$$

where pH is the measured pH and pH_s is the pH of the water if it were in equilibrium with CaCO₃ at the existing calcium ion [Ca²⁺] and bicarbonate ion [HCO₃⁻] concentrations. Systems with a positive SI are oversaturated with respect to CaCO₃ and this tends to lead to the precipitation of CaCO₃ when suitable precipitation nuclei are available such as algae, whereas systems with a negative SI are under-saturated with respect to CaCO₃ and tend to dissolve CaCO₃. The SI for a saturated system is zero i.e. waters in equilibrium with CaCO₃ and have neither CaCO₃

precipitation nor a tendency to dissolve CaCO_3 and so separates conditions where CaCO_3 precipitation is likely ($\text{SI} > 0$) or not ($\text{SI} < 0$). The equations used to calculate the calcite saturation index are shown in Table 2.6, and their use is visualised in Figure 2.13.

The SI was calculated using a complete mineral analysis, therefore initially the ionic strength of the ions present in calcium carbonate (HCO_3^- , CO_3^{2-} , Alk) is required (Eq. 2.40). The ionic strength of a solution is a measure of the concentration of ions in that solution. Ionic compounds, when dissolved in water, dissociate into ions. K_2 refers to the second dissociation constant for carbonic acid (Eq. 2.41) and is a function of water temperature. K_s is the solubility product constant for CaCO_3 and also a function of water temperature (Eq. 2.42). The activity coefficient of electrolyte solutions (γ ; Eq. 2.43) is a dimensionless quantity that represents how close the solution is to ideal behaviour according to Henry's Law and is function of temperature (A ; Eq. 2.44). pH_s represents the pH of the water if it were in equilibrium with CaCO_3 at the existing calcium ion $[\text{Ca}^{2+}]$ and bicarbonate ion $[\text{HCO}_3^-]$ concentrations. The difference between pH and pH_s signifies the SI of calcium carbonate (Eq. 2.39).

Table 2.6 Equations used to calculate calcium carbonate saturation index (SI).

Parameter	Equation	Source	Eq.
Ionic strength	$I = \frac{1}{2} \sum c_i z_i^2$ where c refers to the concentrations of all ions present in solution; z is the charge of the ion	Stumm & Morgan (1981)	2.40
K_2 (T, Kelvin)	$pK_2 = 107.8871 + 0.03252849 T - 5151.79 / T - 38.92561 \log T + 563713.9 / T^2$	Plummer & Busenberg (1982)	2.41
Calcite Solubility Product (T, Kelvin)	$pK_s = 171.9065 + 0.077993 T - 2839.319 / T - 71.595 \log T$	Plummer & Busenberg (1982)	2.42
Davies activity coefficient (T, Celsius)	$\gamma = A (\sqrt{I} / (1 + \sqrt{I}) - 0.3I)$ where $A = 0.0008 T + 0.4881$ and I is ionic strength	Stumm & Morgan (1981)	2.43 2.44
pH_s	$pH_s = pK_2 - pK_s + p[\text{Ca}^{2+}] + p[\text{HCO}_3^-] + 5\gamma$	Snoeyink & Jenkins (1980)	2.45
Saturation Index	$\text{SI} = pH - pH_s$		2.39

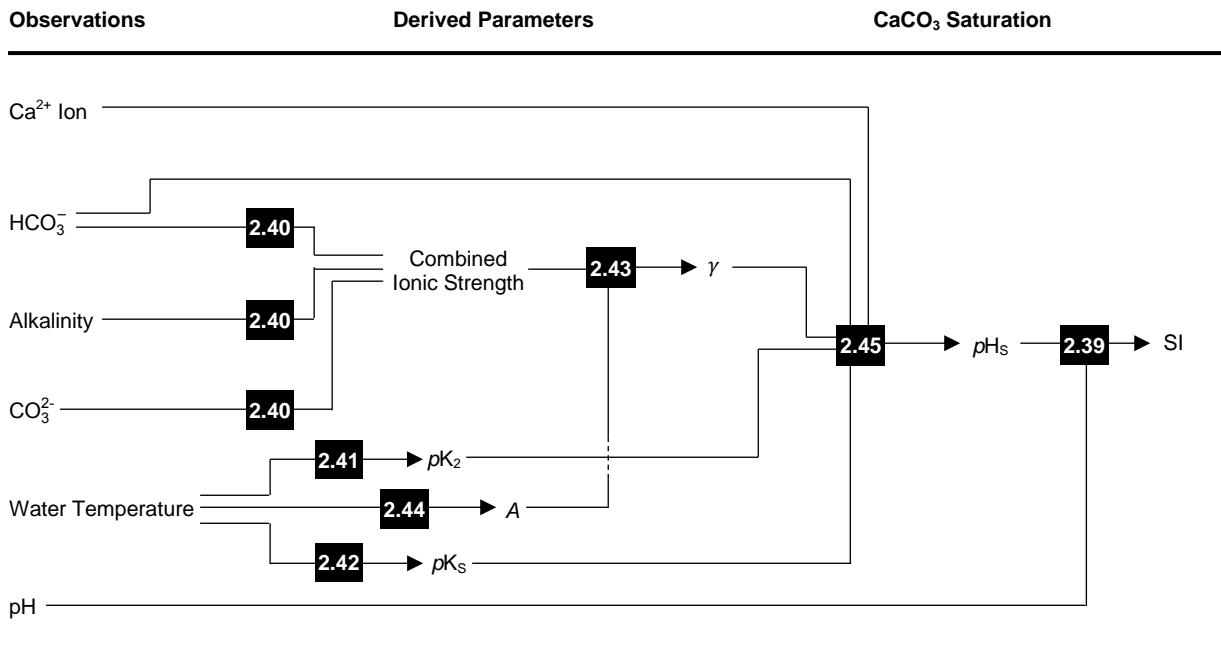


Figure 2.13 Converting measured data to the calcite saturation index. Numbers refer to equations explained in Table 2.6.

2.3.5 Carbon Accumulation and Burial from Trap and Sediment Data

The carbon accumulation rate and burial efficiency of both meres was calculated from a dated master sediment core and sediment trap data (Figure 2.14). The procedure for this is explained below:

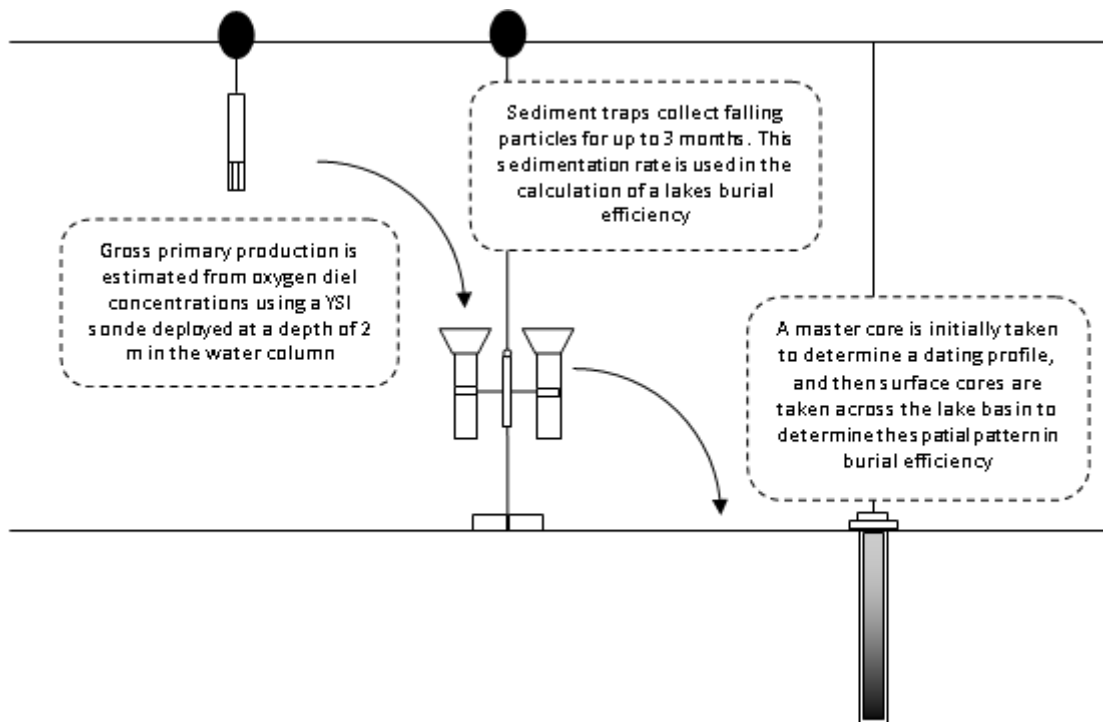


Figure 2.14 Diagram showing the method used to determine carbon sequestration and burial efficiency in Rostherne Mere and Tatton Mere.

2.3.5.1 Sediment Traps

The total organic carbon settling input to the sediment was calculated by using the estimates of GPP and sediment traps, which measure the sedimentation rate. At Rostherne Mere a system of KC Denmark open sediment trap stations were set at 10 m and 22 m within the lake basin collected sinking seston (organic and inorganic particles) through the water column and reset every 3 months. These traps comprise 4 open, clear plastic tubes (450 mm length/ \varnothing 72 mm internal diameter) with a trapping ratio of 1:6.3 and trapping area of 0.10 m². Technicap PPS 4/3 automatic sequencing traps were also set at 10 m and 22 m at Rostherne Mere to collect sediments at a high resolution, 2 week interval. These traps comprise a large open funnel (1310 mm length/ \varnothing 252 mm internal diameter) with a trapping ratio of 1:5.1 and trapping area of 0.05 m² that delivers sediment to 12 individual 500 ml plastic bottles that were programmed to each collect sediment for 2 weeks. The traps were reset every 6 months as dictated by the trapping interval used. At Tatton Mere a single KC Denmark open sediment trap station was set at 7 m and reset at 6 week intervals during the winter and at 3 week intervals during the stratification period.

The organic matter and carbonate content within the sediments traps was determined using LOI at 550°C and 925°C (see section 2.3.5.2). Trap samples were stored frozen and either freeze-dried or thawed out prior to analysis. A small number of samples were subsequently freeze-dried as part of the UKLEON research project. Here samples were initially frozen using Dry Ice then transferred to a Christ BETA 1-8LD freeze-drier, which uses a vacuum to slowly reduce the pressure inside the drier over several hours to allow the frozen water in the material to sublime directly from the solid phase to the gas phase.

2.3.5.2 Sediment Core Collection

The master sediment core for Rostherne Mere (RM_Liv_2011, 112 cm long), taken at 26 m water depth in September 2011, was cut at 1 cm intervals from 0 – 50 cm and 0.5 cm intervals from 50 cm to 112 cm due to sediment compression through the core as further sediment accumulation occurs over time and expected lower sediment accumulations rate pre-20th century. Samples were kept frozen in the laboratories at Loughborough University until needed for analysis. The master sediment core for Tatton Mere (SCM41E, 119 cm long), taken at 11.6 m water depth

in February 2010 by Bennion et al. (2010), was cut at 1 cm intervals throughout except for 0 – 2 cm which was an amalgamated sample.

2.3.5.3 Estimation of Organic Matter and CaCO₃ Content

Organic matter was estimated for trap and core samples using loss-on-ignition (LOI).

LOI is determined by the following method (Dean, 1974):

1. 1g wet weight of sample is dried overnight at 105°C.
2. Once cooled samples are weighed (to 4 decimal places).
3. Samples are transferred to furnace at 550°C for 2 hours.
4. Once cooled samples are reweighed (to 4 decimal places).
5. Difference between dry weight and ash weight is the percentage of dry weight lost on ignition.
6. Remaining ash sample may then be used for carbonate analysis, by heating to 925°C for 4 hours.
7. Once cooled samples are reweighed (to 4 decimal places).
8. Difference between ash weight and weight lost at 925°C is multiplied by 2.274 (the molecular weight of CaCO₃ divided by the molecular weight of CO₂) to derive the carbonate content which can then be expressed as a percentage of the dry weight.

For freeze-dried samples Equation 2.46 was used to calculate the flux of organic matter (g C m⁻² d⁻¹):

$$\text{Flux} = \frac{\text{Total Sample (g)} / \text{Trap Area (m}^2)}{\text{Number of Collecting Days (d)}} \times \frac{\text{Weight \%LOI}}{100} \times 0.46 \quad (2.46)$$

For wet samples Equation 2.47 was used to calculate the flux of organic matter (g C m⁻² d⁻¹):

$$\text{Flux} = \frac{\text{Total Sample (ml)} / \text{Sub Sample (ml)}}{\text{Collecting Days (d)} \times \text{Trap Area (m}^2)} \times \text{Organic Matter (g)} \times 0.46 \quad (2.47)$$

Organic content was converted to organic carbon (OC) for each sample by multiplying the percentage of OM by a factor of 0.46 (Dean, 1974). Fluxes were summed up for each trap sample to give an average estimate for the sampling period.

2.3.5.4 Sediment Core Dating

For the Rostherne Mere master core, 10g wet weight subsamples of the core were taken every 2 cm from 0 – 50 cm and every 4 cm from 50 cm – 112 cm, dried at 50°C, and pulverised after weighing with a mortar and pestle in preparation for lead-210 (^{210}Pb) analysis performed by Dr Dan Engstrom, St. Croix Watershed Research Station, Minnesota, USA.

The analysis of ^{210}Pb is used as a dating technique because once formed, from either sediments or rocks containing uranium-238 (^{238}U) or in the atmosphere from radium-226 (^{226}Ra), it can begin to accumulate in lake sediments. The ^{210}Pb eventually decays, over time, into a non-radioactive form of lead. The half-life of ^{210}Pb is 22.3 years, which means if the sediment layers are undisturbed, as the sediment ages it slowly loses its radioactivity. Cores are typically dated through the analysis of a series of stratigraphic levels from the core surface to a depth where unsupported ^{210}Pb is no longer measurable. It takes approximately 7 half-lives, or 150 years for the ^{210}Pb in a sample to reach near-zero radioactivity (Wetzel, 2001).

^{210}Pb was measured at 16 depth intervals through its grand-daughter product ^{210}Po , with ^{209}Po added as an internal yield tracer. The polonium isotopes were distilled from 0.5 g dry sediment at 550 °C following pretreatment with concentrated HCl and plated directly onto silver planchets from a 0.5 N HCl solution (modified from Eakins & Morrison, 1976). Activity was measured for $1-6 \times 10^5$ s with ion-implanted surface barrier detectors and an Ortec alpha spectroscopy system. Unsupported ^{210}Pb was calculated by subtracting supported activity from the total activity measured at each level; supported ^{210}Pb was estimated from the asymptotic activity at depth (the mean of the lower most samples in the core) or alternatively, from ^{214}Pb activity measured by gamma spectrometry at selected core intervals. From the resulting ^{210}Pb profile, dates and sedimentation rates were determined according to the constant rate of

supply model with confidence intervals calculated by first-order error analysis of counting uncertainty (Appleby, 2001).

The core samples were corrected for sediment focusing, the preferential deposition of fine-grained sediments in deeper regions of the lake basin, to enable a single sediment core to be used to estimate whole basin accumulation. This correction is applied to the whole core and therefore assumes that focusing is constant over time, which may not be a valid assumption in some cases. However, the benefits of using focusing-corrected estimates considerably outweigh possible problems associated with the approach (Engstrom & Rose, 2013). The correction is based a focusing factor for ^{210}Pb flux:

$$\text{FC} = \frac{F(^{210}\text{Pb}_{\text{site}})}{F(^{210}\text{Pb}_{\text{atm}})} \quad (2.48)$$

where $F(^{210}\text{Pb}_{\text{site}})$ is site specific flux of unsupported (excess) ^{210}Pb and $F(^{210}\text{Pb}_{\text{atm}})$ is atmospheric flux of excess ^{210}Pb , both expressed in $\text{Bq m}^{-2} \text{yr}^{-1}$. Following this method, a focusing correction value of 0.7 was calculated for Rostherne Mere.

Dating of the Tatton Mere core was carried out at University College London (UCL) using the well-established technique of spheroidal carbonaceous particle analysis (SCP) (Appleby, 1994). This method was chosen for Tatton Mere as a full SCP record was present, allowing percentiles from the cumulative curve to each be ascribed a date.

Dried sediment was subjected to sequential chemical attack by mineral acids to remove unwanted fractions leaving a suspension of mainly carbonaceous material and a few persistent minerals in water. SCPs are composed mostly of elemental carbon and are chemically robust. The use of concentrated nitric acid (to remove organic material), hydrofluoric acid (siliceous material) and hydrochloric acid (carbonates and bicarbonates) therefore does them no damage. A known fraction of the resulting suspension was evaporated onto a coverslip and mounted onto a microscope slide. The number of SCPs on the coverslip was counted using a light microscope at x450 magnification and the sediment concentration calculated in units

of 'number of particles per gram dry mass of sediment' (gDM⁻¹). The criteria for SCP identification under the light microscope followed Rose (2008). Analytical blanks and SCP reference material (Rose, 2008) were included in each batch of sample digestions. Reference concentrations agreed with the expected values while no SCPs were observed in the blanks. The detection limit for the technique is ~100 gDM⁻¹ and concentrations have an accuracy of ~ ± 45 gDM⁻¹. The core was subsequently dated using cumulative SCP inventory profiles (Rose & Appleby, 2005) where a date for each 10-percentile of the cumulative SCP profile, from the start of the record (0%) to the concentration peak (100%) was allocated to the core.

Using these time-stratigraphic horizons and the thickness of sediment between them, sedimentation rates can be determined using Equation 2.48:

$$\text{Sedimentation rate (cm yr}^{-1}\text{)} = \frac{\text{length between time stratigraphic horizons (cm)}}{\text{time period (yr)}} \quad (2.48)$$

2.3.5.5 Estimating Carbon Burial Efficiency

The organic carbon burial efficiency (Equation 2.49) is calculated as the ratio between organic carbon gross sedimentation rate (g C m⁻² yr⁻¹), derived from mass depositional sediment trap data (Rostherne Mere 22 m deep sequencing trap and Tatton Mere 7 m deep open trap station), and organic carbon net sedimentation rate (g C m⁻² yr⁻¹) into the surface sediments as measured from the master cores taken at each lake. However there is some debate over the method for calculating net sedimentation rate with Gälman et al. (2008) arguing that it is derived from surface sediments > 10 years old, as the majority of C mineralisation takes place within 10 years of initial deposition, and Sobek et al. (2009) maintaining that only sediment layers > 25 years old should be considered due to longer term on-going mineralisation within the sediment.

$$\text{Burial Efficiency \% (BE)} = \frac{\text{OC Net Sedimentation Rate}}{\text{OC Gross Sedimentation Rate}} \quad (2.49)$$

Following Gälman et al. (2008), core sediments < 10 years old were discounted from calculating organic carbon net sedimentation rate (Equation 2.50):

$$\text{OC Net Sedimentation Rate} = \text{Sediment AR (> 10 years)} \times (\text{LOI} / 100) \times 0.46 \quad (2.50)$$

Alongside determining organic carbon content (Section 2.3.5.3); the method devised by Sobek et al. (2009) requires the density and porosity for the sediment layers > 25 years old to be calculated (Eqs. 2.49 – 2.51). Dry bulk density (ρ) of the sediment was calculated from the organic carbon content according to Müller et al. (2005) and assumes that the sediment is a two-phase mixture between silicate and carbonate minerals (density $\sim 2.65 \text{ g cm}^{-3}$) and organic matter (density $\sim 1 \text{ g cm}^{-3}$) (Equation 2.49):

$$\rho \text{ (g cm}^{-3}\text{)} = -0.0523 \text{ (OC\%)} + 2.65 \quad (2.51)$$

From dry bulk density (ρ , g cm^{-3}) and water content (WC%), porosity (Φ) was calculated as follows (Equation 2.50):

$$\Phi = \text{WC\%} / (\text{WC\%} + (1 - \text{WC\%}) \rho) \quad (2.50)$$

Finally, the net sedimentation rate was calculated from the sedimentation rate (SR, mm yr^{-1}), dry bulk density and porosity (Equation 2.51):

$$\text{OC Net Sedimentation Rate} = \text{SR (> 25 years)} \times \rho / \Phi \quad (2.51)$$

2.3.6 Summary of Data Acquisition

A summary of all field and laboratory data required for the calculation of carbon fixation, flux and burial efficiency in Rostherne Mere and Tatton Mere are shown in Table 2.7. All field data was collected and where stated processed at Loughborough University. Where facilities weren't available external laboratories were utilised and are denoted by superscript numbers.

Table 2.7 Summary of project data acquisition. Items marked with superscript numbers denote external laboratory work where ⁽¹⁾ Lancaster Environment Centre, ⁽²⁾ BGS, Keyworth, ⁽³⁾ St. Croix Watershed Research Station, Minnesota and ⁽⁴⁾ UCL.

Field Data	Laboratory Data	Data Calculations
Lake Bathymetry	TP ⁽¹⁾ & SRP ⁽¹⁾	Lake Metabolism
Air Temperature	TN ⁽¹⁾ & Nitrate-N ⁽¹⁾	NEP = GPP – R
Solar Radiation	Ca ²⁺ ⁽²⁾	Inorganic Carbon
Barometric Pressure	Alkalinity	DIC=[CO ₂ aq]+[H ₂ CO ₃]+[HCO ₃ ⁻]+[CO ₃ ²⁻]
Wind Speed	DOC	CO ₂ Flux
Wind Direction	POC	Calcium Carbonate Flux
Water Temperature	LOI	OC Flux
O ₂ Concentration	Freeze-drying	OC Accumulation & Focusing
pH	²¹⁰ Pb Core Dating ⁽³⁾	OC Burial Efficiency
Conductivity	SCP Core Dating ⁽⁴⁾	
CO ₂ Concentration		
Lake Cores		
Lake Sediment Traps		

3.1 METEOROLOGICAL DATA

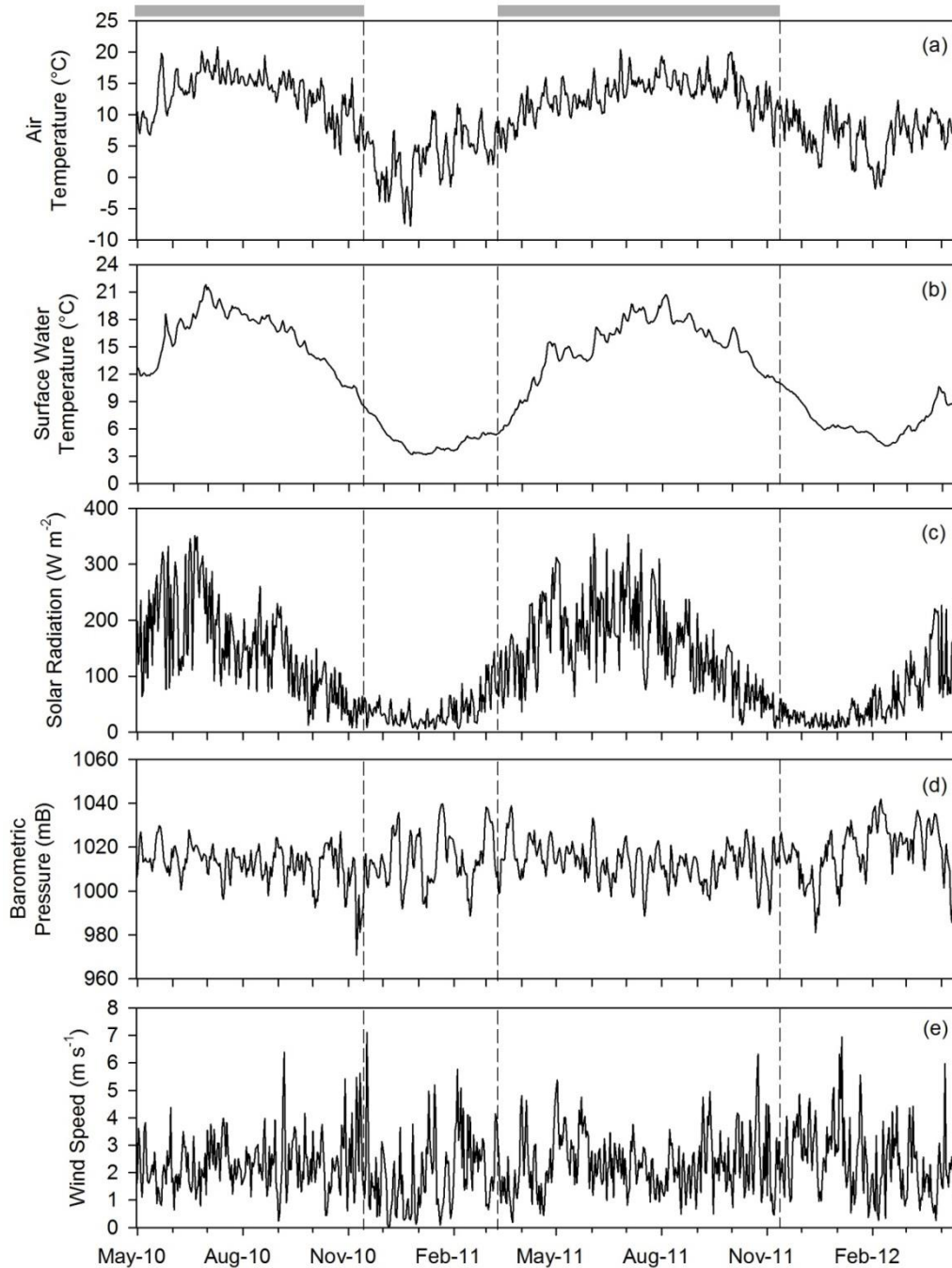


Figure 3.1 Meteorological data recorded at the automatic weather station deployed on Rostherne Mere for the period of study. All data are daily means. (a) Air temperature ($^{\circ}\text{C}$), (b) surface water temperature ($^{\circ}\text{C}$), (c) solar radiation (W m^{-2}), (d) barometric pressure (mB) and (e) wind speed (m s^{-1}). Periods of lake stratification are shown with grey bars and dashed lines.

The climate of Cheshire East is temperate maritime. Between May 2010 and May 2012 the mean air temperature was 10.9°C, with a mean high of 20.8°C in 2010 and 20.4°C in 2011 and a mean low of -7.8°C in 2010 and -1.5°C in 2011 (Figure 3.1a). The mean surface water temperature in Rostherne Mere was 12.6°C, with a mean high of 21.8°C in 2010 and 20.7°C in 2011, the mean low of 3.2°C occurred in both 2010 and 2011 (Figure 3.1b). Air temperature is highly correlated with surface water temperature in Rostherne Mere ($r^2 = 0.84$; $p < 0.01$) and Tatton Mere ($r^2 = 0.84$; $p < 0.01$).

Solar radiation maximum values occurred during July 2010 and June 2011, and lowest values during January 2011 and 2012 (Figure 3.1c). The highest recorded average pressure was 1035 mB in December 2010 and 1039 mB in January 2011. The lowest recorded average pressure was 970 mB in November 2010 and 981 mB in December 2011. The average wind speed between May 2010 and May 2012 was 2.3 m s⁻¹, and informed the selection of low wind speed constants for use in calculating net ecosystem production (Figure 3.1e).

3.2 ROSTHERNE MERE

3.2.1 Water Chemistry

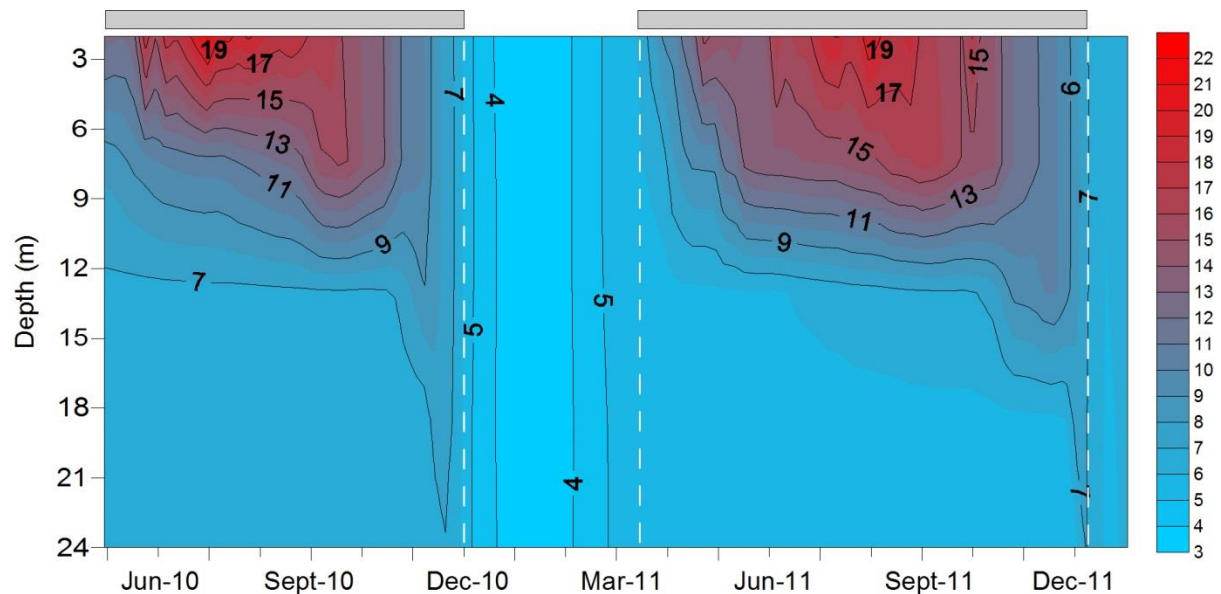


Figure 3.2 Depth-time plot of temperature (°C) measured in Rostherne Mere from May 2010 to April 2012. Periods of lake stratification are shown with grey bars and dashed lines.

Rostherne Mere is a warm monomictic, eutrophic lake system. Figure 3.2 shows temperature stratification over the period of study and highlights the very distinct monomictic mixing regime. Stratification is initiated in mid-March and continues until mid-November when it breaks down and the lake remains mixed for the remainder of the year. A water temperature of approximately 7°C seems critical for the onset and breakdown of stratification. Stratification is very intense during June, July and August with surface water temperatures reaching up to 22°C creating a very small epilimnion, typically only 4 – 5 m deep. Once stratification has begun to break down the lake becomes isothermal within a matter of weeks. No significant ice cover was observed during the study period.

Table 3.1 Summary of phosphorus and nitrogen nutrient availability in Rostherne Mere 2010 – 2012. Water column mean concentration \pm SD.

		Total P ($\mu\text{g L}^{-1}$)	SRP ($\mu\text{g L}^{-1}$)	Total N ($\mu\text{g L}^{-1}$)	Nitrate-N ($\mu\text{g L}^{-1}$)
19 May 2010	0.5m	168	148	1540	907
	12m	232	221	1820	1392
	24m	254	250	1930	1395
	Mean	218 \pm 45	206 \pm 53	1763 \pm 201	1231 \pm 281
14 Sept 2010	0.5m	97	21	920	18
	12m	336	316	2000	1411
	24m	914	871	2780	956
	Mean	449 \pm 420	403 \pm 432	1900 \pm 934	795 \pm 710
27 Jan 2011	0.5m	313	291	1630	710
	12m	324	300	1680	752
	24m	325	301	1680	760
	Mean	321 \pm 7	298 \pm 6	1666 \pm 29	741 \pm 27
27 May 2011	0.5m	222	186	1290	846
	12m	303	274	1940	1278
	24m	437	387	2300	1221
	Mean	321 \pm 109	282 \pm 101	1850 \pm 512	1118 \pm 235
02 Nov 2011	0.5m	178	105	82	116
	12m	199	110	87	128
	24m	933	870	2170	22
	Mean	437 \pm 430	362 \pm 440	1290 \pm 1204	89 \pm 58
08 Mar 2012	0.5m	323	290	1840	1356
	12m	306	288	1840	1283
	24m	310	286	1850	1225
	Mean	313 \pm 9	288 \pm 2	1840 \pm 6	1288 \pm 66

Levels of total phosphorus (TP) and total nitrogen (TN) are both high in Rostherne Mere (Table 3.1) but do show variability through the water column and with time. During the period of study surface water nutrient means were $216 \pm 88 \mu\text{g P L}^{-1}$ (mean \pm SD; $n = 6$) and $1217 \pm 639 \mu\text{g N L}^{-1}$ ($n = 6$) respectively. The hypertrophic (TP > $100 \mu\text{g L}^{-1}$; TN > $1200 \mu\text{g L}^{-1}$) levels of P suggest that N is likely to be the growth limiting nutrient within Rostherne Mere. Variability in water column concentrations are linked to stratification as during mixed months the concentrations of both P and N are virtually uniform (27 Jan 2011 and 08 Mar 2012), whereas during stratified months (19 May 2010, 14 Sept 2010, 27 May 2011 and 02 Nov 2011) the epilimnion nutrients are heavily depleted in contrast to those in the hypolimnion.

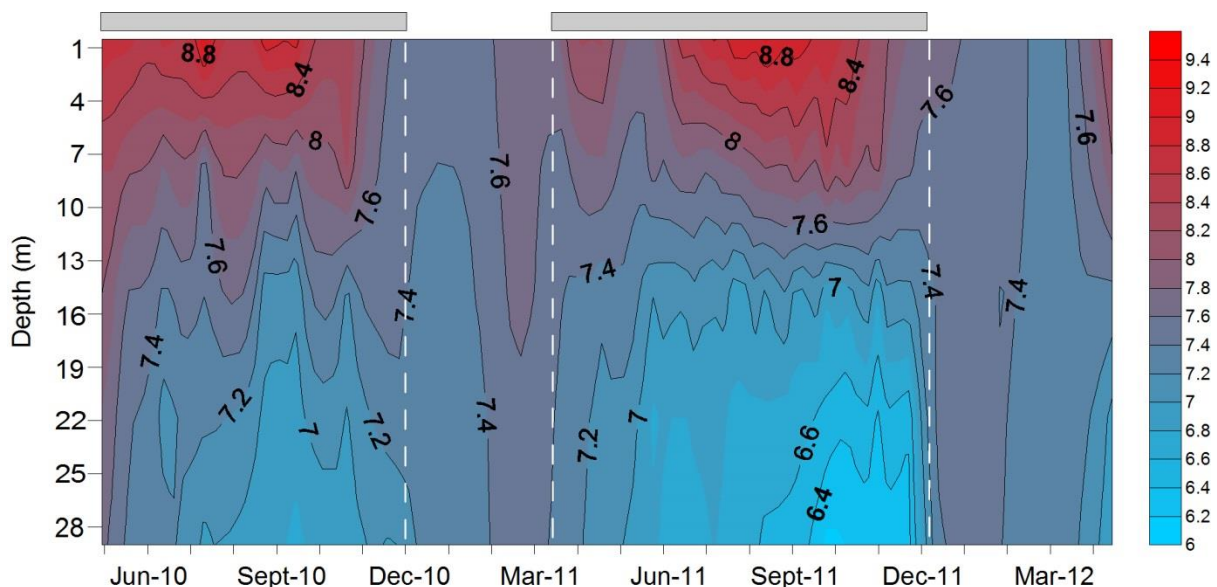


Figure 3.3 Depth-time plot of pH measured in Rostherne Mere from May 2010 to April 2012

The pH of Rostherne Mere exhibits marked seasonality, reaching 9.3 within the epilimnion and falling to 6.1 in the hypolimnion during the summer months of 2010 and 2011; winter values averaged 7.4 ± 0.5 ($n = 193$; Figure 3.3).

The mean transparency at Rostherne Mere was recorded at 2.8 ± 1.5 m ($n = 31$; Figure 3.4). Highest transparency was measured during the mixed phase, December 2010 and January 2011 respectively (6.0 & 6.2 m), with lowest transparency occurring during both July and August 2010 & 2011 (1.1 m).

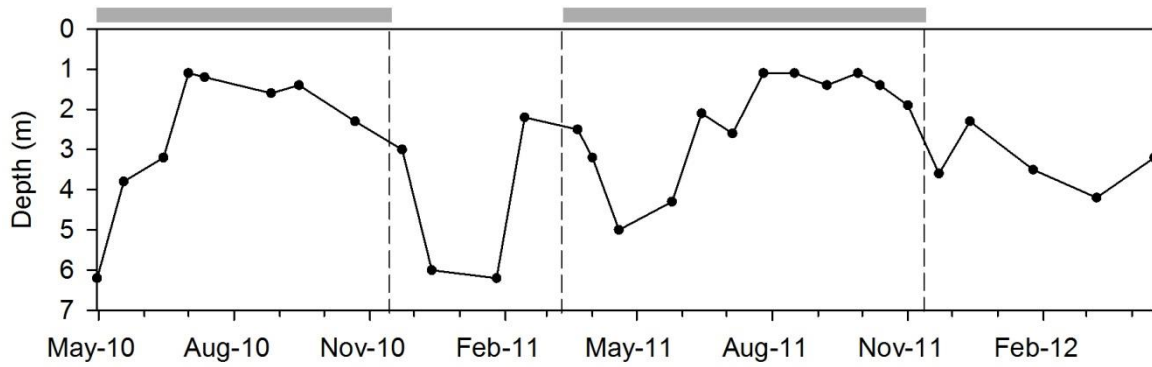


Figure 3.4 Secchi disc depths recorded in Rostherne Mere from May 2010 to April 2012

3.2.2 Organic Carbon Production

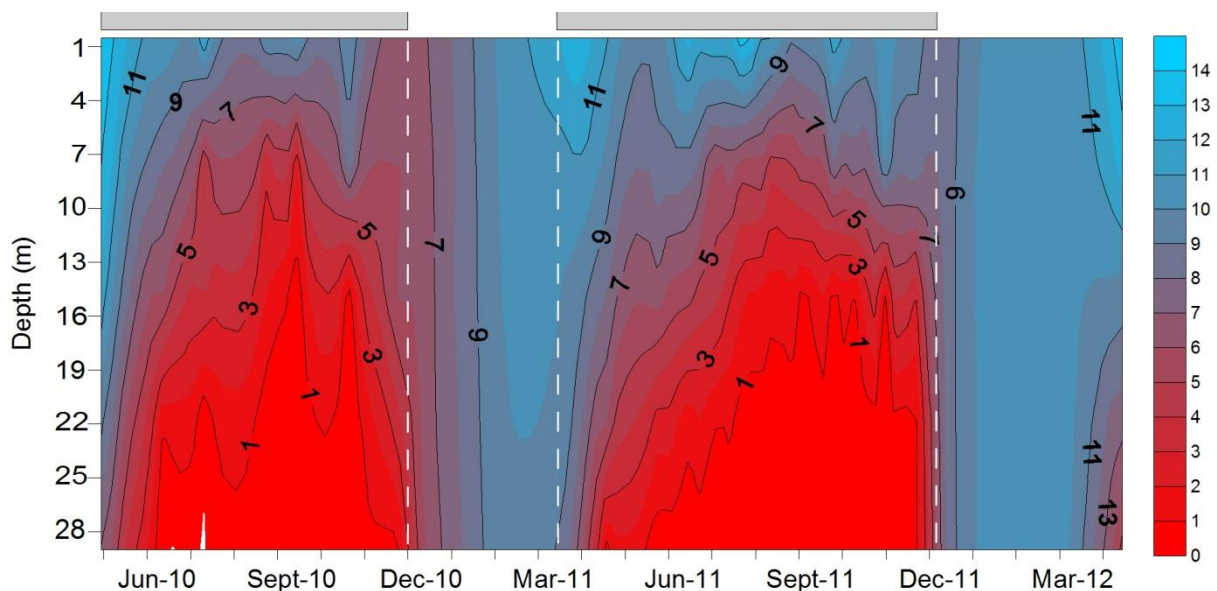


Figure 3.5 Depth-time plot of dissolved oxygen (mg L^{-1}) measured in Rostherne Mere from May 2010 to April 2012.

Alongside thermal stratification (Figure 3.2), Rostherne Mere also experiences dissolved oxygen (O_2) stratification (Figure 3.5). Summer oxygen super saturation in the epilimnion ($> 14 \text{ mg L}^{-1}$) is echoed by hypoxia ($< 2 \text{ mg L}^{-1}$) in the hypolimnion. Low oxygen concentrations develop quickly in the hypolimnion with the onset of stratification and depletion rises quickly from depth as oxygen is consumed, leaving over 50% of the lake hypoxic. This trend persists until lake turnover, when

concentrations steadily increase as oxygenated water from the epilimnion is mixed down into the anoxic hypolimnion.

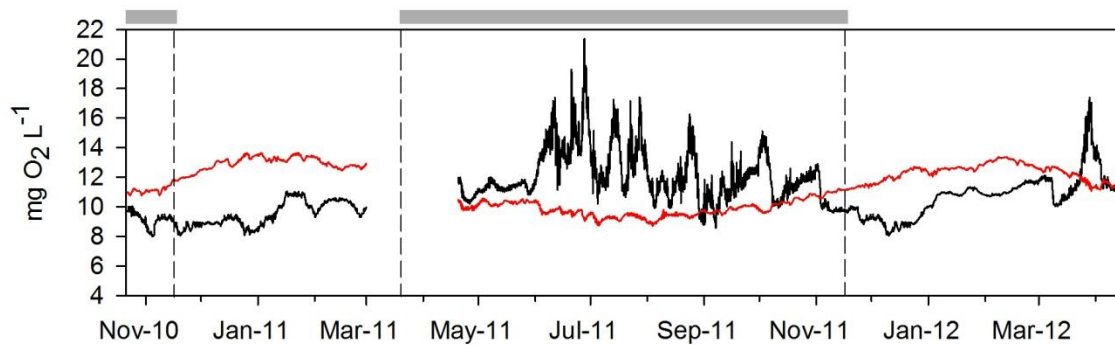


Figure 3.6 Hourly surface oxygen concentration (mg L^{-1}) for Rostherne Mere. Black line is measured surface concentration; red line is oxygen saturation concentration.

Figure 3.6 shows hourly O_2 data compared to the expected oxygen saturation. The lake is under saturated with oxygen during the winter months when the lake is fully mixed and temperatures are at their lowest (lowest oxygen values recorded in December 2010 and 2011). Similarly the lake is super saturated with oxygen during the summer months when the lake is stratified and photosynthesis only occurs in the top 4 – 5 m of the water column (highest oxygen values were recorded in June 2011).

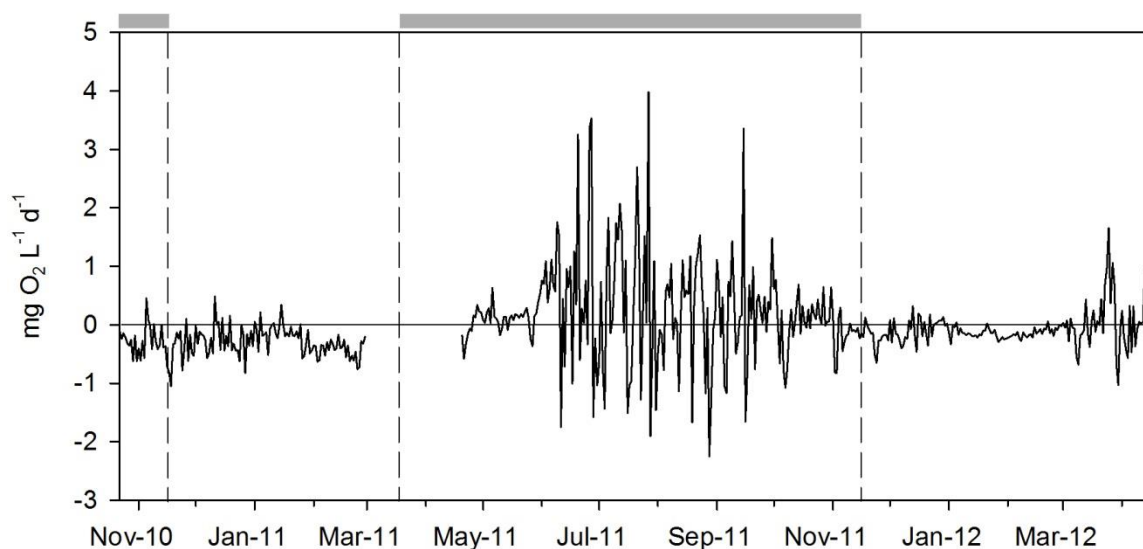


Figure 3.7 Daily net ecosystem production (NEP) calculated in Rostherne Mere from Nov 2010 to Apr 2012. Positive values represent a flux of O_2 out of the lake and negative values represent a flux of O_2 into the lake.

Utilising the data in Figure 3.7, the NEP of Rostherne Mere was calculated (following the method set out in Section 2.3.3) to show that for 2011 the lake is a net autotrophic, producing more carbon through photosynthesis than is lost through respiration ($2.24 \pm 0.8 \text{ mg O}_2 \text{ L}^{-1}$; converted to C fixation $0.37 \pm 0.25 \text{ g C m}^{-2} \text{ d}^{-1}$). The level of photosynthetic production during stratification is very high ($7.94 \pm 0.9 \text{ mg O}_2 \text{ L}^{-1}$; converted to C fixation $3.05 \pm 0.19 \text{ g C m}^{-2} \text{ d}^{-1}$) but losses due to respiration in winter months are nearly as high ($-5.70 \pm 0.2 \text{ mg O}_2 \text{ L}^{-1}$; converted to C fixation $2.70 \pm 0.34 \text{ g C m}^{-2} \text{ d}^{-1}$), meaning that overall there is net autotrophy within Rostherne Mere. The data are summarised in Table 3.2.

Table 3.2 Summary of seasonal NEP values calculated in Rostherne Mere. Mean NEP values are average \pm SD; mean C fixation value average \pm SD generated from sensitivity testing.

	Mean Monthly NEP $\text{mg O}_2 \text{ L}^{-1}$	Mean Stratified NEP $\text{mg O}_2 \text{ L}^{-1}$	Mean Daily C Fixation $\text{g C m}^{-2} \text{ d}^{-1}$	Total C Fixation $\text{g C m}^{-2} \text{ yr}^{-1}$
Study Period (n = 16)	0.97 ± 0.7	-	0.30 ± 0.22	135.1 ± 99
2011 (n = 10)	2.24 ± 0.8	7.94 ± 0.9	0.37 ± 0.25	135.6 ± 91

The mean DOC concentration for the study period was $7.2 \pm 0.5 \text{ mg C L}^{-1}$ (n = 387) with a small annual variation between 2010 ($7.0 \pm 0.6 \text{ mg C L}^{-1}$; n = 146) and 2011 ($7.4 \pm 0.4 \text{ mg C L}^{-1}$; n = 210). DOC concentration in both the epilimnion and hypolimnion varied seasonally (Figure 3.8a). The peak epilimnetic concentration occurred in July 2011 (8.0 mg C L^{-1}) and hypolimnetic DOC concentration peaked in September 2010 (9.4 mg C L^{-1}) and September 2011 (9.1 mg C L^{-1}). Lowest DOC levels occurred in February 2011 (6.8 mg C L^{-1}), with the concentration being uniform through the water column.

DOC loading is extremely variable in Rostherne Brook, as a result of seasonal rainfall and river discharge patterns (Figure 3.8b). DOC peaked during winter, February 2011 (9.4 mg C L^{-1}) and December 2011 (11.7 mg C L^{-1}), and was lowest during late summer, September 2010/11 ($2.3/2.7 \text{ mg C L}^{-1}$).

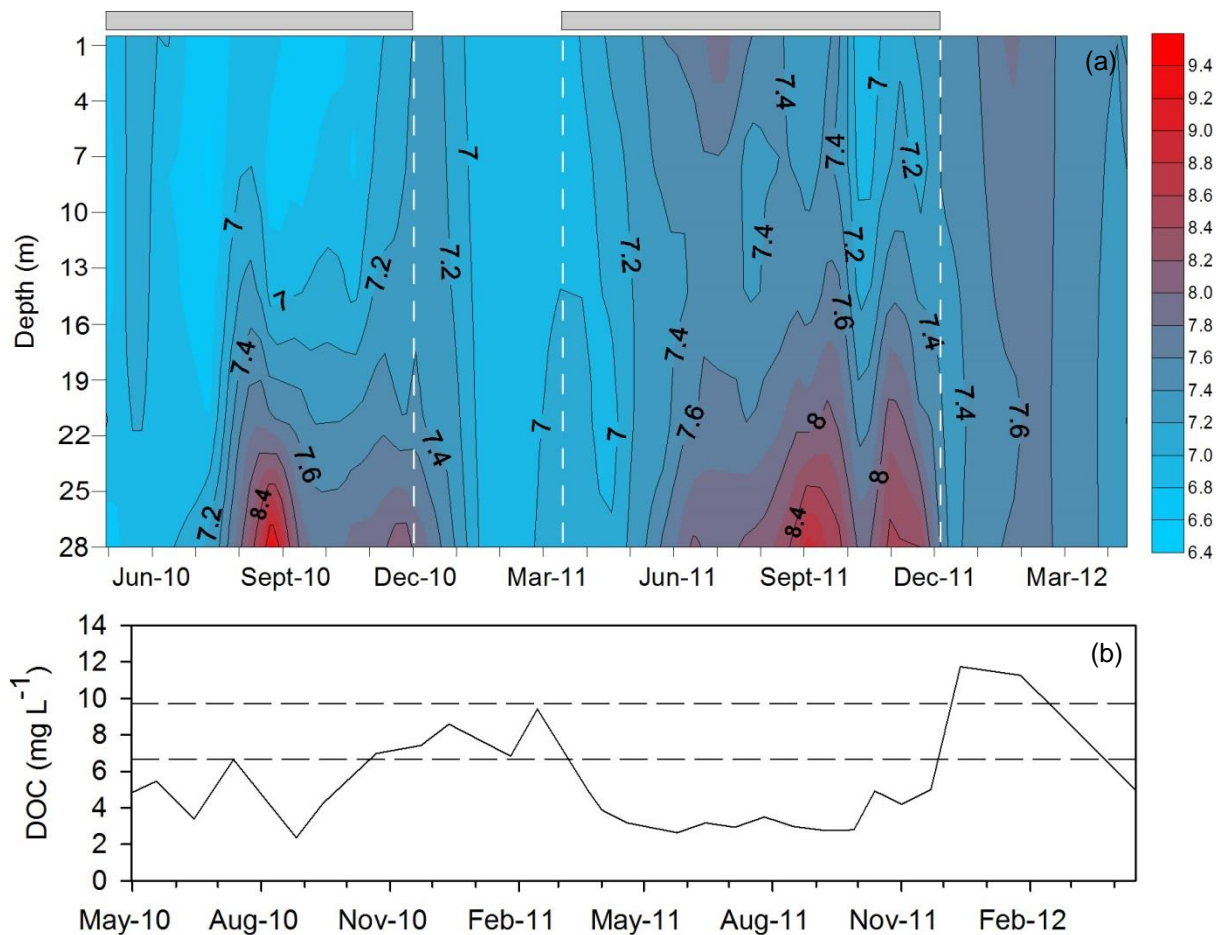


Figure 3.8 (a) Depth-time plot of DOC (mg L^{-1}) measured in Rostherne Mere from May 2010 to April 2012. (b) Levels of DOC (mg L^{-1}) discharged from Rostherne Brook, range of DOC measured in Rostherne Mere denoted by dashed line.

3.2.3 Inorganic Carbon

Levels of carbon dioxide (CO_2) within Rostherne Mere exhibit an inverse distribution to O_2 profile, where the peak occurs in the hypolimnion rather than the epilimnion (Figure 3.9). The rapid onset of stratification in mid-March leads to under saturation of CO_2 in the epilimnion by April and the epilimnion remains under saturated until stratification breaks down in November. Mean summer epilimnion CO_2 concentration was $190 \mu\text{mol mol}^{-1}$, whilst the hypolimnion concentration peaked at over $11,500 \mu\text{mol mol}^{-1}$ in December 2010 and 2011. Due to the very small epilimnion, over 85% of the water column was supersaturated with CO_2 for most of the year ($> 395 \mu\text{mol mol}^{-1}$). The breakdown of stratification and mixing of the water column significantly dilutes the CO_2 concentration, meaning winter water column mean CO_2 concentration was $\sim 1700 \mu\text{mol mol}^{-1}$. This implies that during the mixed

phase the lake was permanently super saturated with CO₂ and did not totally de-gas back to atmospheric CO₂ concentrations before the next period of stratification occurred.

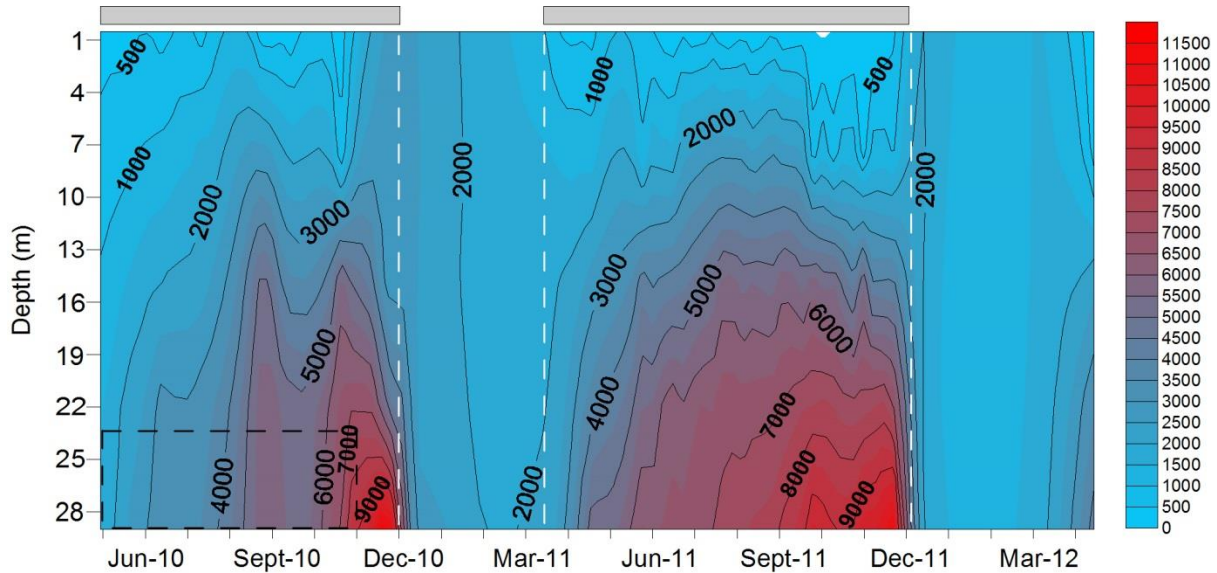


Figure 3.9 Depth-time plot of CO₂ concentration ($\mu\text{mol mol}^{-1}$) measured in Rostherne Mere from May 2010 to April 2012. The black dashed box represents data that was missing and generated using kriging interpolation.

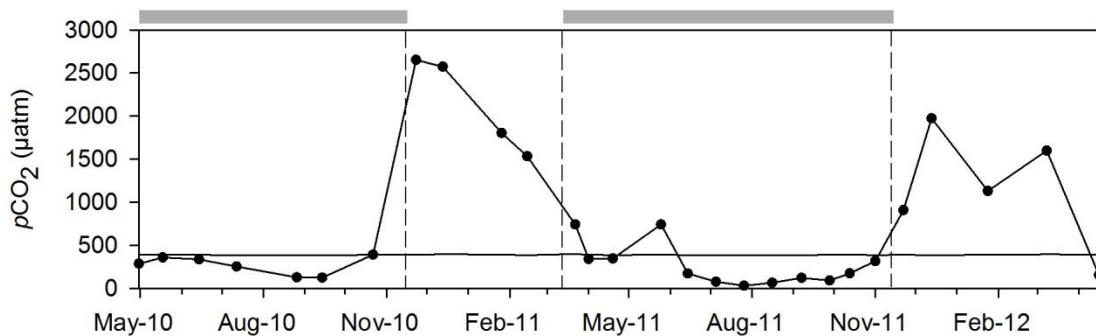


Figure 3.10 Monthly surface $p\text{CO}_2$ (μatm) measured in Rostherne Mere from May 2010 to April 2012. Horizontal black line represents overlying atmospheric $p\text{CO}_2$ (μatm). Values above this line represent super saturation of CO₂ and values below represent under saturation CO₂.

Figure 3.10 emphasises the seasonal pattern of surface $p\text{CO}_2$ concentration in Rostherne Mere. Periods of under saturation typically occurred during stratification and super saturation during the mixed phase. However super saturation did occur during May 2011 as a result of wind speeds with enough energy to temporarily break

stratification and mix epilimnetic waters into the hypolimnion. The study mean surface water $p\text{CO}_2$ was $662 \mu\text{atm}$, with a 2010 mean of $789 \mu\text{atm}$ and a 2011 mean of $590 \mu\text{atm}$.

Areal rates of surface water CO_2 flux (calculated following the method set out in Section 2.3.4) indicate that Rostherne Mere is a net source of CO_2 to the atmosphere (Figure 3.11; Table 3.3). Between May 2010 and May 2012 the lake is emitting $9.47 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ($41.52 \text{ g C m}^{-2} \text{ yr}^{-1}$). The 2011 mean is slightly lower at $7.64 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ($33.51 \text{ g C m}^{-2} \text{ yr}^{-1}$). As expected, during the stratified period, Rostherne Mere is a net sink of CO_2 from the atmosphere ($-4.54 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$), as a result of $p\text{CO}_2$ under saturation for the majority of the stratified cycle (Figure 3.10).

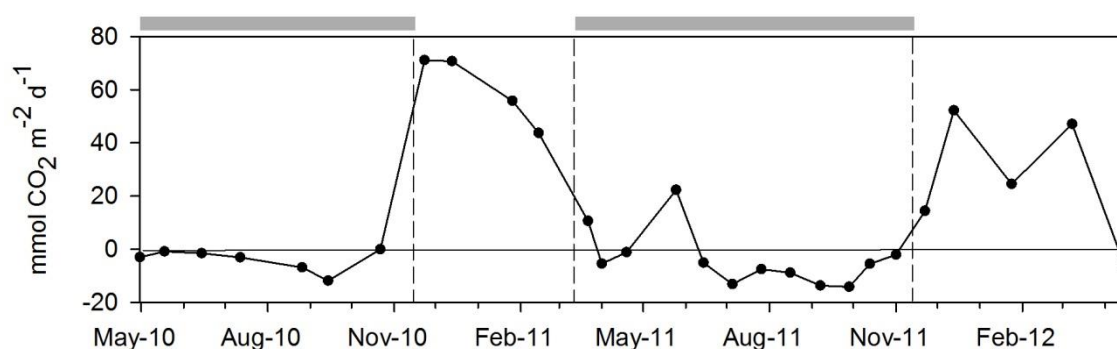


Figure 3.11 Monthly surface CO_2 flux ($\text{mmol m}^{-2} \text{ d}^{-1}$) in Rostherne Mere from May 2010 to April 2012. Positive values represent an outward flux of CO_2 from the lake to the atmosphere and negative values represent inward flux of CO_2 from the atmosphere in to the lake.

Table 3.3 Summary of CO_2 flux calculated in Rostherne Mere. Values \pm SD.

	Mean CO_2 flux $\text{mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$	Mean Stratified CO_2 flux $\text{mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$	Mean Daily C flux $\text{g C m}^{-2} \text{ d}^{-1}$	Total C flux $\text{g C m}^{-2} \text{ yr}^{-1}$
Study Period (n = 28)	10.75 ± 26	-4.54 ± 4.2	0.13 ± 0.2	47.09 ± 73
2010 (n = 9)	12.72 ± 33	-3.91 ± 4.1	0.15 ± 0.4	55.71 ± 146
2011 (n = 16)	7.64 ± 23	-4.94 ± 4.7	0.10 ± 0.2	33.48 ± 72

The concentration of calcium (Ca^{2+}) within the water column of Rostherne Mere is highly variable with both depth and time (Figure 3.12). The concentration is most variable in the surface waters (0.5 m) and shows particularly rapid changes during the summer months when stratification is strongest. In 2010, within the space of 2 weeks the level of calcium within the epilimnion drops from 52.9 mg Ca L^{-1} to 39.1 mg Ca L^{-1} . This sudden drop is echoed by a sharp rise in the CO_3^{2-} standing stock (Figure 3.18) and under saturation of CO_2 in the epilimnion. Variability is much less pronounced further down the water column (12m & 24 m) but does show change over time as the lake moves from being stratified, where Ca^{2+} concentrations are higher than the epilimnion, to fully mixed when eventually the concentration is uniform throughout the entire water column.

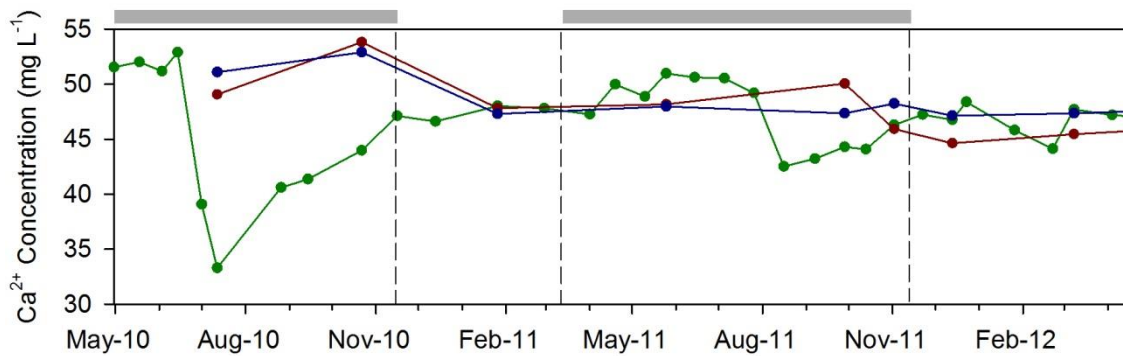


Figure 3.12 Summary of calcium (Ca^{2+}) availability in Rostherne Mere 2010 – 2012. Green line represents 0.5 m, red line represents 12 m and blue line represents 24 m.

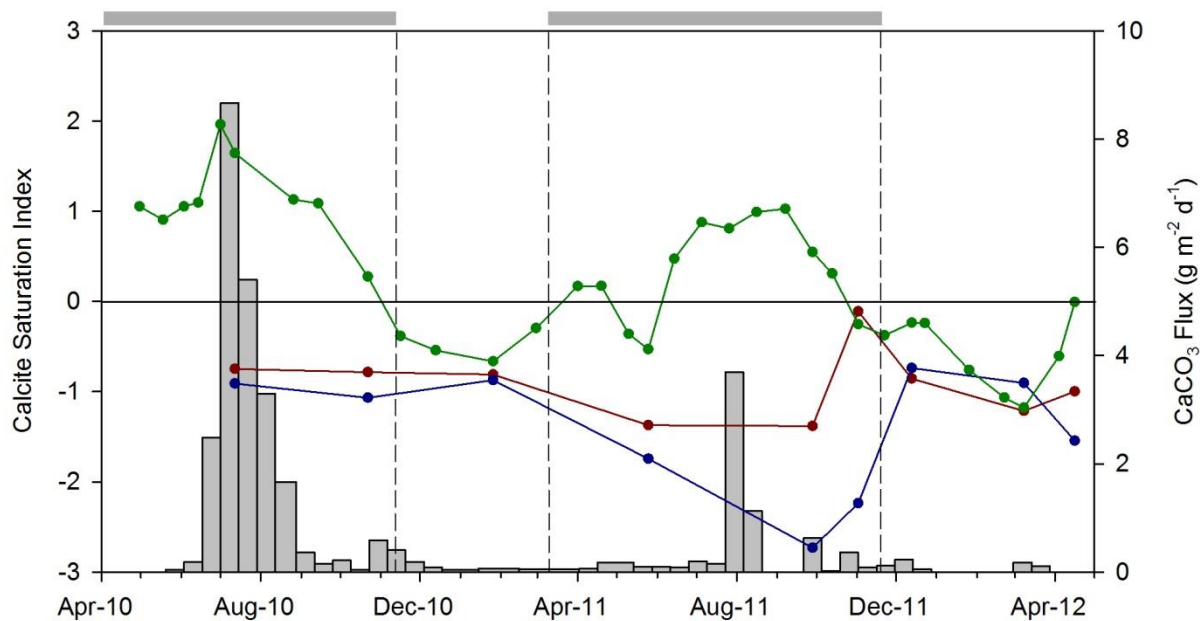


Figure 3.17 Summary of calcite saturation index (lines) and shallow sequencing trap CaCO₃ flux data (bars) in Rostherne Mere 2010 – 2012. Values of saturation > 0 suggest the water is oversaturated with CaCO₃ and values < 0 signify CaCO₃ undersaturation. Green line represents 0.5 m, red line represents 12 m and blue line represents 24 m.

Monthly patterns in the DIC pool (Figure 3.18a) show an overall decline of total DIC over the study period ($r^2 = 0.56$). There is a decline from a mean water column concentration of $1548 \mu\text{mol L}^{-1}$ in 2010 to $1135 \mu\text{mol L}^{-1}$ in 2011. As a result of HCO_3^- constituting approximately 83% of the total DIC pool in Rostherne Mere over the study period there was an equally important concentration decline ($r^2 = 0.59$). Due to the complex nature of inorganic carbon there were no similar reductions in CO_3^{2-} and CO_2 concentrations. Levels of CO_3^{2-} within the water column, typically the epilimnion, pulse due to high pH and low CO_2 concentrations. Average highs of around $15 \mu\text{mol L}^{-1}$ (July and August 2010; August and September 2011) can result in the precipitation of CaCO₃ (Figure 3.17). Typically CO_3^{2-} only constitutes 0.5% of the inorganic carbon measured in Rostherne Mere over the study period. The overall concentration of CO_2 rapidly increases after stratification, from $\sim 100 \mu\text{mol L}^{-1}$ during the mixed phase, to over $250 \mu\text{mol L}^{-1}$ by August 2010 & 2011. The CO_2 concentration reflects the huge increases in hypolimnetic CO_2 as a result of respiration (Figure 3.18c and 3.18d). On average, CO_2 forms 16.5% of the inorganic

carbon pool, but this can be as low as 5% in winter (February 2011) and as high as 30% in summer (July 2011).

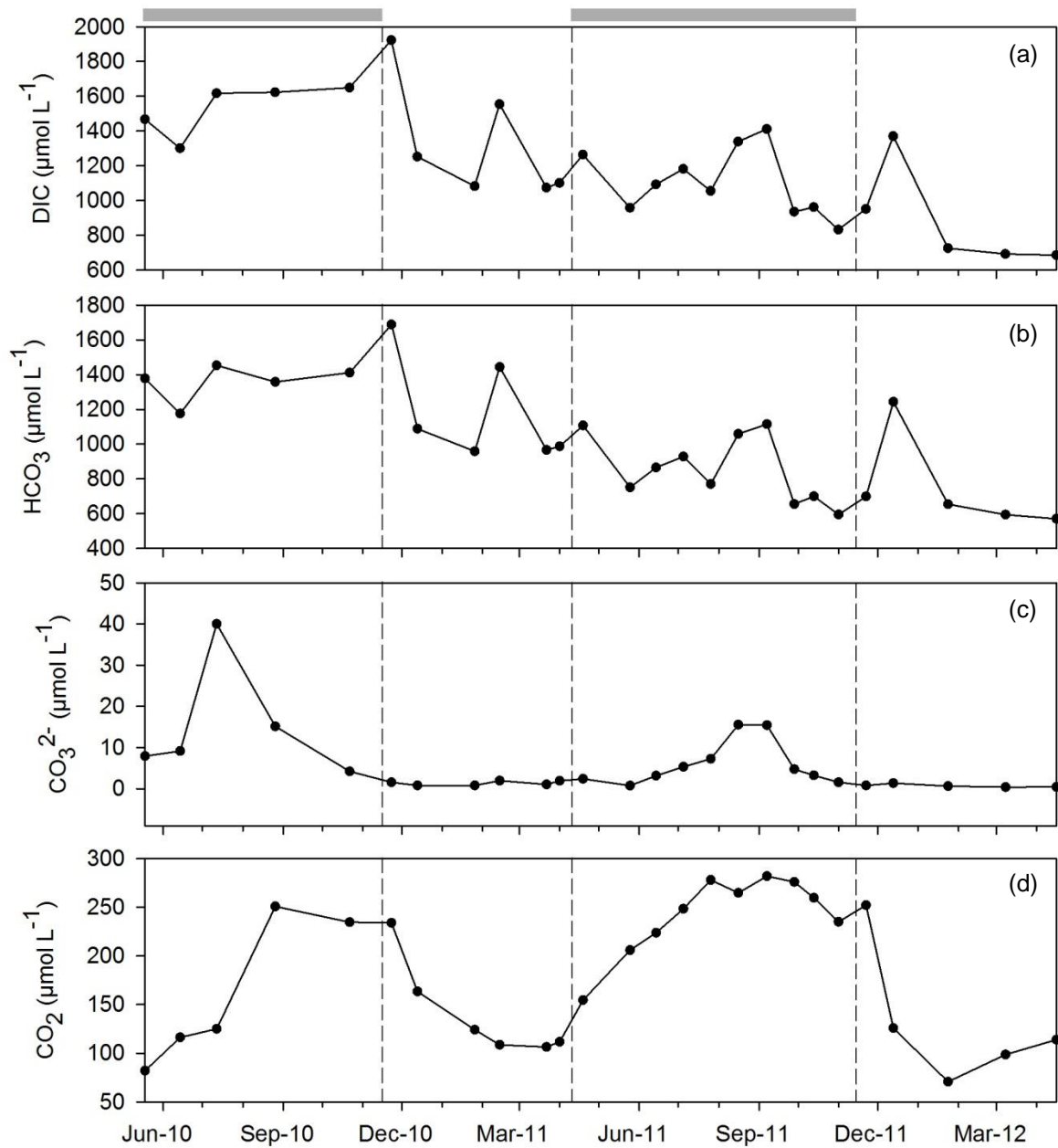


Figure 3.18 Monthly water column means for DIC fractions calculated in Rostherne Mere from May 2010 to April 2012.

Standing stocks of total dissolved inorganic carbon and CO₂ were calculated from the concentration data (Figure 3.19). The overall patterns in total standing stocks matched the concentration figures and showed that overall DIC fell from a peak of 159,242 kg C in July 2010 to just 54,141 kg C in April 2012. Although there are

seasonal fluxes in stocks, yearly mean showed a 30% drop in dissolved organic carbon. The standing stock of total CO₂ merely replicates the seasonal trend in CO₂ accumulation in the hypolimnion, with little annual mean variation (2010: 10,100 kg C; 2011: 11,750 kg C). However, declining total DIC stocks and stable CO₂ stocks mean that the overall percentage of inorganic carbon composed of CO₂ has increased from 7% in 2010 to 12% in 2011.

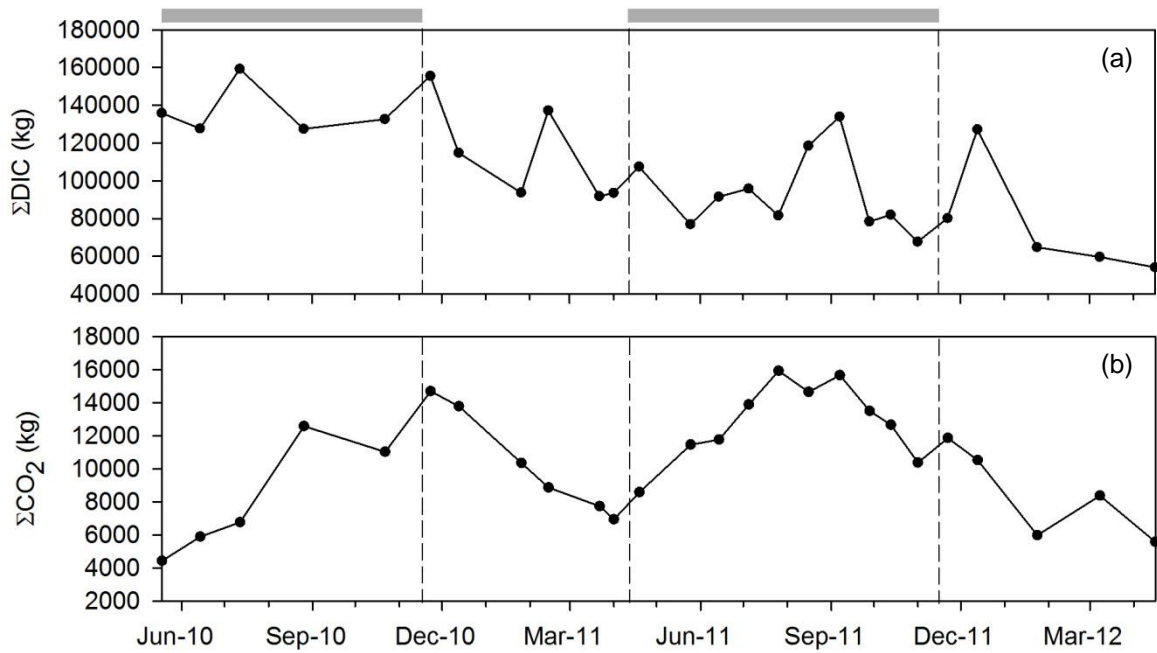


Figure 3.19 Monthly total inorganic carbon stocks (kg C) calculated for Rostherne Mere from May 2010 to April 2012.

3.2.4 Sediment Data

A combination of open traps and sequencing traps were deployed at 12m and 24m in Rostherne Mere and collected a total of $227.5 \pm 7 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($n = 20$; 12m sequencing trap), $142.3 \pm 6 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($n = 13$; 24m sequencing trap between June 2011 and April 2012) and $30.3 \pm 9 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($n = 3$; 12m open trap) and $47.5 \pm 5 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($n = 3$; 24m open trap) between May 2010 and April 2012 (Figure 3.20). This equates to approximately $134.6 \pm 7 \text{ g C m}^{-2} \text{ yr}^{-1}$ (both sequencing traps) during 2011. Data from the two automatic sequencing traps were used in the C-balance for Rostherne Mere.

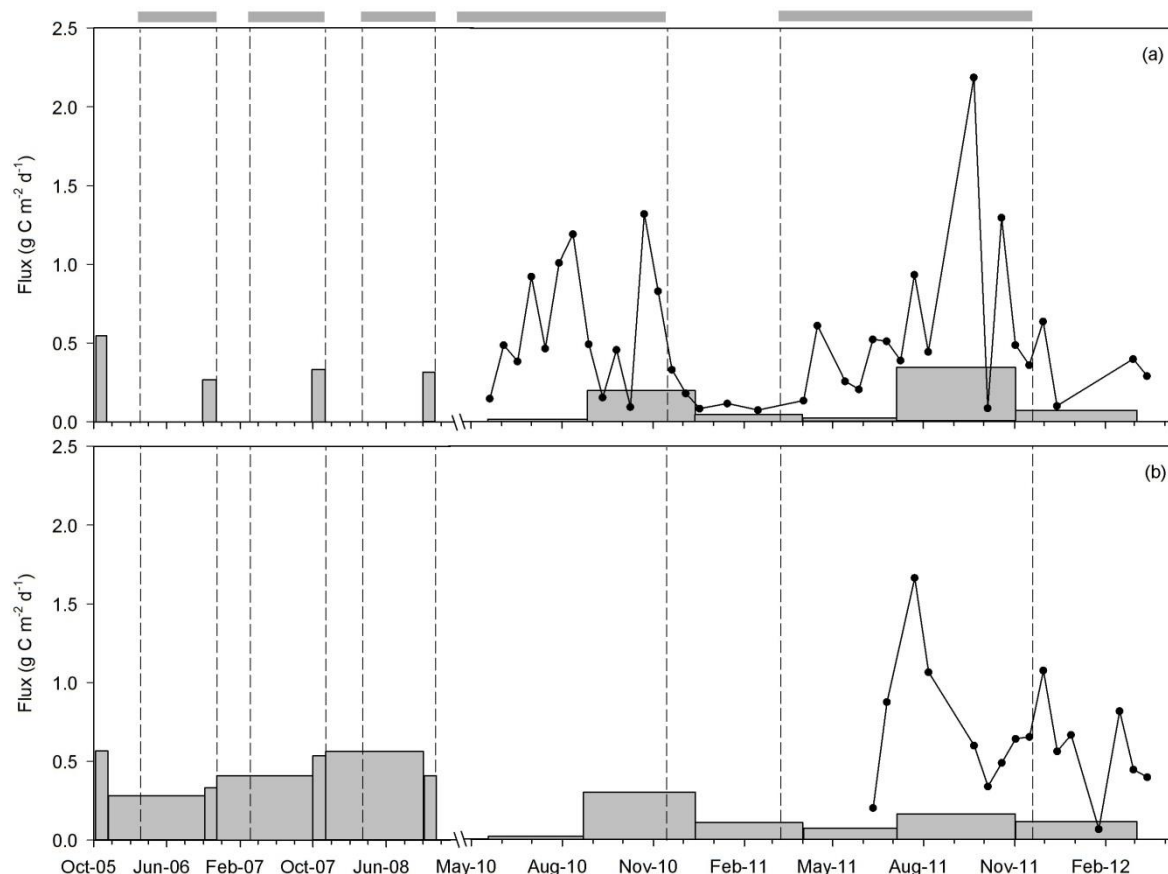


Figure 3.20 Rostherne Mere organic carbon flux ($\text{g C m}^{-2} \text{ d}^{-1}$) from sediment trap data October 2005 to April 2012. a) Shallow traps set at 8 – 10 m, b) Deep traps set at 22 – 25 m. Grey bars refer to open sediment traps and are scaled for deployment time. Scatter plot refers to sequencing sediment traps, typically set for 2 week collection periods.

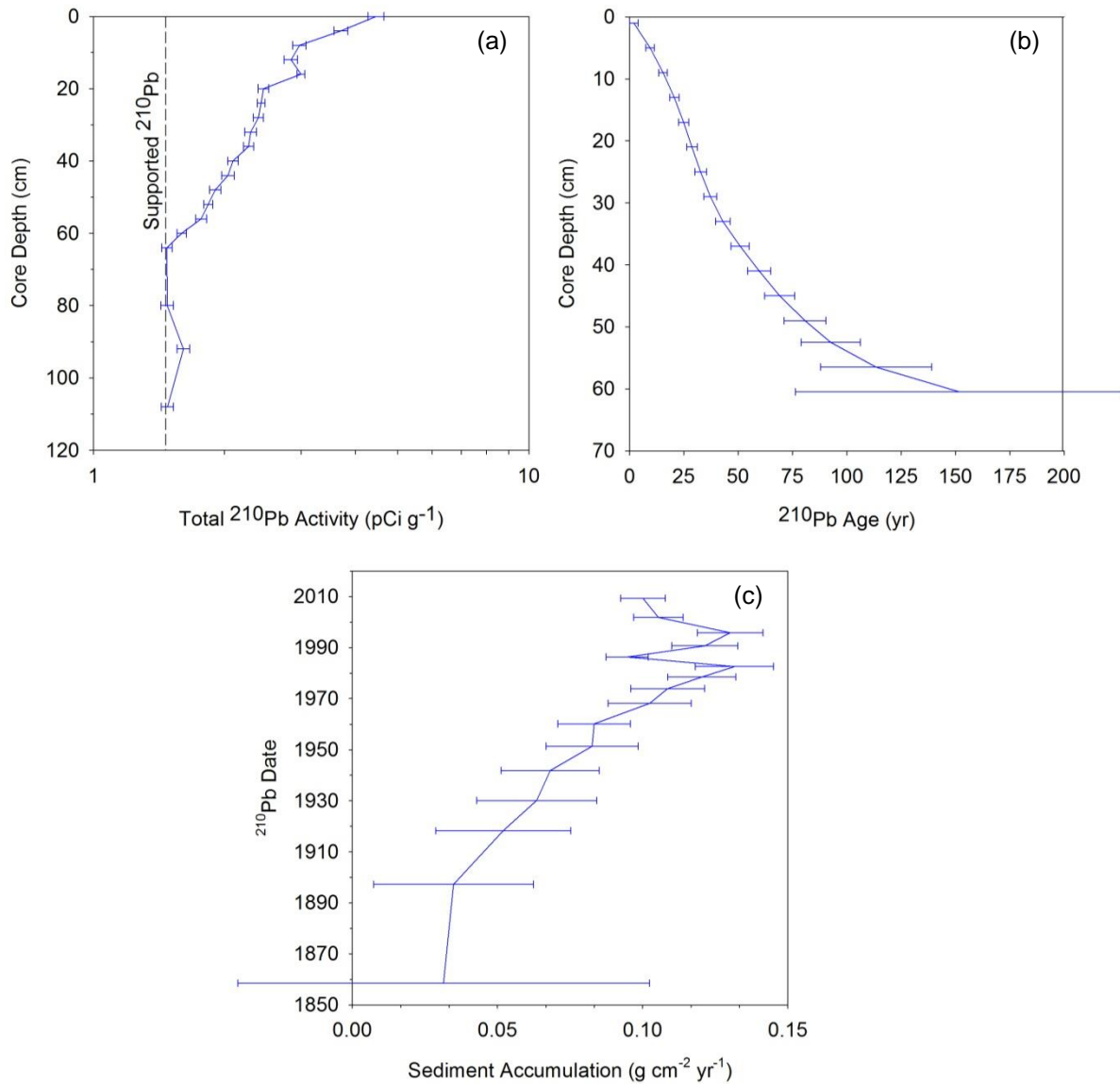


Figure 3.21 RM_Liv_2011 (Rostherne Mere Open Water Core) dating results. (a) Total ^{210}Pb activity (pCi g^{-1}) through the core. (b) Sediment ^{210}Pb age (yr). (c) Sediment accumulation rates ($\text{g cm}^{-2} \text{yr}^{-1}$) since 1850.

The open water core from Rostherne Mere (RM_Liv_2011) was dated using the ^{210}Pb method; the results of the analysis are shown in Figure 3.21. The dates and sediment accumulation rates from the ^{210}Pb analysis were used to calculate the rate OC accumulation ($137.3 \text{ g C m}^{-2} \text{yr}^{-1}$ in 2002) and then corrected for sediment focusing, ~ 0.7 , to provide a mean OC accumulation rate for the entire lake basin ($96.1 \text{ g C m}^{-2} \text{yr}^{-1}$) (Table 3.4).

Table 3.4 Summary of RM_Liv_2011 (Rostherne Mere Open Water Core) sediment core data.

Top of Interval	Base of Interval	Model Date	Date Error	Sedimentation Rate	Sediment Accumulation	Sediment Acc. Error	Organic C Accumulation	OC Focus Corrected
cm	cm	A.D.	± SD	cm ⁻² yr ⁻¹	g m ⁻² yr ⁻¹	± SD	g C m ⁻² yr ⁻¹	g C m ⁻² yr ⁻¹
0	1	2010	2.00	-	1000	0.007	130.94	91.66
4	5	2002	2.04	0.47	1053	0.008	137.34	96.14
8	9	1996	2.01	0.62	1300	0.011	158.90	111.23
12	13	1991	2.18	0.81	1213	0.011	162.48	113.74
16	17	1987	2.37	1.01	946	0.007	132.16	92.52
20	21	1983	2.47	1.15	1315	0.013	150.47	105.33
24	25	1979	2.69	1.15	1202	0.011	139.37	97.56
28	29	1974	2.99	1.00	1085	0.012	114.47	80.13
32	33	1968	3.43	0.80	1023	0.014	107.90	75.53
36	37	1960	4.23	0.61	832	0.012	80.95	56.67
40	41	1952	5.29	0.47	825	0.015	82.62	57.84
44	45	1942	6.92	0.36	681	0.016	64.90	45.43
48	48	1930	9.64	0.29	634	0.020	58.99	41.30
52	52.5	1918	13.72	0.24	519	0.023	48.59	34.02
56	56.5	1897	25.71	0.20	348	0.027	31.31	21.92
60	60.5	1859	76.09	0.16	314	0.070	28.67	20.07

The OC burial efficiency of Rostherne Mere (Table 3.5) was calculated using two competing methods (Sobek et al., 2009 and Gälman et al., 2008). OC deposition is derived from sediment trap data (Figure 3.20) and OC burial is derived from the dated core RM_Liv_2011. The Gälman et al. (2008) method discounts the first 10 years of the core and estimates OC burial efficiency to be 71%, whereas the Sobek et al. (2009) method discounts the first 25 years of the core and estimates OC burial efficiency to be 99%.

Table 3.5 Rostherne Mere organic carbon burial in sediments, deposition onto the sediment as determined by sediment traps, and burial efficiency.

Method	No. of years discounted	OC Deposition g C m⁻² yr⁻¹	OC Burial g C m⁻² yr⁻¹	Burial Efficiency %
This Study	10	134.8	96.1	71
Sobek et al. (2009)	15	134.8	133.2	99

3.3 TATTON MERE

3.3.1 Water Chemistry

Tatton Mere is a warm monomictic, eutrophic lake system, however Figure 3.22 shows thermal stratification over the period of study is weakly defined and warmer water can mix down into the lower lake depths during stratification. Mean lake temperature for the study period was 10.2°C. Weak stratification is typically initiated in early April and continues until mid-October when it breaks down and the lake remains mixed for the remainder of the year. A temperature of approximately 10°C seems critical for the onset and breakdown of stratification. Stratification intensified during July and August with surface water temperatures reaching up to 20°C creating a very small epilimnion, typically only 3 – 4 m deep. Once stratification has begun to break down the lake becomes isothermal slowly cooling through the following months, reaching a low of 3.0°C during February 2011 and 2012. Temperature is variable during mixed periods, most likely as a result of groundwater inputs. No ice cover was observed during the study period.

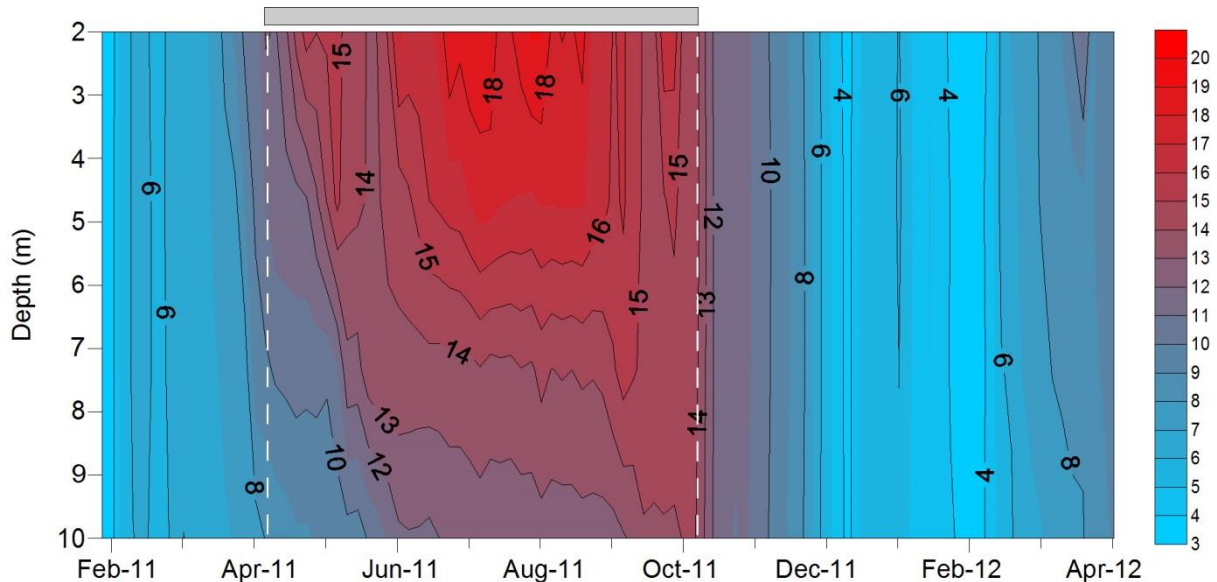


Figure 3.22 Depth-time plot of temperature (°C) measured in Tatton Mere from Feb 2011 to April 2012. Periods of lake stratification are shown with grey bars and dashed lines.

Levels of TP and TN are both high in Tatton Mere (Table 3.6) during the period of study, surface water means were $442 \pm 170 \mu\text{g P L}^{-1}$ ($n = 5$) and $827 \pm 202 \mu\text{g N L}^{-1}$

(n = 5) respectively. The hypertrophic (TP > 100 µg L⁻¹; TN > 1200 µg L⁻¹) levels of P suggest that N is likely to be the growth limiting nutrient within Tatton Mere. Concentration variability within the water column can be linked to stratification and biological uptake, as during mixed months the concentrations are virtually uniform (24 Nov 2010, 15 Feb 2011 and 02 Nov 2012) whereas during productive months (17 Aug 2011) the epilimnion nutrients are heavily depleted in contrast to those in the hypolimnion.

Table 3.6 Summary of nutrient availability in Tatton Mere 2010 – 2012. Water column mean concentration ± SD.

		Total P (µg L⁻¹)	SRP (µg L⁻¹)	Total N (µg L⁻¹)	Nitrate-N (µg L⁻¹)
24 Nov 2010	0.5 m	360	338	763	434
15 Feb 2011	0.5 m	381	350	1110	547
17 Aug 2011	0.5 m	444	343	590	Readings Too Low
	5 m	490	412	500	
	10 m	1905	1839	2580	
	Mean	947 ± 831	865 ± 845	1220 ± 1176	
02 Nov 2011	0.5 m	731	629	730	144
	5 m	727	621	790	164
	10 m	751	626	740	155
	Mean	736 ± 13	625 ± 4	750 ± 32	154 ± 10
08 Mar 2012	0.5 m	296	262	940	459
	5 m	323	266	950	412
	10 m	314	286	1040	525
	Mean	311 ± 14	271 ± 13	977 ± 55	465 ± 57

The pH of Tatton Mere also shows some seasonality within the lake, with pH reaching 9.5 within the epilimnion and falling to 6.4 in the hypolimnion during the summer months of 2011, winter values averaged 7.8 ± 0.3 (n = 117; Figure 3.23).

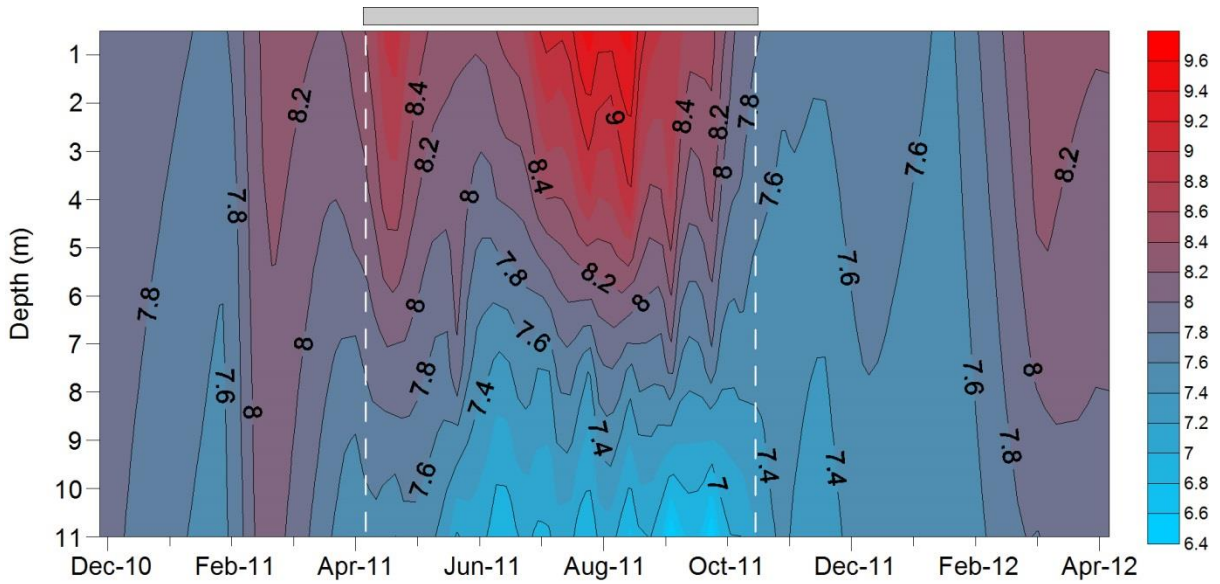


Figure 3.23 Depth-time plot of pH measured in Tatton Mere from Dec 2010 to April 2012.

The mean transparency at Tatton Mere was recorded at 2.6 ± 0.9 m ($n = 19$). The highest transparency was measured during the mixed phase, April 2011 and 2012 respectively (4.1 and 4.5 m; Figure 3.24), with lowest transparency occurring during July and August 2011 (1.3 m). The decreasing secchi disc depth throughout the period of lake stratification is consistent with increasing temperatures, oxygen super saturation and CO_2 under saturation in the epilimnion.

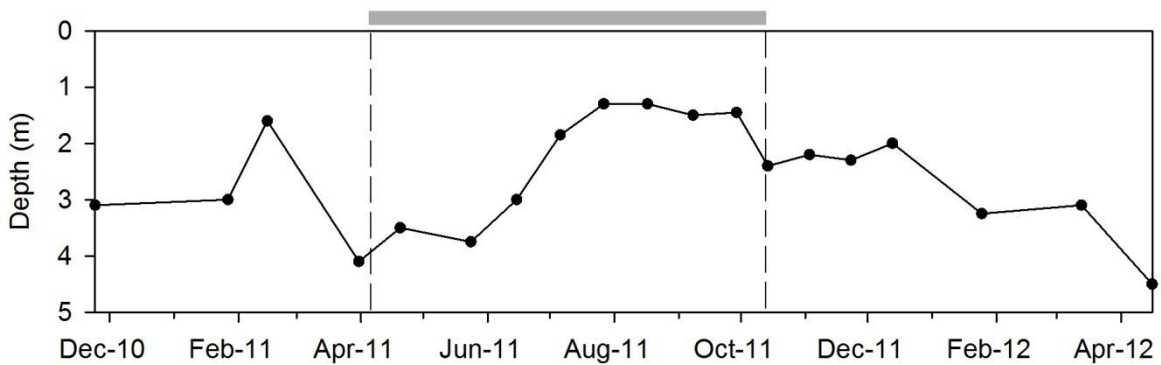


Figure 3.24 Secchi disc depths measured in Tatton Mere from Dec 2010 to April 2012.

3.3.2 Organic Carbon Production

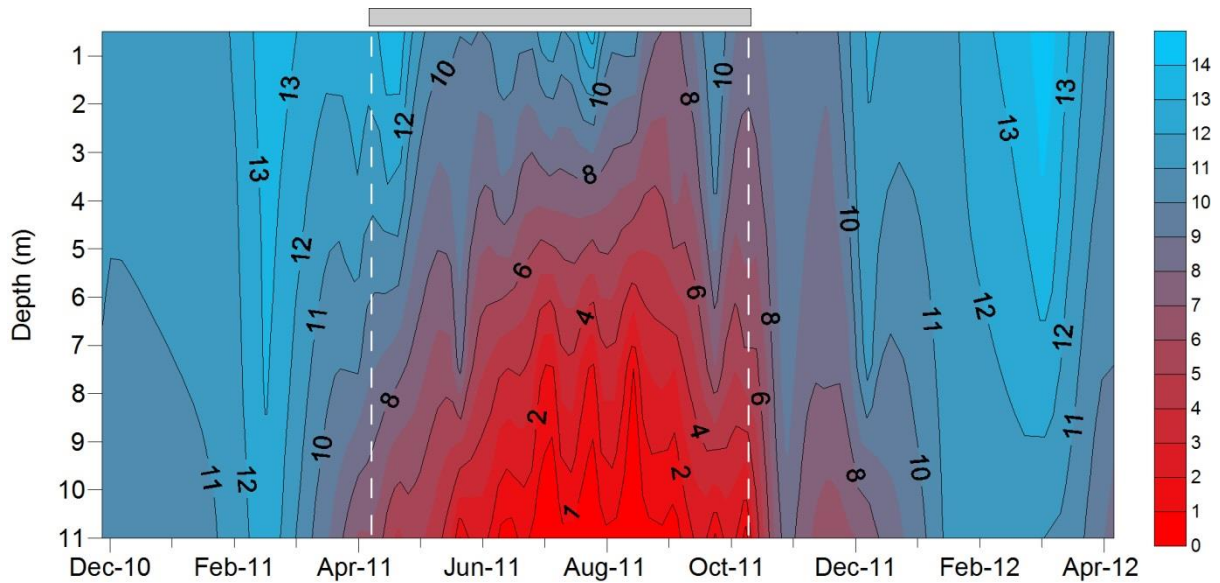


Figure 3.25 Depth-time plot of dissolved oxygen (mg L^{-1}) measured in Tatton Mere from Dec 2010 to April 2012.

Dissolved oxygen stratification is more stable than temperature stratification within Tatton Mere (Figure 3.25). Summer oxygen super saturation in the epilimnion ($>14 \text{ mg L}^{-1}$) is contrasted by hypoxia ($< 2 \text{ mg L}^{-1}$) in the hypolimnion. Low oxygen concentrations develop in the hypolimnion with the onset of stratification and steadily decline as oxygen is consumed. The zone of hypoxia within the lake increases from June through to September leaving 60% of the lake with either low O_2 concentration or anoxia during the summer months. This trend persists until lake turnover, when O_2 concentration steadily increases as oxygenated water from the epilimnion is mixed down into the hypoxic hypolimnion.

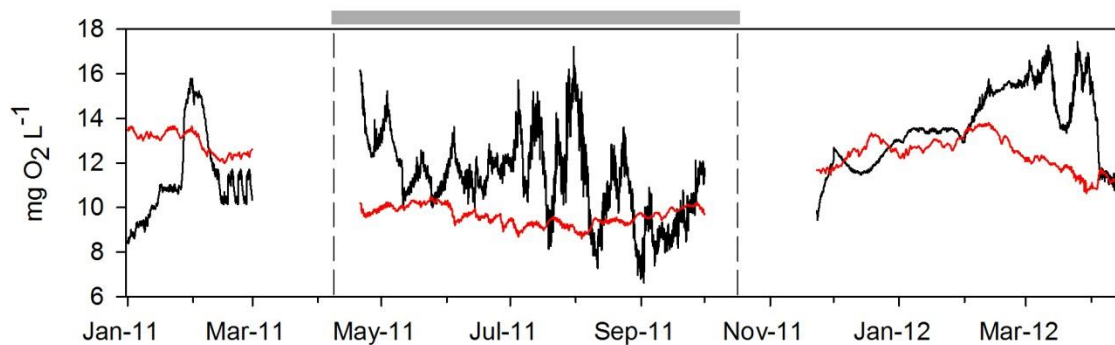


Figure 3.26 Hourly surface oxygen data for Tatton Mere. Black line is measured surface concentration; red line is the oxygen saturation concentration.

Figure 3.26 shows hourly O₂ concentration data is compared to the expected O₂ saturation. The lake is typically under saturated with O₂ during the winter months when the lake is fully mixed and temperatures are at their lowest, however warm spring periods in February 2011 and March 2012 (Figure 3.1) led to spikes in oxygen associated with early algal blooms. Similarly the lake is typically super saturated with oxygen during the summer months when the lake is stratified and photosynthesis is only occurring in the top 3 – 4 m of the water column, however high wind speeds in September 2011 (Figure 3.1) is likely to have led to a mixing of epilimnetic and hypolimnetic waters causing a drop in the overall surface oxygen concentration (highest oxygen values recorded in July 2011 & March 2012; lowest values recorded in September 2011).

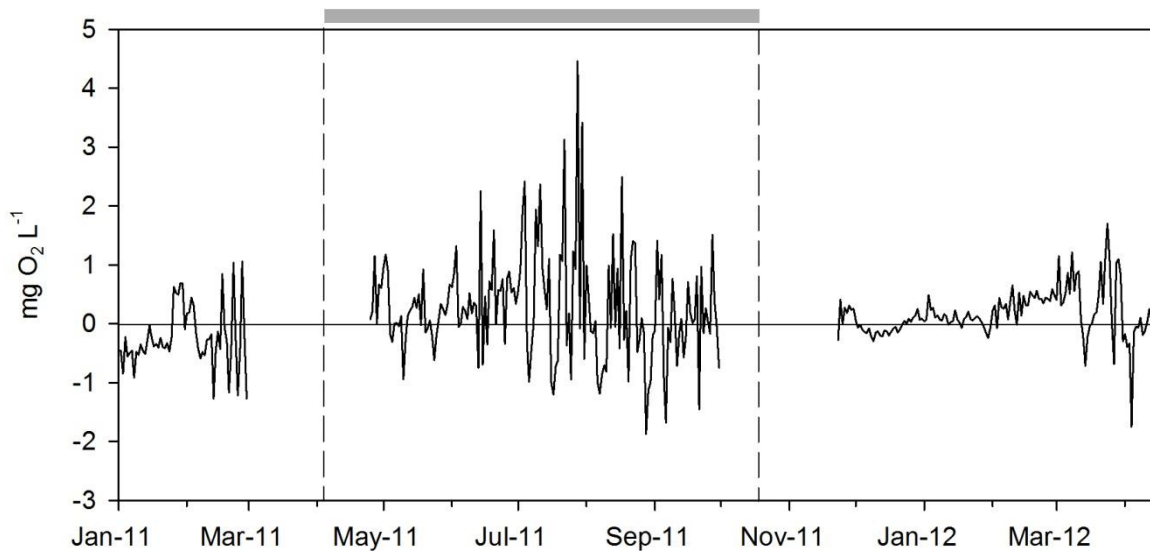


Figure 3.27 Daily Net Ecosystem Production (NEP) calculated for Tatton Mere between January 2011 and April 2012. Positive values represent a flux of O₂ into the lake and negative values represent a flux of O₂ out of the lake.

Utilising the data in Figure 3.26, the NEP of Tatton Mere was calculated (following the method set out in Section 2.3.3) and shows that for 2011 the mere is net autotrophic, producing more carbon through photosynthesis than is lost through respiration ($2.38 \pm 0.8 \text{ mg O}_2 \text{ L}^{-1}$; converted to C fixation $0.32 \pm 0.24 \text{ g C m}^{-2} \text{ d}^{-1}$). The level of photosynthetic production during stratification is very high ($7.44 \pm 0.9 \text{ mg O}_2 \text{ L}^{-1}$; converted to C fixation $2.17 \pm 0.19 \text{ g C m}^{-2} \text{ d}^{-1}$), with losses due to respiration

in winter months being nearly as high ($-5.05 \pm 0.4 \text{ mg O}_2 \text{ L}^{-1}$; converted to C fixation $1.84 \pm 0.36 \text{ g C m}^{-2} \text{ d}^{-1}$). The data are summarised in Table 3.7.

Table 3.7 Summary of seasonal NEP values calculated in Tatton Mere. Mean NEP values are average \pm SD; mean C fixation value average \pm SD generated from sensitivity testing.

	Mean Monthly NEP $\text{mg O}_2 \text{ L}^{-1}$	Mean Stratified NEP $\text{mg O}_2 \text{ L}^{-1}$	Mean Daily C Fixation $\text{g C m}^{-2} \text{ d}^{-1}$	Total C Fixation $\text{g C m}^{-2} \text{ y}^{-1}$
Study Period (n = 15)	3.65 ± 0.7	-	0.50 ± 0.26	180.9 ± 94
2011 (n = 11)	2.38 ± 0.8	7.44 ± 0.9	0.32 ± 0.24	118.6 ± 88

The Mean DOC concentration for the study period was $4.4 \pm 0.3 \text{ mg C L}^{-1}$ (n = 174), but varied in both the epilimnion and hypolimnion seasonally (Figure 3.28). The peak epilimnetic concentration was measured in January 2012 (4.9 mg C L^{-1}). The hypolimnetic DOC concentration peaked in September 2011 (5.4 mg C L^{-1}). Lowest DOC levels were measured in March 2011 for both the epilimnion (3.8 mg C L^{-1}) and hypolimnion (4.0 mg C L^{-1}).

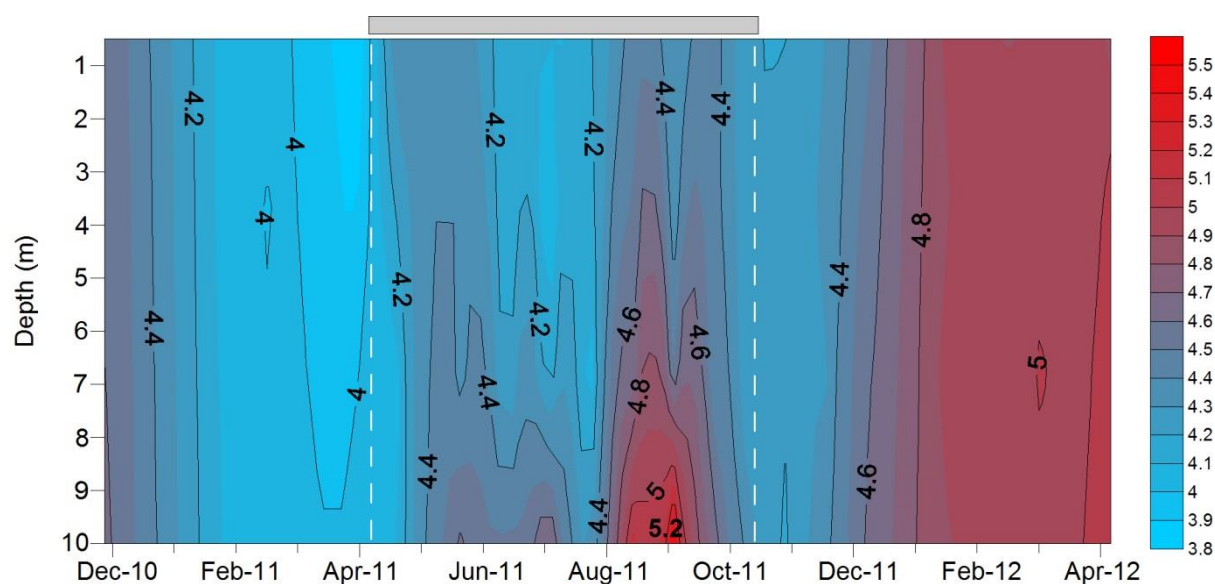


Figure 3.28 Depth-time plot of DOC (mg L^{-1}) measured in Tatton Mere from Dec 2010 to April 2012.

3.3.3 Inorganic Carbon

Levels of CO₂ within Tatton Mere exhibit an inverse stratification, where the peak occurs in the hypolimnion rather than the epilimnion (Figure 3.29). The onset of stratification in early April leads to under saturation of CO₂ in the surface waters and a steady increase in hypolimnetic concentration. Mean surface summer surface CO₂ concentration is 150 μmol mol⁻¹, whilst the hypolimnion concentration peaks at over 7,500 μmol mol⁻¹ in September 2011. Over 50% of the water column has high CO₂ concentrations during the summer months. The breakdown of stratification and mixing of the water column significantly dilutes the CO₂ concentration, with winter water column mean concentration being ~1100 μmol mol⁻¹. As a result, during the mixed phase the lake gradually de-gases CO₂ to the atmosphere and the lake eventually returns to CO₂ equilibrium with the atmosphere.

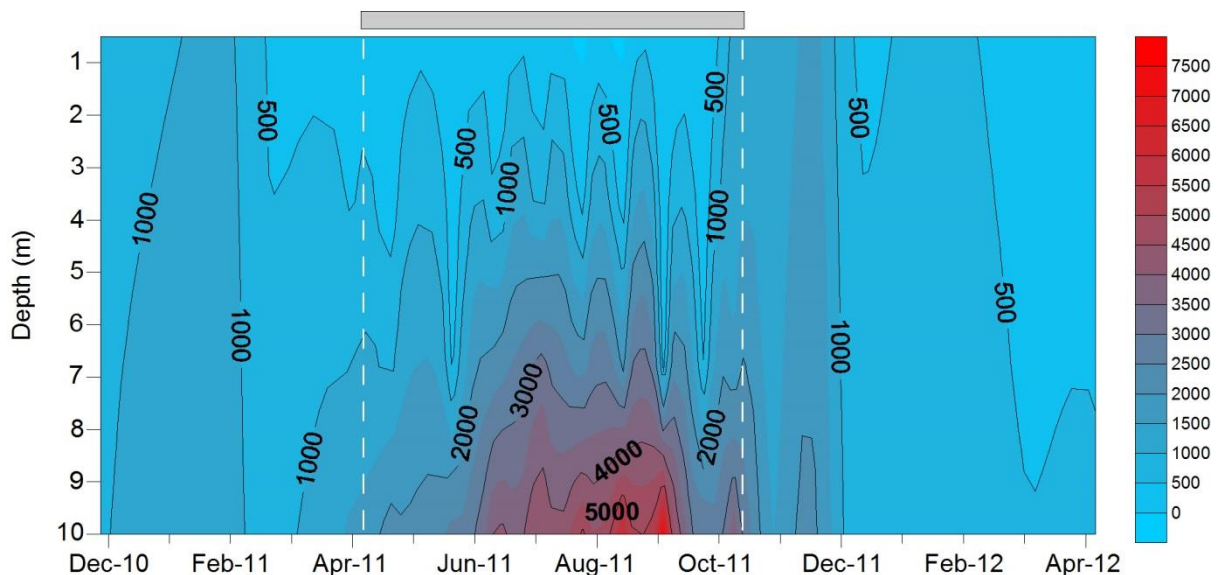


Figure 3.29 Depth-time plot of CO₂ (μmol mol⁻¹) measured in Tatton Mere from Dec 2010 to April 2012.

Figure 3.30 emphasises the seasonal pattern of surface pCO₂ concentration in Tatton Mere. Periods of under saturation typically occurred during stratification and super saturation during the mixed phase. The study mean surface water pCO₂ was 560 μatm, with a 2011 mean of 540 μatm.

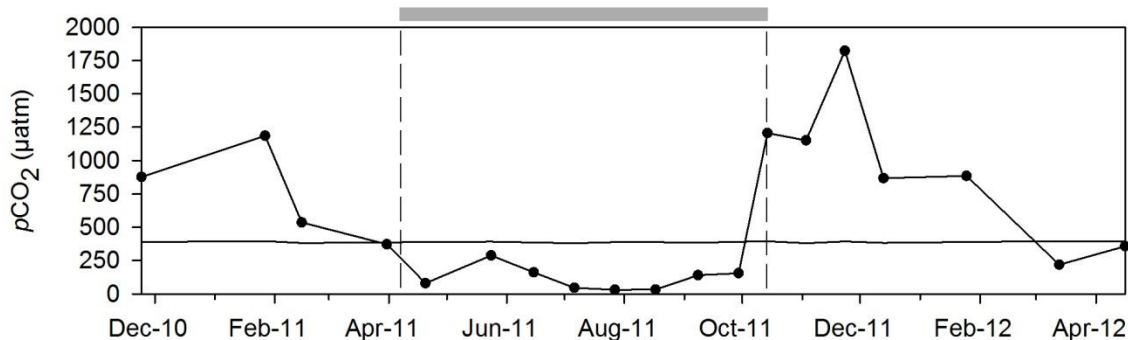


Figure 3.30 Monthly surface $p\text{CO}_2$ (μatm) measured in Tatton Mere from Dec 2010 to April 2012. Horizontal black line represents overlying atmospheric $p\text{CO}_2$ (μatm). Values above this line represent super saturation of CO_2 and values below represent under saturation CO_2 .

Areal surface water CO_2 flux (calculated following the method set out in Section 2.3.4) indicates that Tatton Mere is a net source of CO_2 to the atmosphere (Figure 3.31; Table 3.8). On average the lake emits $8.38 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ($36.74 \text{ g C m}^{-2} \text{ y}^{-1}$). The 2011 mean is slightly lower than this figure at $7.92 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ($34.71 \text{ g C m}^{-2} \text{ d}^{-1}$). As expected, during the stratified period, Tatton Mere is a net sink of CO_2 from the atmosphere ($2011: -3.49 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$), as a result of $p\text{CO}_2$ under saturation during the stratified cycle (Figure 3.30).

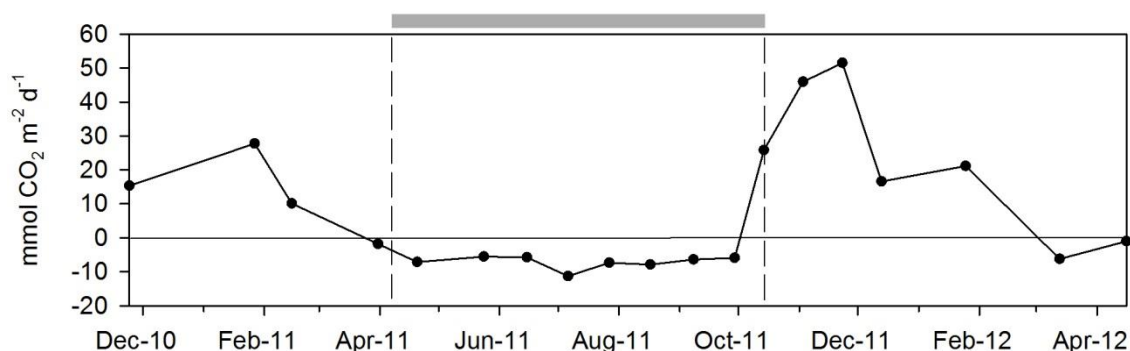


Figure 3.31 Monthly surface CO_2 flux ($\text{mmol m}^{-2} \text{ d}^{-1}$) in Tatton Mere from December 2010 to April 2012. Positive values represent an outward flux of CO_2 from the lake to the atmosphere and negative values represent inward flux of CO_2 from the atmosphere in to the lake.

Table 3.8 Summary of CO₂ flux calculated in Tatton Mere. Values ± SD.

	Mean CO ₂ flux mmol CO ₂ m ⁻² d ⁻¹	Mean Stratified CO ₂ flux mmol CO ₂ m ⁻² d ⁻¹	Mean Daily C flux g C m ⁻² d ⁻¹	Yearly C flux g C m ⁻² y ⁻¹
Study Period (n = 19)	7.78 ± 19	- 3.49 ± 11	0.10 ± 0.2	34.12 ± 83
2011 (n = 12)	7.92 ± 20	- 3.49 ± 11	0.09 ± 0.2	34.68 ± 91

The concentration of calcium (Ca²⁺) within the water column of Tatton Mere shows moderate variation between depths and over time (Figure 3.32). The concentration follows a similar trend at both 0.5 m and 10 m, but as the lake enters stratification in April epilimnetic Ca²⁺ levels drop below hypolimnetic levels. The lowest surface concentration is found during April 2011 at 36.9 mg Ca L⁻¹, similarly the lowest concentration at depth also occurs in April 2011 at 40.2 mg Ca L⁻¹. A spike in the CO₃²⁻ standing stock (Figure 3.34) and under saturation of CO₂ in the epilimnion occur during July and August 2011 when there is the greatest difference between epilimnion and hypolimnion Ca²⁺ concentrations. During the mixed phase at Tatton Mere concentrations of Ca²⁺ are virtually identical.

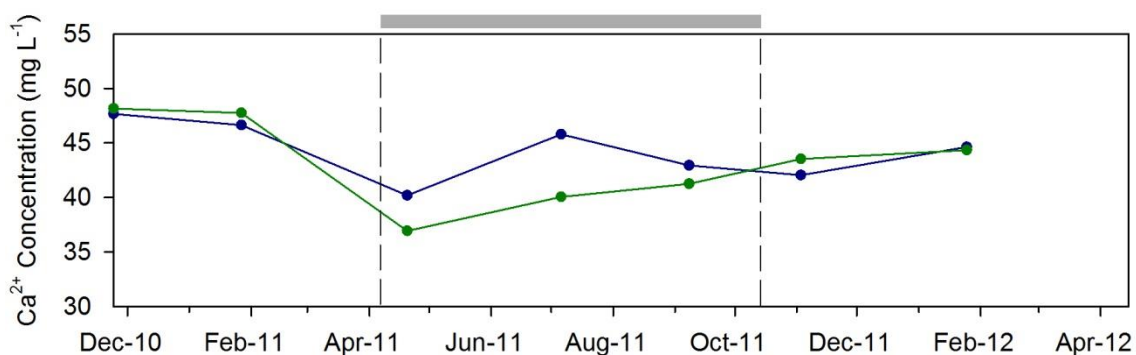


Figure 3.32 Summary of calcium (Ca²⁺) availability in Tatton Mere 2010 – 2012. Green line represents 0.5 m and blue line represents 10 m.

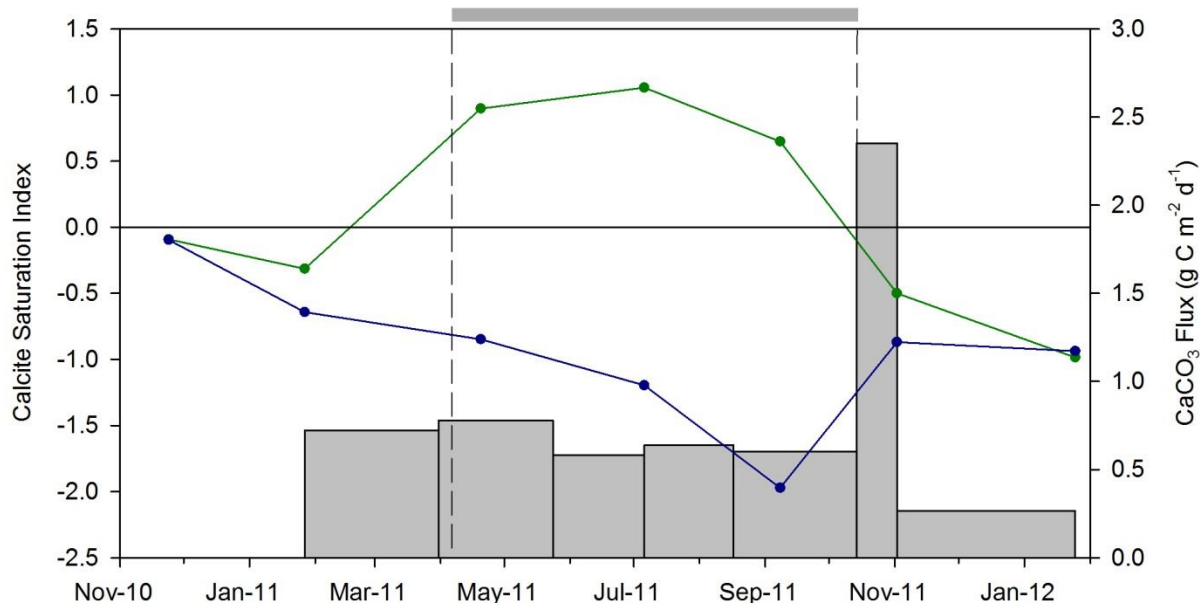


Figure 3.33 Summary of calcite saturation index (lines) and shallow sequencing trap CaCO₃ flux data (bars) in Tatton Mere 2010 – 2012. Values of saturation > 0 suggest the water is oversaturated with CaCO₃ and values < 0 signify CaCO₃ undersaturation. Green line represents 0.5 m and blue line represents 10 m.

Monthly patterns in the DIC pool (Figure 3.34a) show some variation in total DIC over the study period, but no overall decline. The highest water column concentration of 1454 $\mu\text{mol L}^{-1}$ occurs in November 2010, but similar peaks of 1330 $\mu\text{mol L}^{-1}$ in August 2011 and 1322 $\mu\text{mol L}^{-1}$ in October 2011 do occur. Lowest levels of DIC were found in January 2012 (602 $\mu\text{mol L}^{-1}$). The HCO₃⁻ pool in Tatton Mere is important in comparison to CO₃²⁻ and CO₂, as it constitutes on average 93% of total inorganic carbon. Due to the complex nature of inorganic carbon there were not similar patterns in CO₃²⁻ and CO₂ concentrations. Levels of CO₃²⁻ within the water column, typically the epilimnion, pulse due to high pH and low CO₂ concentrations. Average highs of around 70 $\mu\text{mol L}^{-1}$ (August & September 2011) can result in the precipitation of CaCO₃ (Figure 3.33). Typically CO₃²⁻ only constitutes 1.5% of the inorganic carbon measured in Tatton Mere over the study period. The overall concentration of CO₂ increases steadily after stratification, from ~40 $\mu\text{mol L}^{-1}$ during the mixed phase, to over 80 $\mu\text{mol L}^{-1}$ by August 2011. The CO₂ concentration reflects the increases in hypolimnetic CO₂ (Figure 3.34c and 3.34d) as a result of respiration. On average, CO₂ forms only 5% of the inorganic carbon pool, but this

can be as low as 2% in winter (February 2011) and as high as 10% in summer (June 2011).

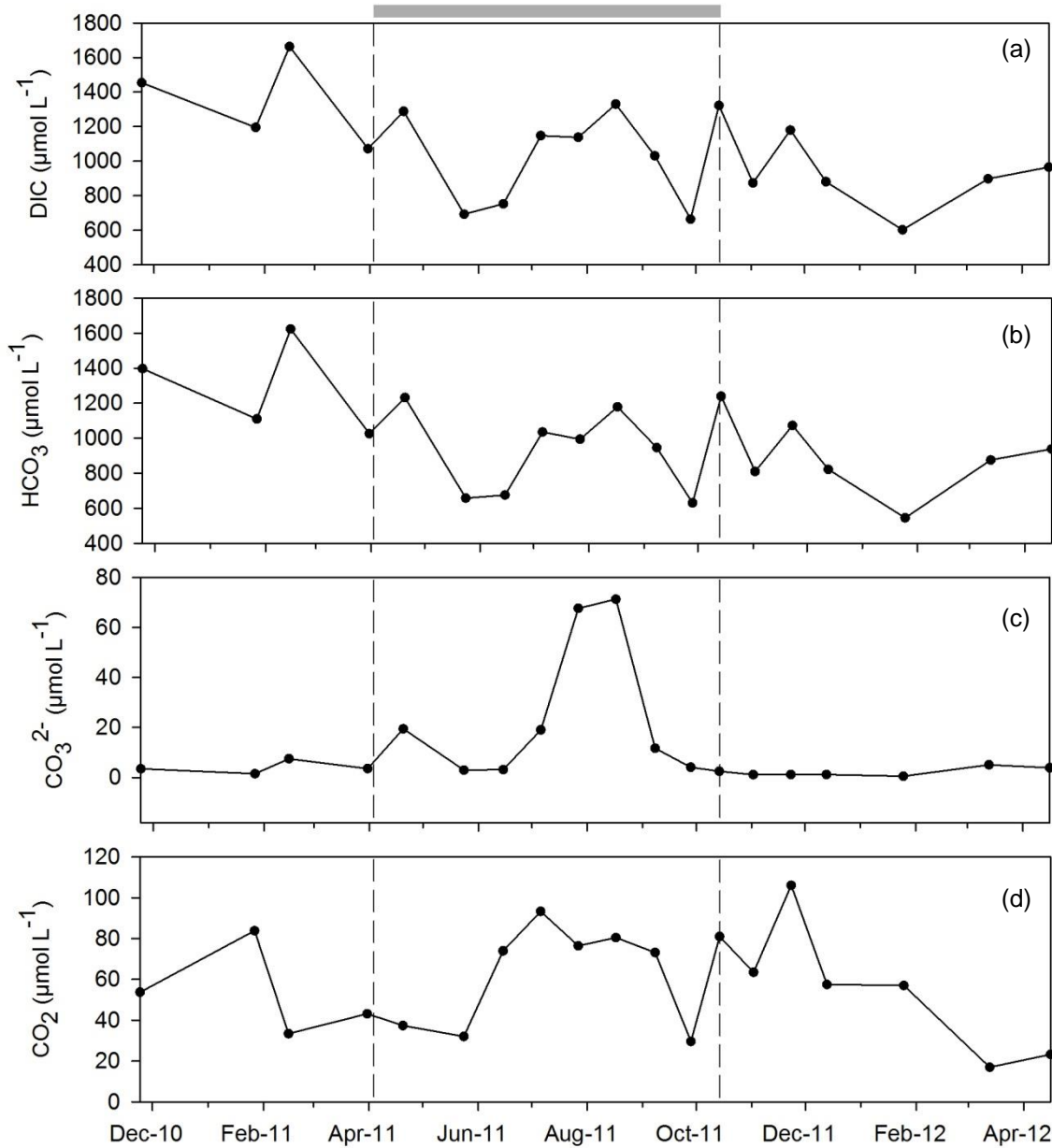


Figure 3.34 Monthly water column means for DIC fractions calculated in Tatton Mere from Dec 2010 to April 2012.

Standing stocks of total dissolved inorganic carbon and CO₂ were calculated from the concentration data (Figure 3.35). The overall patterns in total standing stocks match the concentration figures and show that overall DIC peaked at 26,915 kg C in February 2011 with the low of 9,594 kg C occurring in January 2012. The standing

stock of total CO₂ shows peaks during the mixed phase (January 2012: 1,274 kg C; November 2011: 1,586 kg C) and relatively consistent stocks of ~400 kg C during stratification.

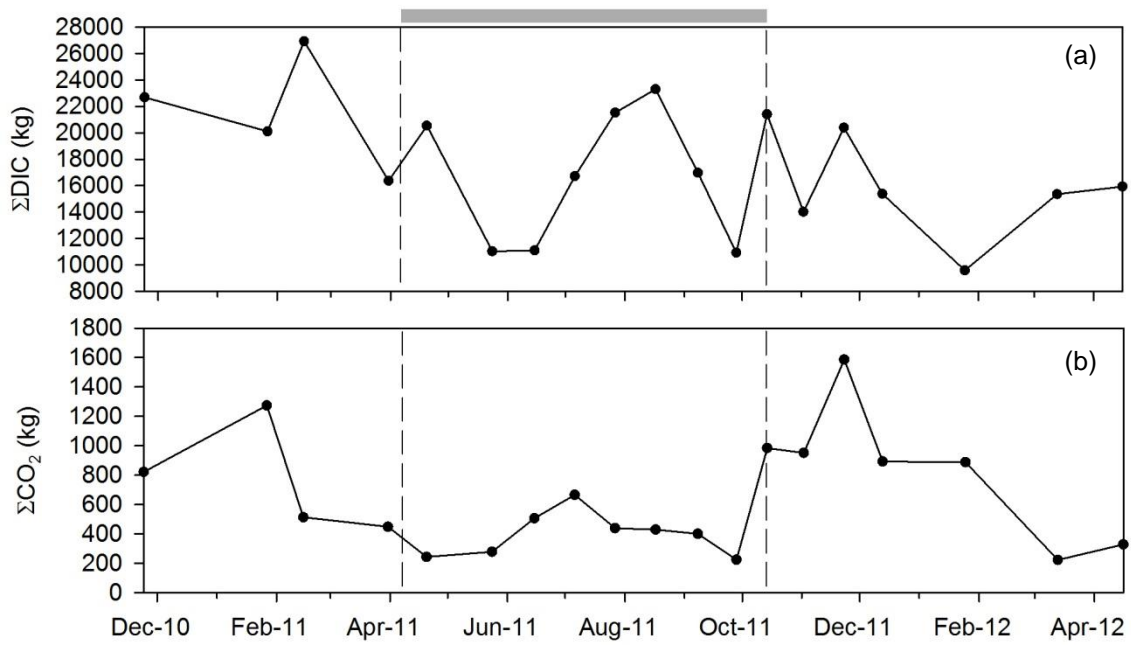


Figure 3.35 Monthly total inorganic carbon stocks calculated for Tatton Mere from Dec 2010 to April 2012.

3.3.4 Sediment Data

The open trap deployed at Tatton Mere collected a total of $41.4 \pm 3 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($n = 8$) between January 2011 and April 2012 (Figure 3.36). This equates to approximately $33.5 \pm 2 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($n = 6$) during 2011. However the open trap potentially under-trapped sediment due its location within the lake basin, but can be corrected by comparing the difference between open trap and sequencing trap data at Rostherne Mere over the same 12 month period. Using a correcting factor of 3, a more representative figure of $100.5 \text{ g C m}^{-2} \text{ yr}^{-1}$ can be used to signify OC deposition when calculating the OC sedimentation rate of Tatton Mere.

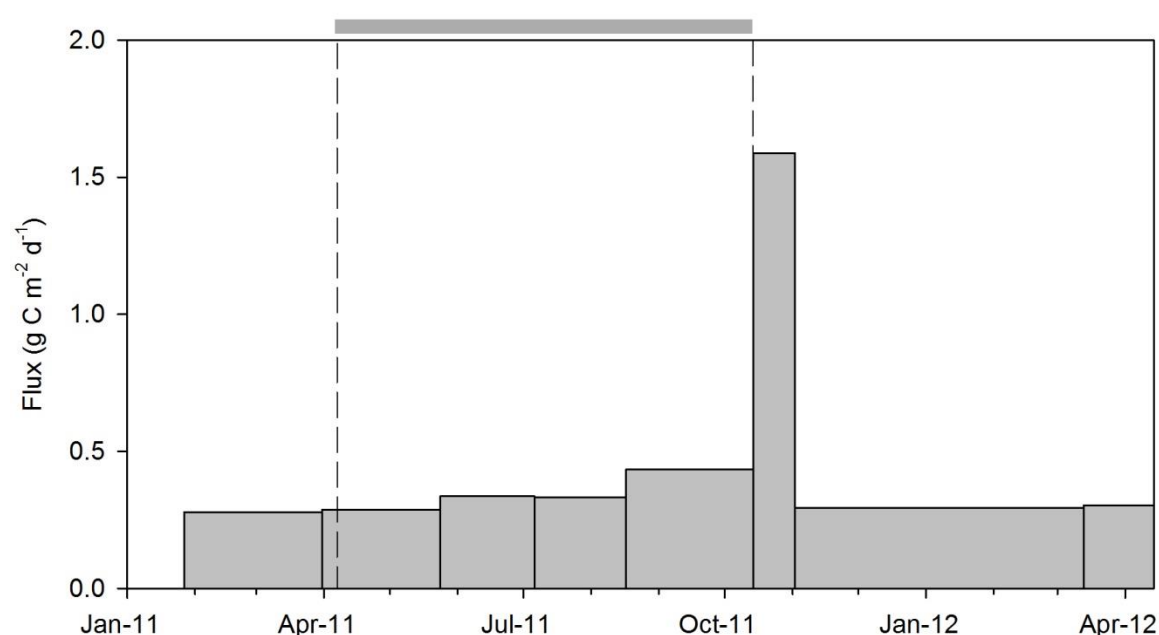


Figure 3.36 Tatton Mere organic carbon flux ($\text{g C m}^{-2} \text{ d}^{-1}$) from sediment trap data January 2011 to April 2012. Grey bars refer to an open sediment trap, set at 7 m, and are scaled for deployment time.

The SCP concentrations for the open water core taken at Tatton Mere (SCM41E) are shown in Figure 3.37. SCPs initially occur at 79 - 80 cm, from which concentrations steadily increase to around 45 cm and then more rapidly to 20 cm when they increase dramatically to a peak of over 51000 gDM^{-1} at 14 – 15cm. Concentrations then decrease rapidly again to the sediment surface.

In this core the SCP concentration peak is well defined and although the sample resolution means it could lie between 11 and 18 cm, it is most likely to fall in the

middle of this range, meaning a depth of 14 – 15 cm is assigned the date of 1978 ± 4 . The mean sediment accumulation rate for the last 35 years would therefore be 0.48 cm yr^{-1} . The rapid increase feature (~ 1950) is not obvious in SCM41E, but extrapolation of the mean sedimentation rate for 1978 – 2010 would put 1850 at ~ 70 – 75 cm. This is not so far out from the observed start of the SCP record and therefore it is likely that the SCP record is intact. This being the case we can use the cumulative SCP inventory approach (Rose & Appleby, 2005) to date this core. This provides a date for each 10-percentile of the SCP record providing 11 dates rather than three using the alternative approach. Dates modelled from this cumulative SCP chronology for SCM41E are given in Table 3.9.

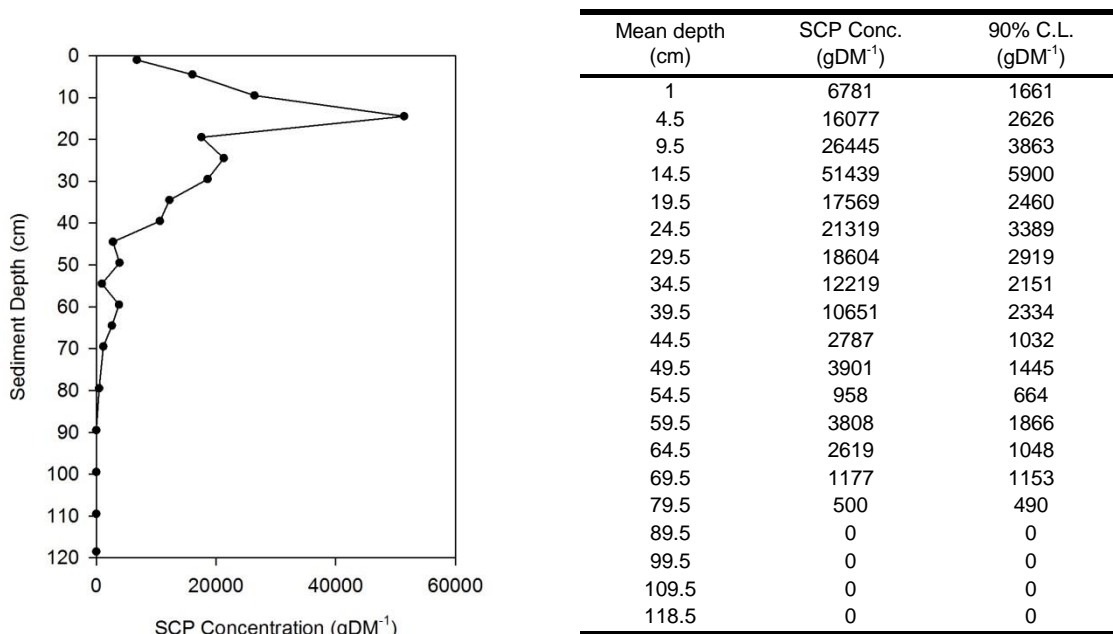


Figure 3.37 SCP profile and concentrations for SCM41E (Tatton Mere Open Water Core), recreated from Bennion et al. (2010) dataset.

Table 3.9 Summary of SCM41E (Tatton Mere Open Water Core) sediment core data. Original data taken from Bennion et al. (2010).

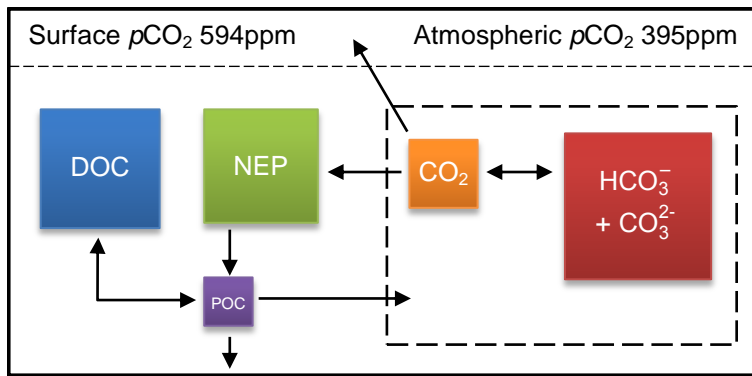
Top of Interval cm	Base of Interval cm	Model Date A.D.	Sedimentation Rate cm ² yr ⁻¹	Sediment Accumulation g m ⁻² yr ⁻¹	Organic C Accumulation g C m ⁻² yr ⁻¹
0	2	2010	-	500	61.79
5	6	2000	0.48	559	62.51
9	10	1992	0.50	657	66.70
13	14	1984	0.48	649	70.02
17	18	1975	0.46	625	65.76
21	22	1966	0.45	557	60.72
25	26	1957	0.43	583	63.07
29	30	1947	0.42	626	68.56
33	34	1938	0.42	597	67.84
37	38	1928	0.41	540	64.93
41	42	1918	0.41	525	68.10
45	46	1908	0.40	509	71.01

The OC burial efficiency of Tatton Mere (Table 3.10) was calculated using two competing methods (Sobek et al., 2009 and Gälman et al., 2008). OC deposition is derived from sediment trap data (Figure 3.35) and OC burial is derived from the dated core SCM41E (Bennion et al., 2010). The Gälman et al. (2008) method discounts the first 10 years of the core and estimates OC burial efficiency to be 62%, whereas the Sobek et al. (2009) method discounts the first 25 years of the core and estimates OC burial efficiency to be 71%.

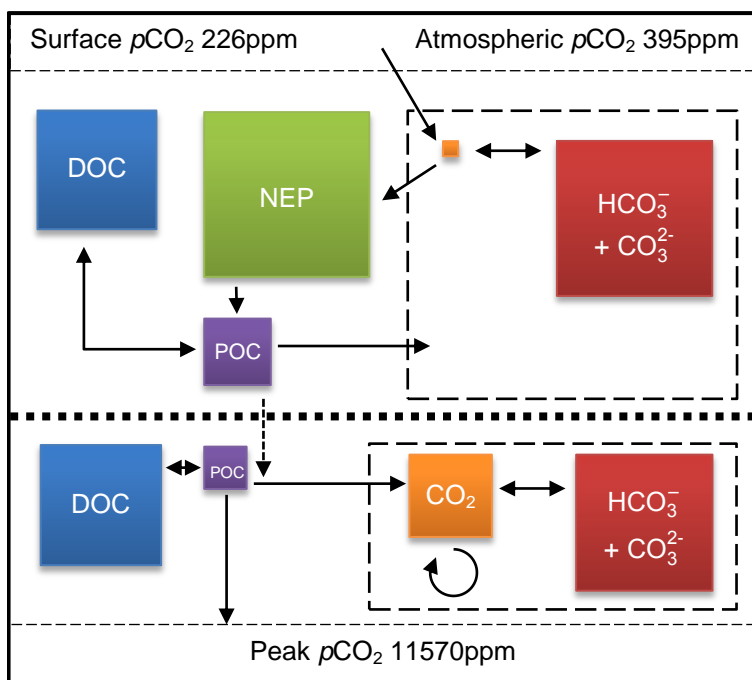
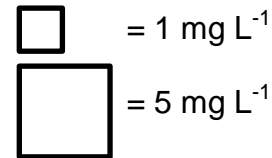
Table 3.10 Tatton Mere organic carbon burial in sediments, deposition onto the sediment, as determined by sediment traps and burial efficiency.

Method	No. of years discounted	OC Deposition g C m ⁻² yr ⁻¹	OC Burial g C m ⁻² yr ⁻¹	Burial Efficiency %
This Study	10	100.5	62.51	62
Sobek et al. (2009)	15	100.5	71.79	71

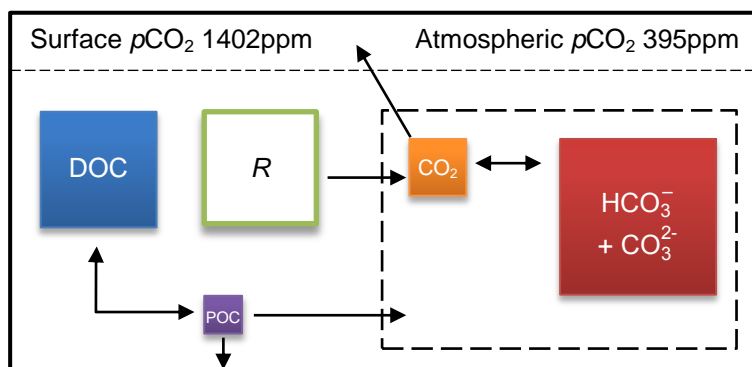
3.4 LAKE CARBON POOL COMPARISON



(a) Carbon pools for 2011. Values are integrated water column values. Box areas are scaled to the sizes of carbon pools:



(b) Carbon pools for 2011 stratified period. Values above black dashed line are epilimnion values (up to 6m – mean for season). Values below black dashed line are hypolimnion values.



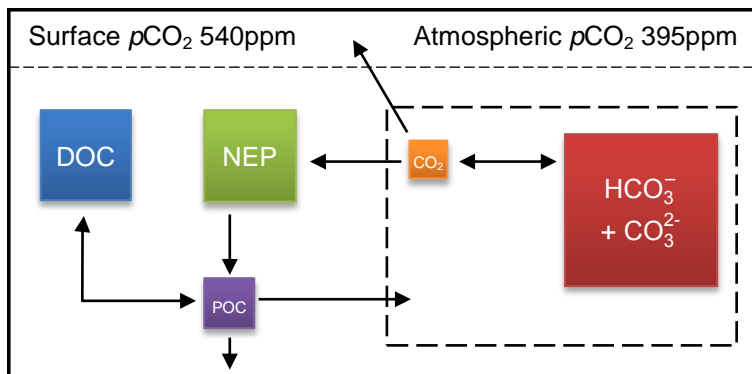
(c) Carbon pools for 2011 mixed period. Values are integrated water column values. *R* value represents negative NEP.

Figure 3.38 Graphical representation of Rostherne Mere carbon pools and interactions.

A visual interpretation of the 2011 carbon pools in Rostherne Mere and Tatton Mere are presented in Figures 3.38 and 3.39. The largest pool in both systems is DIC, comprising HCO_3^- , CO_3^{2-} and CO_2 , which shows some variability in size through the year as a result of photosynthesis and respiration. However, there is a larger CO_2 stock within Rostherne Mere compared to Tatton Mere due to its greater volume. In both lakes the DIC pool is largest in winter during the mixed period when respiration is at its greatest meaning the lakes become supersaturated with CO_2 and de-gas to the atmosphere (Figure 3.38c and 3.39c).

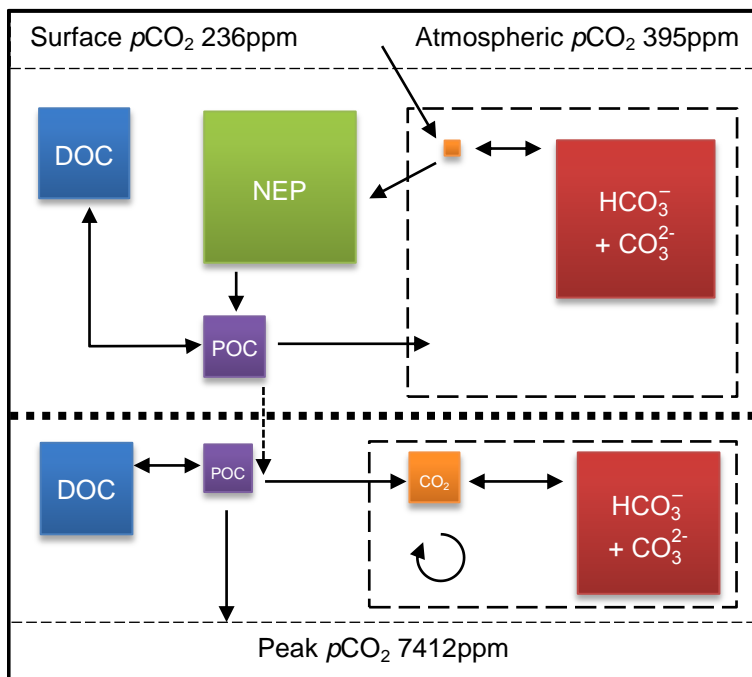
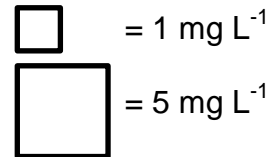
During stratification the epilimnion becomes depleted of CO_2 , causing the DIC pool to be at its lowest during the yearly lake cycle, the under saturation within the epilimnion means CO_2 is drawn into the surface waters from the atmosphere to increase the concentration but very high levels of photosynthesis cause the epilimnion to be consistently under saturated with CO_2 . The CO_3^{2-} pool is at its greatest during the summer period and typically leads to precipitation of CaCO_3 within the surface waters, however during the summer the hypolimnion is depleted of CO_3^{2-} as a result of the larger CO_2 pool from respiration and low pH values mean that the CaCO_3 saturation threshold is severely reduced and CaCO_3 dissolution occurs. This CO_2 stock in the hypolimnion increases through stratification, as it is unable to mix with the epilimnion, to its largest concentration throughout the year (Figure 3.38b and 3.39b).

Productivity within both meres is overall positive for the year but is larger in Rostherne Mere than Tatton Mere. Positive NEP occurs during the summer months within the epilimnion but shifts to negative NEP in winter when respiration is dominant. DOC pools are extremely stable throughout the year in both Rostherne Mere and Tatton Mere, suggesting it is unlikely the lakes are subsidised by large amounts of external, catchment DOC during the winter months. The production and breakdown of POC within the water column is shown in Figure 3.38b and 3.39b where high productivity during the summer increases the surface POC load but as it sinks through the hypolimnion is broken down through respiration, suggesting the likely amount of carbon reaching the sediments is much reduced on the values produced in the epilimnion.

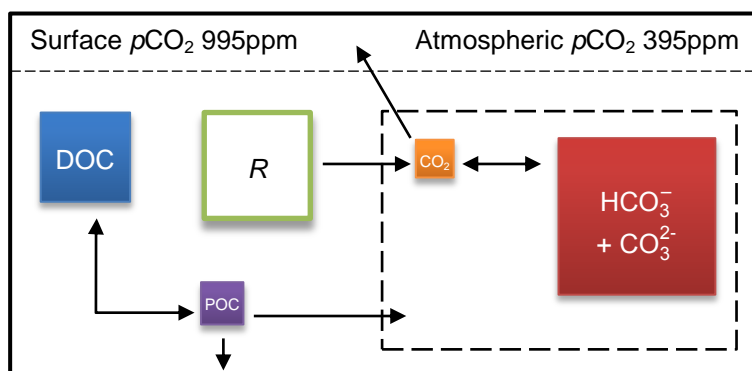


(a) Carbon pools for 2011. Values are integrated water column values.

Box areas are scaled to the sizes of carbon pools:



(b) Carbon pools for 2011 stratified period. Values above black dashed line are epilimnion values (up to 4m – mean for season). Values below black dashed line are hypolimnion values.



(c) Carbon pools for 2011 mixed period. Values are integrated water column values. *R* value represents negative NEP.

Figure 3.39 Graphical representation of Tatton Mere carbon pools and interactions.

4.1 DISCUSSION OUTLINE

Following the flow of C through Rostherne Mere and Tatton Mere, from its initial fixation in the surface waters by photosynthesis, flux and transformation through the water column and ultimate burial in the lake sediments (Figure 4.1), this discussion aims to investigate the processes driving the C-dynamics in the Cheshire-Shropshire meres. In particular it will address:

- The drivers of NEP in the Cheshire-Shropshire meres.
- Loss and recycling of C within the water column.
- Lake CO₂ dynamics.
- C-burial efficiency of both individual lakes and the wider Cheshire-Shropshire meres.
- The significance of C-storage in lakes, regionally and nationally and the implications for future management.
- How the Cheshire-Shropshire meres compare to other lake regions.
- A methodological review of the techniques used during this project.

There has been a considerable shift in aquatic ecosystems research, particularly lakes, in an attempt to improve our understanding of their C-dynamics (Tranvik et al., 2009; Cole et al., 2007). Research areas of particular interest include ecosystem metabolism (e.g. Van de Bogert et al., 2012; Sadro et al., 2011; Coloso et al., 2010; Staehr & Sand-Jensen, 2007), C-burial efficiency (e.g. Sobek et al., 2009, 2011; Gälman et al., 2008) and the long term stability of aquatic C-dynamics (e.g. Anderson, et al., 2014; Tranvik et al., 2009; Alin & Johnson, 2007). These ecosystem properties are increasingly subject to high-frequency measurement, especially since the development of sophisticated and portable sensors (Staehr, et al., 2010; Hanson et al., 2008; Van de Bogert et al., 2007), which have enabled the implementation of various collaborative projects across the globe, from regional to international scales, mapping high-frequency changes in environment and ecological processes with a particular focus on C-dynamics in many cases (e.g. Tranvik et al., 2009; Downing et al., 2006).

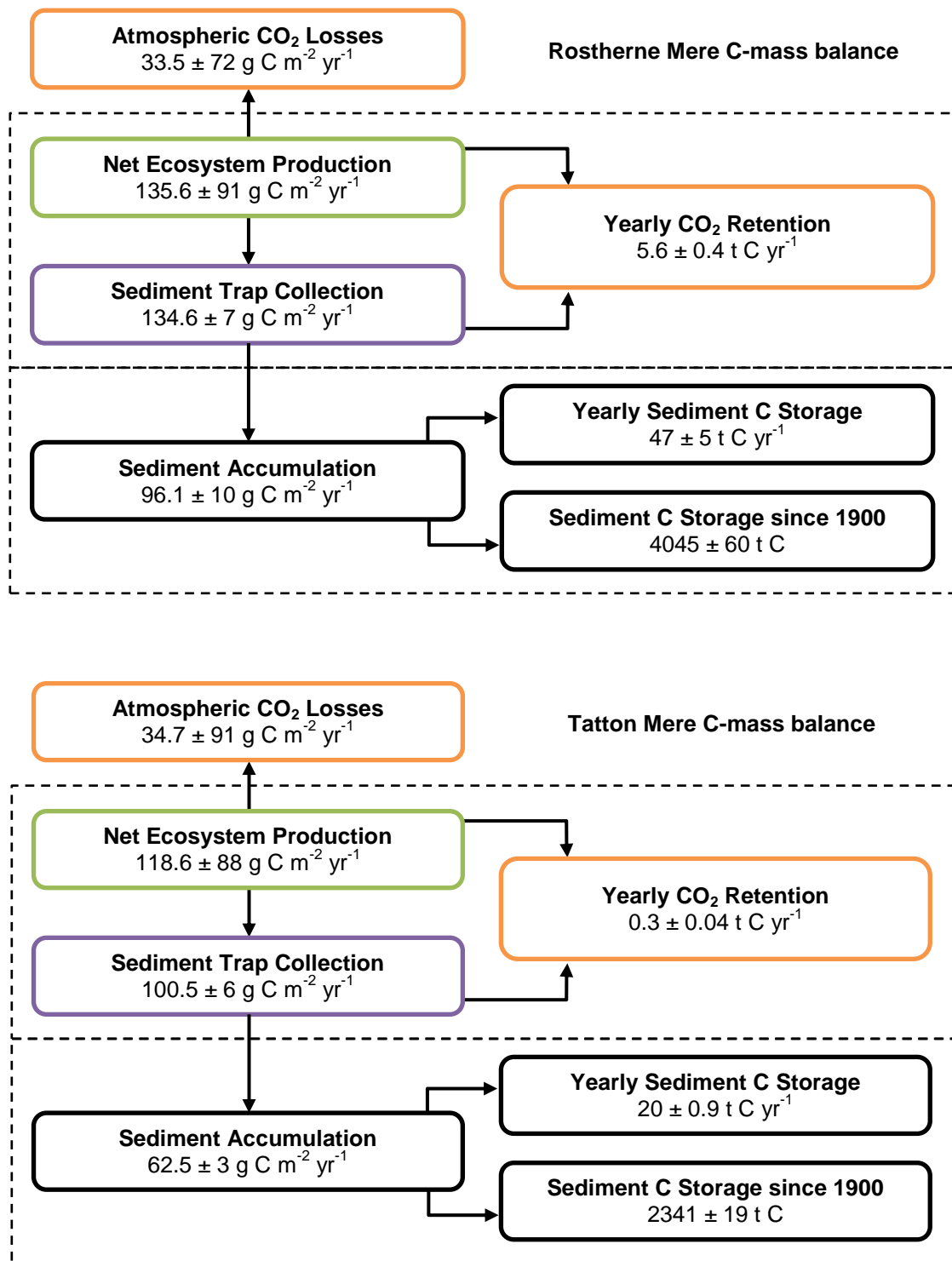


Figure 4.1 Summary of 2011 C-mass balance for Rostherne Mere and Tatton Mere; atmospheric CO₂ losses are calculated as part of net ecosystem production, but presented here as a net loss from the lake. Yearly CO₂ retention is excess free-CO₂ measured within the water column at the beginning of 2012 stratification cycle that was not evaded from the lake during turnover. Sensitivity testing expressed as uncertainty bounds (\pm).

However, there are significant variations in the estimates given for lake C-dynamics from these studies, largely due to the variability of lake productivity. This variability is typically as a result of lake type and trophic status, lake size, the number of lakes within different studies and an incomplete understanding of lake metabolism, as current techniques tend only provide a partial measurement of processes (e.g. extrapolating to whole year from a season, spot sampling etc.) (Cole et al., 2007; Einsele et al., 2001).

4.2 CARBON FIXATION

Quantifying the rate of C-fixation within the boundaries of a lake system is an essential element of NEP calculation and determining the ability of a lake to store or export C (Cole et al., 2000). The rate of primary productivity is typically dependent upon nutrient supply (largely N and P), but can be limited by other factors such as temperature and light availability (Søndergaard et al., 2003; Reynolds & Davies, 2001). The majority of research into lake productivity to date has focussed on boreal lakes as they are, globally, most abundant (Sobek et al., 2007; Downing et al., 2006). This imbalance, however, has led to the perception that most lakes are oligotrophic, heavily loaded with catchment-derived DOC and therefore net heterotrophic (Sand-Jensen & Staehr, 2007; Duarte & Prairie, 2005; Hanson et al., 2003). In contrast, temperate lake systems tend to be more nutrient rich, usually due to anthropogenic activity, in comparison to oligotrophic lakes, yet despite their visibility and accessibility, are poorly understood due to fewer studies or longer term datasets being available to assess critically their impact on the C-cycle (Downing et al., 2008; Gelda & Effler, 2002).

4.2.1 Trophic State & Lake Metabolism

The metabolism of lakes, typically presented as NEP, has become widely employed as a proxy for lake productivity. By estimating metabolism (or net production) lakes can be subsequently described as either autotrophic, a net C sink if $GPP > R$, or heterotrophic, a net C source if $GPP < R$. Previous studies have determined that DOC and TP are often the most important drivers of metabolism in lakes (Hanson et al., 2003; Cole et al., 2000; del Giorgio & Peters, 1994).

Table 4.1 Calculated areal net carbon production rates for different groups of lakes. Positive values signify net autotrophy and negative values signify net heterotrophy.

Group	Lake Type	Calculated areal carbon production rates	Time period of emission rate	Source
Cheshire-Shropshire Meres	Eutrophic	0.30 g C m ⁻² d ⁻¹	Annual average	This study
		0.62 g C m ⁻² d ⁻¹	Summer average (165 days)	
Gribsø, Denmark	Dystrophic	- 0.47 g C m ⁻² d ⁻¹	Up-scaled to annual values from 8 month study period	Staehr et al. (2010)
Slotssø, Denmark	Mesotrophic	- 0.45 g C m ⁻² d ⁻¹		
Onondaga Lake, NY	Eutrophic	0.75 g C m ⁻² d ⁻¹	Up-scaled to annual values from 4 month study period	Gelda & Effler (2002)
Paul Lake, MI	Oligo/Meso boundary	- 0.062 g C m ⁻² d ⁻¹	Up-scaled to annual values from seasonal datasets	Coloso et al. (2010)
Peter Lake, MI		0.076 g C m ⁻² d ⁻¹		
Lake Hampen, Denmark	Mesotrophic	0.061 g C m ⁻² d ⁻¹	69 day study period (during stratification)	Staehr et al. (2012)

Hanson et al. (2004) modelled the influence of TP and DOC on the C dynamics of lakes representing a range of lake trophic status (oligotrophic, mesotrophic, eutrophic and dystrophic) and demonstrated that the majority of lakes, globally, would be expected to be net heterotrophic on an annual basis. Heterotrophy is characteristically driven by high DOC loading and low TP concentrations (e.g. Sand-Jensen & Staehr, 2009; Duarte & Prairie, 2005). The majority of the DOC load in heterotrophic lakes has been imported from the surrounding catchment and the introduction of this terrestrial C has been found to subsidise bacterial respiration and lead to elevated levels of CO₂ within the water column and increase net CO₂ emissions to the atmosphere (e.g. Maberly et al., 2012; Lennon, 2004). However, the research model also highlighted that lakes with a low DOC burden and moderate to high TP levels were net autotrophic on an annual basis. This was the case for both Rostherne Mere and Tatton Mere, which were found to be net autotrophic on an annual basis (Annual NEP – RM: 135.6 g C m⁻² yr⁻¹; TM: 116.8 g C m⁻² yr⁻¹). Following on from Prairie et al. (2002), who suggested the autotrophy/heterotrophy boundary lay between a DOC loading range of 4 – 6 mg L⁻¹, Hanson et al. (2004) found that when DOC concentrations in lakes exceeded 8 mg L⁻¹, these lakes were consistently heterotrophic. Epilimnetic DOC concentrations in both Rostherne Mere

(7.2 mg L⁻¹) and Tatton Mere (4.4 mg L⁻¹) fall below this DOC boundary of 8 mg L⁻¹ (Figures 3.8; 3.28).

Table 4.1, however, highlights the high levels of variability in metabolism estimates among lakes and even within trophic classifications. Obviously DOC, TP and TN have a significant role in influencing lake metabolism, but other factors such as stratification regime, light availability and anthropogenic land-use changes can impact productivity and respiration within a lake (Coloso et al., 2010; Tsai et al., 2008).

The lakes of this study and Gelda & Effler (2002) were classified as eutrophic and showed net autotrophy on an annual basis, however, the research by Gelda & Effler (2002) estimated yearly C production from a 4 month (summer) study period, whilst the estimates for Rostherne Mere and Tatton Mere were generated from a full year's monitoring. However, if only summer data was used to calculate the NEP of the Cheshire-Shropshire meres, the estimate would potentially be twice that of the full year dataset (Table 4.1). Despite annual net autotrophy within the Cheshire-Shropshire meres, there was distinct seasonal variability. Net autotrophy was observed when the lakes were stratified and net heterotrophy was observed during periods of overturn (Figure 3.8; 3.25). Coloso et al. (2010) and Staehr et al. (2010) both utilised shorter, seasonal studies to estimate annual C production, however there are issues surrounding when to conduct seasonal surveys and how long these surveys should last (Coloso et al., 2011; Staehr et al., 2010). Finally, Staehr et al. (2012) presented C production rates from a 69 day study, during peak levels of production, which cannot be representative of a lakes overall levels of productivity.

Table 4.2 Summer near-surface average nutrient concentrations ($\mu\text{g L}^{-1}$) for classifying lakes into different trophic state categories (adapted from Kalff, 2001)

Trophic State	Inorganic N	Total N	Total P
Oligotrophic	< 200	< 350	< 10
Mesotrophic	200 – 400	350 – 650	10 – 30
Eutrophic	300 – 650	650 – 1200	30 – 100
Hypertrophic	500 – 1500	> 1200	> 100

Nutrient loading, especially catchment P loading, has been a long established problem in the Cheshire-Shropshire meres (Carvalho, 1993; Nelms, 1984; Reynolds & Sinker, 1976). The mean annual levels of TN and TP within both Rostherne Mere (1217 $\mu\text{g N L}^{-1}$; 216 $\mu\text{g P L}^{-1}$) and Tatton Mere (826 $\mu\text{g N L}^{-1}$; 442 $\mu\text{g P L}^{-1}$) suggest they are not just eutrophic but exhibit the characteristics of hypertrophic systems (Table 4.2). Typically P is seen as the most likely nutrient to limit productivity within a lake because it is naturally scarce and, although many cyanobacteria have the ability to exploit and fix N from the atmosphere, if there is an N deficiency within the water column they can utilise P to stimulate production (Schindler, 1977).

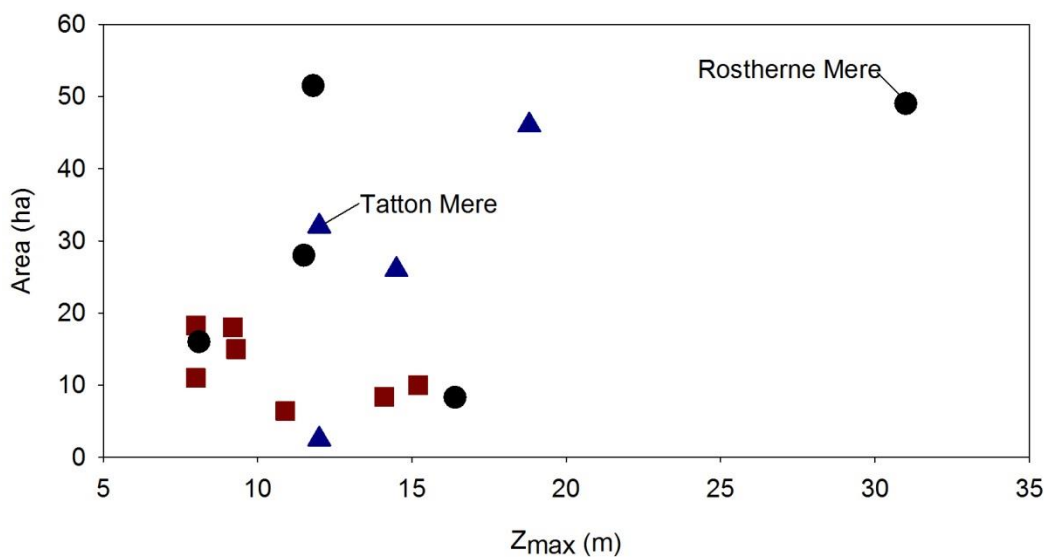


Figure 4.2 Redfield Ratios for the 16 deepest meres. Black circles are lakes with no clear nutrient limitation; red squares are lakes that are likely to be P limited and blue triangles are lakes that are likely to be N limited.

Using the Redfield Ratio, the atomic ratio of N and P found in plankton (16 N: 1 P), it can be determined which nutrient, if any, is deficient and likely restricting growth within a lake. If the ratio of N:P > 20, P is scarce relative to N meaning P is potentially limited, but if N:P < 10, N is likely to be limiting; if N:P < 20 but > 10, neither nutrient is considered limiting. Of the deepest 16 lakes on the Cheshire-Shropshire Plain, 7 could be classified as P limited, 4 as N limited and 5 as not nutrient deficient (Table 4.3). The P limited lakes tend to be small (< 20 ha) and relatively shallow ($r = -0.582$), whilst there is virtually no pattern to N limitation or nutrient deficiency (Figure 4.2). Rostherne Mere can be classified as neither N or P limited with a N:P ratio of 12.46, implying another factor is probably contributing to

limiting growth (e.g. light or a micronutrient), while Tatton Mere is likely N limited with a N:P ratio of 4.13.

Anthropogenic activity within a catchment, such as agriculture or sewage discharge, usually leads to a release of P into aquatic habitats altering its availability for synthesis into organic matter (Søndergaard et al., 2003). Typically the eutrophication of lakes is exacerbated by natural factors such as water residence time (WRT) and thermal stratification which allows the accumulated P to be recycled and released on an annual basis between the sediment and water column. This is especially problematic on the Cheshire-Shropshire Plain, where the larger meres have WRT in excess of 1 year. Attempts to improve water quality over the last 20 years have seen an overall reduction in P concentrations through reducing external loading, however the majority of the lakes in the area remain eutrophic due to annual P recycling within the lake system itself (Moss et al., 2005).

In thermally stratified lakes, such as those in the Cheshire-Shropshire meres, the majority of P recycling occurs during the summer months in the hypolimnion, where the concentration steadily increases. As successive surface blooms of particulate organic matter (POM) are broken down in the hypolimnion, both C and P become mobilised and free-O₂ is consumed through respiration. As anaerobic conditions begin to dominate the lake hypolimnion during summer the release of phosphate into the water column is promoted. Initially this phosphate is trapped in the hypolimnion, but once the hypolimnion mixes into the upper waters, as the thermocline erodes, the phosphate becomes mixed through the entire water column (Tables 3.1; 3.6). During the winter months, once overturn is complete and the lake becomes isothermal, the primary method of P recycling occurs through the precipitation of iron phosphate onto sediment particles and transfer into sediments. This precipitation of iron phosphate reduces any potential P losses during winter from increased river and groundwater discharge and will be released back into the water column the following spring, with the onset of low redox conditions. Consequently the concentration of P within a eutrophic, stratifying lake system may be maintained or even gradually increase (e.g. even if external P loading falls over time) (Allott, 2011; Reynolds & Davies, 2001).

Table 4.3 Summary of lake depth, area and chemical variables for the 16 deepest meres (> 8m Z max) on the Cheshire-Shropshire Plain. Data collated from Fisher et al. (2009) and this project.

Mere	Area (km ²)	Z max (m)	A/Z max	Known Summer Stratification	TP (µg L ⁻¹)	TN (µg L ⁻¹)	N:P Ratio	N/P Limited
Berrington Pool	0.03	12	2.08		113	720	14.09	-
Betton Pool	0.06	10.9	5.87		96.8	1500	34.27	P
Blake Mere	0.08	14.1	5.95	✓	62	1380	49.23	P
Bomere Pool	0.10	15.2	6.57		48.8	1000	45.33	P
Cole Mere	0.28	11.5	24.34	✓	262	1370	11.56	-
Comber Mere	0.52	11.8	43.64	✓	362	900	5.49	N
Croze Mere	0.15	9.3	16.12	✓	55	1320	53.09	P
Ellesmere	0.46	18.8	24.46	✓	894	1210	2.99	N
Marbury Big Mere	0.11	8	13.75		251	2610	23.00	P
Mere Mere	0.16	8.1	19.75		86.8	1800	45.87	P
Newton Mere	0.08	16.4	5.06	✓	196	1330	15.01	-
Oak Mere	0.18	8	22.87		61	330	11.96	-
Pick Mere	0.18	9.2	19.56		96	1010	23.27	P
Rosterne Mere	0.49	31	15.80	✓	216	1217	12.46	-
Tatton Mere	0.32	12	26.66	✓	442	826	4.13	N
White Mere	0.26	14.5	17.93	✓	694	1440	4.59	N

However oxygen availability is not the only process to have an effect on the binding and release of P from sediments. The process has also been found to be sensitive to changes in pH and alkalinity in calcareous lakes. The ability of calcareous lakes to buffer phosphorus loading is associated with co-precipitation of P and calcium carbonate from the water column (Søndergaard et al., 2003; Otsuki & Wetzel, 1974).

With such elevated levels of nutrients found in the water column of many of the Cheshire-Shropshire meres, it is likely that another process is responsible for limiting productivity. In such nutrient rich lakes, algae can become so abundant the self-shading can begin to limit the crop (Moss et al., 2005; Reynolds & Davies, 2001). As a result, this reduction in light penetration becomes the growth limiting factor, rather than nutrients, and under such conditions blue-green algae frequently become dominant especially if they have the ability to 'over-winter' on the sediments and survive until the following growth season. Rostherne Mere and Tatton Mere have been found to be dominated by blue-green algae, especially species such as *Microcystis* which is known to be a common light-limited population (Moss et al., 1994; Reynolds & Bellinger, 1992), suggesting that self-shading could be limiting growth rates within the water column of these lakes.

4.3 CARBON FLUX

The majority of lakes globally are supersaturated with CO₂ in respect to the atmosphere; this makes them a net source of C to the atmosphere (Sobek & Tranvik, 2005; Cole et al., 1994). Table 4.4 compares data from a variety of studies highlighting the global trend of surface water CO₂ super-saturation. Algesten et al. (2004) estimated flux using the relationship between DOC and CO₂ in a subset of lakes then extrapolating the result to many oligotrophic lakes in northern and central Sweden. Kortelainen et al. (2006) sampled 177 oligotrophic lakes 4 times throughout the year to infer annual flux rates. Alin and Johnson (2007) gathered previously published pCO₂ and wind speed data to estimate yearly flux rates. Lazzarino et al. (2009) used summer CO₂ values and average wind speeds from oligotrophic and mesotrophic lakes to estimate yearly flux rates.

The data from the Cheshire-Shropshire Meres and Balmer & Downing (2011) highlights the seasonal variability of surface CO₂ in lakes, particularly eutrophic

systems. The Cheshire-Shropshire meres are consistently under-saturated with CO₂ during summer when productivity is high and free-CO₂ is utilised in photosynthesis leading to CO₂ being drawn down from the atmosphere into the lake (a negative flux). After overturn the large volumes of CO₂ that have built up in the hypolimnion are mixed into the entire water column and gradually diffuse into the atmosphere and ultimately make the meres net sources of CO₂ on an annual basis (Figures 3.13; 3.30).

Table 4.4 Calculated areal CO₂ emission rates for different groups of lakes. Positive values reflect a flux out of the lake to the atmosphere and negative values reflect a flux into the lake from the atmosphere.

Group	Calculated areal carbon emission rates	Time period of emission rate report	Source
Cheshire-Shropshire Meres	34 g C m ⁻² yr ⁻¹ – 8.7 g C m ⁻²	Calculated annual flux Calculated total summer flux (165 days)	This study
North American Agricultural	– 0.1 g C m ⁻² yr ⁻¹	Estimated annual flux from summer data (123 days)	Balmer & Downing (2011)
Finnish lakes	42 g C m ⁻² yr ⁻¹	Estimated annual flux	Kortelainen et al. (2006)
Large lakes of the world (>500 km ²)	62 g C m ⁻² yr ⁻¹	Estimated annual flux	Alin & Johnson (2007)
Florida lakes	328 g C m ⁻² yr ⁻¹	Estimated annual flux	Lazzarino et al. (2009)

The flux of carbon within a lake system relates to the processing of both autochthonous and allochthonous matter. Boreal systems are typically loaded with terrestrially-derived DOC and poor nutrient availability and autotrophic C production, meaning the majority of the organic matter degradation within the lake is heterotrophic (Jonsson et al., 2007; Sobek et al., 2006; Hudson et al., 2003). In eutrophic lakes there is typically an abundant supply of nutrients to support large algal blooms, often multiple blooms per year, with a usually lower ratio of terrestrially derived DOC subsidising bacterial processes meaning autotrophy is prevalent (Staehr et al., 2011, 2012; Sadro et al., 2011). However Maberly et al. (2012) have discovered, contrary to previous understanding, that a net efflux of CO₂ from lakes

represents net heterotrophy as a result of terrestrial DOC imports (Duarte & Prairie, 2005). They show that in relatively clear-water lakes such as the English Lake District high CO₂ concentrations can also result from the direct input of already fixed and broken down terrestrial CO₂ through hydrological pathways such as rivers and groundwater. They have demonstrated that if levels of terrestrially derived DOC are low with a lake system, which implies a low contribution to lake respiration, but concentrations of CO₂ are high, this CO₂ can derive from terrestrially fixed C that has already been broken down in the soil.

4.3.1 Sediment Traps

The flux of particulate matter within Rostherne Mere and Tatton Mere was measured using sediment traps. Understanding the flux of C through the water column is vital in determining potential C losses, typically through the transformation of OC to IC by bacterial and photo-oxidation (Stets et al., 2009; Cole et al., 2007; Graneli et al., 1996). Sediment traps can also be used to calculate the flux of OC to the sediment surface within lakes and this technique has widespread use (Sobek et al., 2006, 2011; Algesten et al., 2004). There was little or no loss found between the upper (epilimnion) and lower (hypolimnion) traps in Rostherne Mere during the study period (Figure 3.18). This could be as a result of high OM settling velocities, high levels of OM preservation within the traps or low levels of mineralisation within the water column, with the majority of OM mineralisation occurring in the sediment surface due to the short distance to the anoxic zone in the summer months due to stratification.

4.3.2 CO₂ Regeneration

The regeneration of CO₂ within the water column, or *in-situ* losses of OC, have received some attention recently (Sobek et al., 2003; Jonsson et al., 2001; den Heyer & Kalff, 1998) and research suggests that levels of OC mineralisation are typically lower *in-situ* than in surface sediments. However there is also an element of IC transformation as CaCO₃, precipitated in the surface waters of many highly productive lakes, including Rostherne Mere and Tatton Mere, will be dissolved lower down the water column to maintain inorganic carbon equilibrium, as the hypolimnion becomes more acidic and concentrations of free-CO₂ increase (Wetzel, 2001; Figures 3.15; 3.32).

There is also evidence from this study to suggest that deeper, strongly stratifying eutrophic lakes may potentially retain CO₂ over periods longer than the annual stratification cycle. For example, despite mixing each winter, levels of CO₂ remained well above atmospheric levels in Rostherne Mere throughout the overturn period and this remaining CO₂ (5.6 ± 0.4 t C) was once again trapped in the hypolimnion the following spring with the onset of stratification (Figure 4.1). As Rostherne Mere has a residence time of approximately 2 years, it would require the lake to be isothermal and fully mixed for ~11.5 years for the trapped CO₂ to be returned to the atmosphere and the lake to fully de-gas (peak loss rate at Rostherne Mere 1 g C m⁻² d⁻¹).

4.3.3 Other Losses

Alongside the generation and loss of CO₂ from lakes as a result of C mineralisation, CH₄ and the re-release of previously bound metals and nutrients is likely to occur. The flux of CH₄, in particular, is complex and depends on many factors, including temperature, water depth and the amount of organic C available. It is believed that CH₄ will represent a small fraction of the overall C flux within the lake, and therefore was not measured in this study (Lennon et al., 2006; Matthews et al., 2003).

4.4 CARBON STORAGE

The storage potential of lakes is directly affected by their size, levels of production and loss within the system; typically oligotrophic and mesotrophic lakes have very low recorded C burial rates (e.g. < 10 g C m⁻² yr⁻¹ Anderson et al., 2013; ~28 g C m⁻² yr⁻¹, Gälman et al., 2008; 21 g C m⁻² yr⁻¹, Jonsson et al., 2007) when compared to eutrophic and hypertrophic lakes (e.g. 68 g C m⁻² yr⁻¹ this study; 88 g C m⁻² yr⁻¹ Heathcote & Downing, 2011). However these values have to be taken into context with other system processes, such as C fixation and C loss, to provide an understanding of the overall C-balance within a lake. Lake C burial estimates can be determined from mass balance budgets, where the burial component is the difference between total inputs and losses to the sediment (Sobek et al., 2006), or sediment core analysis (Anderson et al., 2014). The focus of this study, two small, very eutrophic lake systems, had a mean C AR of 68 g C m⁻² yr⁻¹ (RM, 96.1 g C m⁻² yr⁻¹; TM, 62.5 g C m⁻² yr⁻¹) derived from sediment core analysis, where only the first 10 years of the core are discounted from analysis (see Section 4.4.2).

4.4.1 Sediment Focusing

A major consideration when undertaking C burial calculations is the phenomenon of sediment focusing. Originally described by Likens & Davis (1975), sediment focusing is used to describe the observed increase in net sediment accumulation in the deepest part of a lake basin. The processes behind sediment focusing can vary between basins and seasons, however without correction the estimates provided from a typical single deep core method is likely to lead to an overestimation of C burial (Engstrom & Rose, 2013; Molot & Dillon, 1996). Sediment focusing correction was performed on the Rostherne Mere core (RM_Liv_2011) using the ^{210}Pb flux correction method (Engstrom & Rose, 2013), reducing the C AR by ~30% ($131 \text{ g C m}^{-2} \text{ yr}^{-1}$ corrected to $92 \text{ g C m}^{-2} \text{ yr}^{-1}$), as the bathymetry of the basin suggests that focusing is likely to occur. Although focusing is very likely to occur at Tatton Mere, focusing correction was not performed on the Tatton Mere core (SCM41E; Bennion et al., 2010) as SCP dating was used in the analysis and ^{210}Pb flux was not available for the core.

The most common processes associated with sediment focusing that might occur at Rostherne Mere are sliding and slumping of sediment on the slopes, intermittent complete mixing during the overturn period and peripheral wave attack around the shallow shore zone. Each of these processes has been shown to redistribute sediment from shallow regions to deep waters and is typically observed in both the sediment core record and sediment trap data (Hilton et al., 1986; Hilton, 1985). Small increases in sediment trap accumulation were observed after the overturn period in both Rostherne Mere (Figure 3.18) and Tatton Mere (Figure 3.35); however the latter is likely to be as a result of methodological error, and water column mixing at overturn is liable to lead to the re-suspension and deposition of some material from across the basin.

4.4.2 Burial Efficiency

Although lakes are extremely efficient at storing C when compared to other systems, such as terrestrial and ocean environments (Tranvik et al., 2009; Alin & Johnson, 2007; Dean & Gorham, 1998), a degree of mineralisation will continue to occur in the sediment surface after deposition (Sobek et al., 2009). Typically the burial efficiency of a lake will vary as a result of a number of factors, but the most important are the C

source (terrestrial or aquatic), oxygen exposure time and sedimentation rate (Sobek et al., 2009). There is, however, a degree of uncertainty within the literature over the length of time significant mineralisation persists. The sediments at Rostherne Mere below 12 – 15 m are anoxic for ~9 months of the year and anoxic at Tatton Mere for ~7 months of the year, during the stratification cycle. This means the sediments are not exposed to oxygen during the peak levels of GPP and therefore rates of mineralisation could be reduced at both lakes. Sobek et al., (2009) and others calculate burial efficiency in lake cores on sediment layers > 25 years old and create a steady-state model of core C burial. However Gälman et al. (2008) demonstrated that maximum OC mineralisation rates occur in sediments < 5 years old and drops dramatically after ~10 years and only discount sediment layers < 10 years old. Following these methods, burial efficiency calculations for both Rostherne Mere and Tatton Mere yielded varying results (Table 4.5).

Table 4.5 Rostherne Mere and Tatton Mere OC burial efficiency determined by competing methods.

Method	No. years excluded	RM BE %	TM BE %
Gälman et al. (2008)	10	71	62
Sobek et al. (2009)	15	99	71

This discrepancy in burial efficiency is undoubtedly as a result of the Sobek et al. (2011) method over-estimating OC burial rates due to the implication that lake OC burial rates are constant and steady over the last 100 – 150 years. However, in Rostherne Mere and other European eutrophic lakes, the rate of OC burial has changed significantly since 1900, increasing rapidly with a period of pronounced eutrophication ~1950 A.D. linked to the introduction of artificial fertilisers and land use changes (Battarbee et al., 2011; Anderson et al., 2014), and then falling again as lake management was introduced to help reduce levels of eutrophication. Rostherne Mere, in particular has seen a pronounced decrease since 1996 following sewage diversion in 1991, from C burial rates in excess of 111 g C m⁻² yr⁻¹ to 92 g C m⁻² yr⁻¹, which has been quite stable over the last couple of decades (Table 3.4).

This means that discounting sediments younger than 25 years, as suggested by Sobek et al. (2009), skews the result in favour of higher OC burial rates. Discounting the first 25 years of the Rostherne Mere core leads to a burial efficiency nearly equal the current levels of gross sedimentation into the surface sediments.

4.4.3 Significance of Lake Carbon Storage

Rostherne Mere and Tatton Mere form part of the Cheshire-Shropshire meres, a group of more than 60 productive lakes that lie within a small geographical area in NW England (Cheshire-Shropshire Plain ~5,400 km²), and have the potential to be annual net carbon stores as a result of their persistent eutrophic status over that last ~150 years (Table 4.6). Annual C storage estimates from this study predict a combined yearly C accumulation rate for the two lakes of 68 ± 4 t C yr⁻¹ (weighted average – see below). Using data obtained from two, dated sediment cores these two lakes have sequestered 6041 ± 97 t C since 1900. This consistent net storage means the carbon is removed from the wider carbon cycle on a long-term basis i.e. not easily available for further use within the lakes metabolism cycle or to be exchanged with the atmosphere.

Table 4.6 Estimates of C accumulation within groups of eutrophic lakes. Yearly C AR based on mean AR 68 g C m⁻² yr⁻¹; Total C AR since 1900 based on mean Total AR 7458 g C m⁻². ^(a) JNCC (2008). Mt C = 1 million t C.

	Total Lake Area	Yearly C AR	Total C AR since 1900
Rostherne Mere and Tatton Mere	0.81 km ²	68 ± 4 t C yr ⁻¹	6041 ± 97 t C
All Cheshire-Shropshire Meres	7.5 km ²	506 ± 32 t C yr ⁻¹	0.05 ± 0.001 Mt C
All UK Eutrophic Waters	1,785 km ² ^(a)	0.12 ± 0.01 Mt C yr ⁻¹	13.3 ± 0.2 Mt C

Up-scaling the data to all the Cheshire-Shropshire meres was based upon a mean yearly C accumulation rate of 68 g C m⁻² yr⁻¹ and total C accumulation since 1900 was based upon a mean total accumulation rate of 7458 g C m⁻². These figures were calculated by weighting the individual lake areal estimates 15% RM: 85% TM, to reflect the composition and distribution of the Cheshire-Shropshire meres total

lake area. Approximately 15% of the total area of the meres will have a depth >18 m with an observed very high C AR when compared to the balance of 85% of total lake area covered by meres with a depth >18 m, reflecting a lower observed C AR. The annual C accumulation rate for the Cheshire-Shropshire meres were therefore estimated to be $506 \pm 32 \text{ t C yr}^{-1}$ and $0.05 \pm 0.001 \text{ Mt C}$ since 1900. However these values are likely an over-estimate of C accumulation rates as the mean data generated by this study only robustly reflects 50% of all the Cheshire-Shropshire meres, as very small/shallow lakes are likely to have annual C accumulation rates below $68 \text{ g C m}^{-2} \text{ yr}^{-1}$.

The same mean yearly and total C accumulation rates were used to estimate C accumulation rates for all eutrophic waters in the UK. No accurate figures exist for total number of eutrophic lakes in the UK, so an estimate for total area of UK eutrophic water was used instead, but this is likely to include reservoirs which are more likely to be a net source of C to the atmosphere due to their low water residence times and rapid siltation (Tranvik et al., 2009). The annual C accumulation rate for all UK eutrophic waters were therefore estimated $0.12 \pm 0.01 \text{ Mt C yr}^{-1}$ and $13.3 \pm 0.2 \text{ Mt C}$ since 1900. The Cheshire-Shropshire meres consequently only contribute about 0.5% of annual UK lake C accumulation and storage.

Table 4.7 Annual natural C sequestration compared to annual UK CO₂ emissions. UK eutrophic waters yearly C sequestration based on mean AR $68 \text{ g C m}^{-2} \text{ yr}^{-1}$. Where ^(a) DECC (2014), ^(b) Forestry Commission (2014), ^(c) this study and ^(d) JNCC (2008). Mt C = 1 million t C.

	Total Area	Total Emissions/Sequestration	Mean Areal Rate
2012 Total UK CO₂ Emissions ^(a)	243,610 km ²	- 128.85 Mt C yr ⁻¹	- 529 t C km ⁻²
2010 UK Forest Carbon Sequestration ^(b)	28,500 km ²	2.9 Mt C yr ⁻¹	101 t C km ⁻²
2011 UK Eutrophic Waters Sequestration ^(c)	1,785 km ² ^(d)	0.12 Mt C yr ⁻¹	68 t C km ⁻²

Lakes are seen to many as efficient long-term stores of carbon and offer potential to offset some of the extra burden placed on the global C-cycle by anthropogenic C

emissions (e.g. Anderson, et al., 2009; Tranvik et al., 2009; Downing et al., 2008; Cole et al., 2007). However current CO₂ emission rates in the UK, and globally, far outstrips the current storage potential of natural sinks such as forests and lakes (Table 4.7). Major UK CO₂ sources include numerous anthropogenic sources such as industrial process, transport and energy supply, but also a number of natural sources including plant and animal respiration and the loss of soils as a result of land-use changes (inc. changes in land management practices; Alonso et al., 2012) though these losses have yet to be accurately quantified. Annual UK CO₂ emissions are ~128.85 Mt C yr⁻¹ (DECC, 2014), which means that annual UK forest C sequestration (2.9 Mt C yr⁻¹; Forestry Commission, 2014) only currently offsets 2.24% of UK yearly CO₂ emissions. This value is, though, significantly larger than the annual UK eutrophic waters C sequestration (0.12 Mt C yr⁻¹; this study) which offsets only 0.09% of yearly UK CO₂ emissions.

The data also show that UK forests are, on average, annually more efficient C-sinks when compared to UK eutrophic waters (~67% C of UK forests), although UK lake sequestration rates can vary dramatically from values close to or in excess UK forest C sequestration rates for hypertrophic lake systems to net C sources for oligotrophic lake systems. The expected annual C sequestration by UK forests is expected to fall over the next ~10 years as future predictions of C sequestration assume restoration of commercial conifer plantations with replanted trees to be native, slower growing species, and that planting of new woodland will continue at the same rate as in 2011 (Forestry Commission, 2014).

4.5 A CROSS-SYSTEM PERSPECTIVE

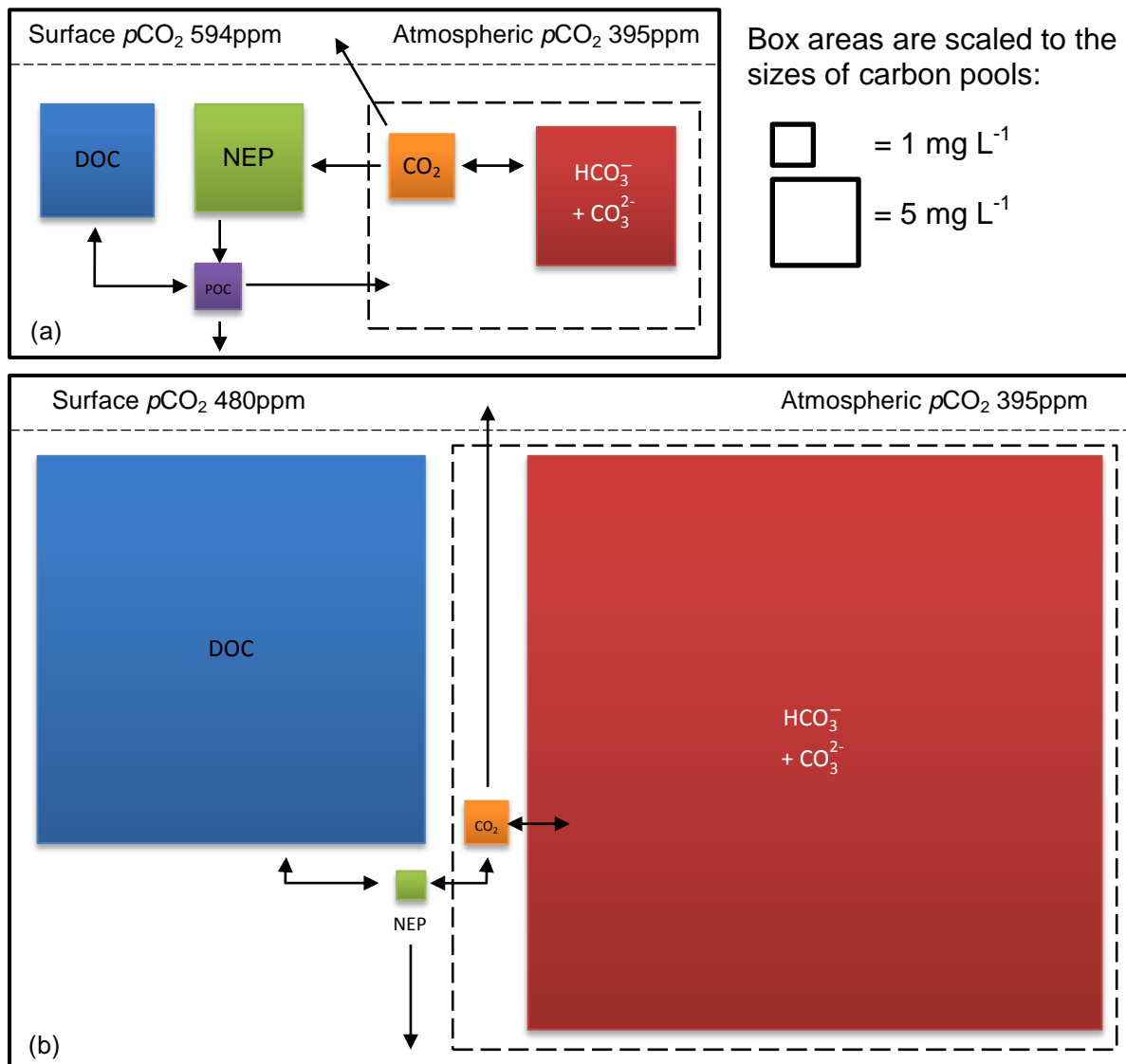


Figure 4.3 Graphical representation of carbon pools for (a) Temperate lake systems; Rostherne Mere (2011) integrated water column, a eutrophic lake and (b) Arctic lake systems; SS4 (1999) integrated water column, an oligotrophic lake (data from Anderson et al., unpublished).

The Cheshire-Shropshire meres are net autotrophic systems, where the annual C production and burial exceed annual rates of C mineralisation (Figure 4.3a). They receive low levels of terrestrially-derived DOC and are P-loaded, supporting high rates of C production within the epilimnion. Despite the prevalence of net autotrophy, the meres are a net source of CO_2 to the atmosphere. The source of this free- CO_2 is unclear as, however, as although there is a contribution from the mineralisation of OC within the surface sediments, the rates of OC mineralisation from the literature

show rates in eutrophic lakes range from $13.6 \text{ mmol C m}^{-2} \text{ d}^{-1}$ at 25m water depth, under anoxic conditions, to $34.9 \text{ mmol C m}^{-2} \text{ d}^{-1}$ in shallower, oxygen exposed sediments (Maerki et al., 2009), and may only account for ~8% of total mineralisation (den Heyer & Kalff, 1998). It is also unlikely that the transfer of CO_2 from the catchment, through rivers and groundwater flux, is a major input into the Cheshire-Shropshire meres as DOC loading is low, well below figures quoted in the literature that would promote net heterotrophy (Figures 3.10; 3.27). Other potential sources of CO_2 within the water column could include the dissolution of silicon (Si), as both Rostherne Mere and Tatton Mere have abundant diatom communities (Carvalho, 1993; Moss et al., 1992; Nelms, 1984) or the re-mineralisation of CaCO_3 , that has been precipitated in the epilimnion of the lakes during periods of peak GPP, but as it sinks into the hypolimnion pH falls and the concentrations of CO_2 rise promoting its breakdown into other DIC fractions (Figures 3.15; 3.32)

The eutrophic meres are a contrast to the oligotrophic lakes found across the arctic and boreal zone, including Greenland (Figure 4.3b). Here the majority of lakes are net heterotrophic on an annual basis as anthropogenic activity and land-use change leads to increased DOC-loading and nutrient availability (Anderson et al., 2009; Ågren et al., 2008; Jonsson et al., 2007). Levels of C production within oligotrophic lakes are extremely small when compared to eutrophic systems. This can be as a result of more frequent mixing regimes, and a much reduced growing season due to their geographic location. The DOC load is usually very large, in this case SS4 has DOC concentrations $> 62 \text{ mg L}^{-1}$, and has been found to subsidise lake respiration in numerous studies (e.g. Duarte & Prairie, 2005). This is likely to be one reason why overall quantities of inorganic carbon (mainly as CO_3^{2-} and HCO_3^-) within the SS4 are substantially higher than those in eutrophic lakes such as Rostherne Mere and Tatton Mere.

4.5.1 Temperate Systems

There are approximately 300,000 small lakes between 0.1 km^2 and 5 km^2 across Europe covering an area $\sim 240,000 \text{ km}^2$ (Kastowski et al., 2011). Of these, 113,338 ($61,880 \text{ km}^2$) could be classified as temperate systems (United Kingdom and mainland Europe excluding the Alps region) and account for ~25% of European lake

surface area. However, they potentially store in excess of 0.32 Mt C yr⁻¹, which is nearly 35% of all European lake C accumulation. This is most likely a conservative estimate as the C accumulation rates are based on a mean European C accumulation rate of 5 g C m⁻² yr⁻¹ (n = 228; Kastowski et al., 2011), whereas Anderson et al. (2014) have estimated that 20th century C accumulation rates across Europe could be as high as 30 g C m⁻² yr⁻¹ (n = 93) for meso-eutrophic lakes, meaning the real estimate of European small lake C accumulation could be in excess of 1.85 Mt C yr⁻¹ (Table 4.8).

Table 4.8 Estimates of C accumulation rates in lake across Europe. Mean C AR multiplied by total lake area. Mt C = 1 million t C.

	Number of Lakes	Mean C AR g C m ⁻² yr ⁻¹	Total C AR
Cheshire-Shropshire meres (This study)	62 (7.5 km ²)	68	506 t C yr ⁻¹ 0.05 Mt C since 1900
All UK eutrophic waters (This study; JNCC, 2008)	- (1,785 km ²)	68	0.12 Mt C yr ⁻¹ 13.3 Mt C Since 1900
0.1 – 5 km² temperate European lakes (Kastowski et al., 2011)	113,338 (61,880 km ²)	5	0.32 Mt C yr ⁻¹ 30.9 Mt C since 1900
Meso-eutrophic European lakes (Anderson et al., 2014)	113,338 (61,880 km ²)	30	1.85 Mt C yr ⁻¹ 185 Mt C since 1900

The estimation of annual C accumulation rates remains unclear, as studies by Tranvik et al. (2009) and Kortelainen et al. (2004) estimated long term global C burial rates to be ~5 g C m⁻² yr⁻¹. These studies, however, mainly focused on long term Holocene averages and made no attempt to correct for more recent C accumulation rates. In areas such as Europe recent C accumulation rates will have been affected by increasing levels of anthropogenic interference, especially eutrophication from both point sources (wastewater treatment) and diffuse sources (agricultural runoff). Anderson et al. (2014) highlights this trend of increasing European C accumulation rates throughout the 20th century as mean C AR measured in lakes (n = 93) increased from 17 g C m⁻² yr⁻¹ in the 19th century to 40 g C m⁻² yr⁻¹ between 1900 and 1950 and to 60 g C m⁻² yr⁻¹. The rates could be even higher for hypertrophic

lakes (TP >100 $\mu\text{g L}^{-1}$) at 100 $\text{g C m}^{-2} \text{yr}^{-1}$ post-1950; these data are supported by C AR measured at Rostherne Mere (TP 216 $\mu\text{g L}^{-1}$; C AR $96.1 \pm 10 \text{ g C m}^{-2} \text{yr}^{-1}$). The increasing C accumulation trend across Europe, especially since 1950, has an impact on any up-scaling calculations as this non-linear trend is difficult to predict in and between lakes. However, in the past 15 – 20 years, there has been an overall decline in C burial in a number of lakes, including Rostherne Mere and Tatton Mere (Tables 3.4 & 3.9; Anderson et al., 2014). The decline is likely as a result of European policy introduced to reduce nutrient loading from both point sources and diffuse sources, because as many as 44% or almost 6500 lakes monitored across Europe, as part of the European Water Framework Directive, are failing to achieve good ecological status or potential. Evidence suggests that the highest pollution pressures on these lakes are agricultural runoff and wastewater treatment (EEA, 2012; Kronvang et al., 1993).

The decision by the European Commission to implement the European Water Framework Directive suggests a long-term management plan to improve the water quality and ecological status of lakes across Europe to a good chemical and ecological status by 2015, and introduces the principle of preventing any further deterioration of status (EEA, 2012). This typically means managing catchments to reduce and control the amount of pollution loading into these systems with the aim of improving overall species diversity, reducing their vulnerability to climate change and improving their recreational quality. This management plan has led to an overall improvement in water quality especially a significant decrease in nutrient loading in lakes, by 31% between 1992 and 2010. The impact of reducing lake nutrient loading will most likely be a reduction in the number of eutrophic lakes or lakes likely to become eutrophic across Europe. This is undoubtedly a positive outcome for species diversity and improving the recreational quality of lakes but has the potential to seriously impact the C accumulation potential for European lakes (Table 4.8), as less productive lakes (oligotrophic and mesotrophic lakes) typically have very low recorded C burial rates (e.g. < 10 $\text{g C m}^{-2} \text{yr}^{-1}$ Anderson et al., 2013; ~28 $\text{g C m}^{-2} \text{yr}^{-1}$ Gälman et al., 2008; 21 $\text{g C m}^{-2} \text{yr}^{-1}$ Jonsson et al., 2007) when compared to eutrophic and hypertrophic lakes (e.g. 68 $\text{g C m}^{-2} \text{yr}^{-1}$ this study; 88 $\text{g C m}^{-2} \text{yr}^{-1}$ Heathcote & Downing, 2011). According to the recent sediment records eutrophic

lakes are sequestering more C than at any other time in their history (Anderson et al., 2014).

4.5.2 Arctic and Boreal Systems

Arctic and boreal lake systems are seen as perhaps having the greatest C storage potential due to their global abundance in comparison to other lake types, and their typical high density within a landscape. With an approximate land coverage in SW Greenland of about 14%, Anderson et al. (2009) calculated that the Holocene standing C stock for small lakes in the area (extrapolating to an estimated 20,000 lakes) to be in the region of 49 Mt C. This value is about half of that estimated C stock for the regional soil pool, but in only 5% of the land area. These standing stock determinations yield organic C accumulation rates of between 3.5 – 11.5 g C m⁻² yr⁻¹. Other lake dense regions, including Finland, have also been intensely studied and Kortelainen et al. (2004) calculated the standing C stock for ~56,000 lakes, extrapolated from a study of 122 lakes, to be in the region of 1900 – 2700 Mt C. These estimates suggest that small lakes buried two-thirds of the C store of all Finnish lakes although they represent only one third of the lake area. While the rates of C accumulation are not as high as those estimated for eutrophic and hypertrophic systems, such studies indicate the importance of incorporating high density lake regions into models of regional C balance. Oligotrophic lakes in the arctic and boreal zone are however, currently most vulnerable to a changing climate, meaning that as temperatures increase, the likelihood of their C-dynamics being disrupted increases. Mixing regimes are likely to change as periods of ice-cover will be reduced and the strength of stratification may be increased. There will also be further catchment changes, in arctic regions in particular, as areas of permafrost decrease and previously frozen soils can be eroded, not only potentially releasing previously long-term stored C into the atmosphere but increase the DOC and nutrient loads to these lakes. This has the potential for greater C evasion from arctic lakes as allochthonous DOC typically consists of recalcitrant compounds that resist microbial decay and are less biologically available for primary production. Such compounds can persist within the water column and restrict primary productivity through their impact on in-lake light climate (Porcal et al., 2009; Cardille et al., 2009; White et al., 2000).

4.6 METHODOLOGICAL EVALUATION

The key uncertainties highlighted by this research are summarised and ranked in order of most significance to the overall analysis:

(i) **Calculation sensitivity testing**; although the fundamental technique for measuring metabolic rates from O_2 diel has not notably changed since its introduction by Odum (1956) and others, new modelling and statistical analysis has begun to provide better estimates for the mixing of O_2 due to wind and flow variability (F; Eq. 2.13), air-water flux coefficients (k ; Eqs. 2.11; 2.12) and oxygen saturation (Eq. 2.6) as a result of extensive laboratory and field tests, allowing uncertainties to be more reliably accounted for when considering lake metabolism (Staeher et al., 2010; Cole & Caraco, 1998; Wanninkhof, 1992). However, these statistical analyses are only valid if the errors associated with their calculation are considered. Evaluating the sensitivity of metabolic rates to potential errors in key assumptions requires simple sensitivity testing. Modifying data models by $\pm 10\%$ to investigate their influence on metabolic rates can illustrate the potential errors associated with incorrect measurements of temperature or barometric pressure, for example, due to poor equipment calibration (Staeher et al., 2010; Dubois et al., 2009; Bade et al., 2004). Equally, estimates of CO_2 storage and flux were based on established calculations (Zeebe & Wolf-Gladrow, 2001; Cole & Caraco, 1998; Wanninkhof, 1992; Millero, 1979) that attempt to minimise the number of uncertainties in calculations such as air-water flux coefficients (k ; Eqs. 2.36; 2.37) and water vapour pressure (p_{H_2O} ; Eq. 2.30), but are obviously somewhat simplified expressions of natural processes to allow meaningful estimates to be made.

(ii) **Photosynthetic quotient (PQ)**; when converting oxygen derived metabolism to carbon units a photosynthetic quotient (Eq. 2.19), the molar ratio of the rate of oxygen production to that of carbon assimilation, is used. Uncertainty exists surrounding the value of PQ as it has been shown to vary between algal species, over time and with nutrient availability (Williams & Robertson, 1991; Grande et al., 1989). There is some agreement that this value is likely to fall between 1.0 – 1.3, though most experimental data are derived from algal cultures and little data exist for natural populations (Williams & Robertson, 1991).

(iii) **Heterogeneity**; the majority of recent studies investigating lake ecosystem metabolism have utilised a high frequency, sonde based 'free-water' approach as these estimates can provide in-situ high frequency, precise measurements from multi-variable sensors over a wide range of timescales (daily, seasonally and annually) (e.g. Coloso et al., 2008; Van de Bogert et al., 2007). However, although the cost of sondes has fallen over recent years they still represent significant investment within a project and typically metabolic estimates are derived from a single sensor placed at one depth within the epilimnion at the centre of a lake (Sadro et al., 2011; Staehr et al., 2010). This means that when calculating metabolic processes in lakes from O₂ concentration for example, heterogeneity is assumed i.e. the concentration is the same throughout the mixed zone as measured at the sonde depth, metabolism is happening at the same rate throughout the mixed zone and littoral areas, despite a mixing depth often lower than that at the centre of the lake, and discounting the greater interaction with sediments in these areas. The degree to which a single sonde can represent whole-lake metabolism depends on a number of factors, including lake morphometry (% of lake area pelagic or littoral), strength of vertical mixing, depth of the active mixing layer (z_{mix}) and the variability in the abundance of phytoplankton and bacteria throughout the water column (Sadro et al., 2011). Van de Bogert et al. (2007) suggests that single-site metabolic estimates may not represent whole-lake metabolism or only pelagic metabolism, but rather something between these two endpoints.

Similarly, there is risk of heterogeneity when estimating C accumulation rates as the majority of studies to date have used a single central basin sediment core to estimate whole lake basin accumulation (e.g. Heathcote & Downing, 2011; Finlay et al., 2010; Bennion et al., 2010). This is achieved by applying a correction factor for sediment focusing towards the centre of the lake, based on the flux of ²¹⁰Pb in the core relative to the atmospheric ²¹⁰Pb flux for the region in which the lake is located. The method assumes: (1) the atmospheric ²¹⁰Pb flux is known with some level of certainty; (2) the sediment constituent of interest is focused to the same degree as ²¹⁰Pb, and (3) focusing to the core site has remained relatively constant over the period of interest. The most appropriate method for addressing over/underestimation of whole lake C accumulation is by using multiple dated sediment cores for each lake basin, but this is an expensive and extremely labour

intensive approach and cannot realistically be applied to budget-limited studies or regional studies of more than 10 lakes (Engstrom & Rose, 2013; Anderson et al. 2014).

(iv) **No. of lakes in study**; when designing a study that involves the potential for up-scaling it is important to determine whether the sample (i.e. number of lakes) is representative of the area or region being subject to investigation. This is because it is impractical (expensive and labour intensive) to consider sampling every lake, there has to be a trade-off between data intensity and sample size, as most scientific research works to limited budgets and equipment. There is a choice between fewer lakes more intensely with a higher data resolution but potentially be representative of fewer lake classifications or do you study more lake classifications less intensely with a lower data resolution but potentially overlook key trends within each classification. For many key variables, however, regional change across all lakes may not be mirrored in similar changes in individual lakes making it difficult to model larger lake regions from a few individual lakes. For example, Cardille et al. (2009) identified in their study that groundwater in modelled lake hydrologic budgets decreased by ~10% with increasing precipitation. However, the decrease was not uniform across all lakes and was not predictable as a proportion of groundwater in lakes of different sizes. Rather, the regional trend was driven by a small number of lakes whose reliance on groundwater declined substantially in wetter scenarios. Lake responses reveal that they are not independent elements reacting to the same perturbation; rather the models show lakes are sometimes coupled and sometimes uncoupled to regional trends, with many of the elements that influence carbon and water budgets having several highly non-linear characteristics. More generally, the variety of behaviour among different lakes appears to be related to a wide array of factors, including lake and watershed size and shape, upstream and downstream connections and the composition of land cover in the lake's watershed (Anderson et al., 2013; Weyhenmeyera & Karlsson, 2009; Cardille et al., 2009; Sobek & Tranvik, 2005).

Another consideration when up-scaling is the ability to model regional, national or supra-national trends using total lake area. The majority of lake studies estimate C accumulation rates on an areal basis, typically $\text{g C m}^{-2} \text{ yr}^{-1}$, meaning the most robust

models have to be calculated using known lake area. Up-scaling from a single or small number of lakes to total number of lakes in a region/nation allows for a potentially greater over/underestimation of C accumulation as total lake area is based on the sample of the study i.e. an assumption that all lakes in the modelled region have the same area as your sample. On smaller scale studies, such as this, an accurate total lake area exists for 63 lakes of the Cheshire-Shropshire plain, whereas the estimates for total eutrophic lake area within the UK, Europe and globally are based on either computer models or 'best guess' estimates from existing published data, meaning data is inferred using the best current knowledge but is still potentially over/underestimating C accumulation on the larger scale.

That is not to say that the up-scaling method cannot be used to give a useful first estimate for assessing larger regional or national trends as although modelling a handful of lakes and up-scaling to thousands simplifies the natural environment, it does allow meaningful estimates to be made where none may currently exist (Cardille et al., 2009).

(v) **Sediment traps and mineralisation**; the use of sediment traps is very widespread when investigating lake sedimentation, with a variety of open and sequencing traps now available to provide a range of sediment data over a number of timescales (days, weeks and months). Both open and sequencing traps were used during this project and a number of issues became apparent during their deployment, most notably *in-situ* sediment mineralisation and water turbulence, especially when using an open trap design.

The mineralisation of sediment in traps is a known issue within the literature (Filstrup et al., 2009; von Wachenfeldt & Tranvik, 2008; Bloesch & Burns, 1980); however it is almost unavoidable due to the timescales involved in sediment trap experiments. Bloesch & Burn (1980) estimated, from a mesotrophic lake basin, that ~10% mineralisation is likely to occur within the trap within a 1 – 2 week period, however when exposure times are increased to 3 months the rate of mineralisation increased to ~30%. Based on these findings an optimal trap reset period is 2 weeks. Both the open and sequencing traps in this study spent the majority of their time in the

hypoxic zone of the lake which has the potential to reduce the amount of mineralisation that will occur (Gudas et al., 2010).

Water turbulence can affect both settling sediment and the re-suspension of sediment from the bottom waters (Bloesch & Burns, 1980). The design of a sediment trap can either minimise or exacerbate water turbulence. For example Bloesch & Burns (1980) conducted experiments on various trap designs and found that open cylindrical traps were the most efficient trapping design (95 – 100%), with sediment settling patterns minimally disrupted by turbulence and open traps with a funnel shape consistently under-trapped (25 – 60%), especially under turbulent conditions. A funnel design was used during this project in an attempt to maximise collection amount per trap and subsequent comparisons with the sequencing traps found that the open traps under-trapped by 3 – 4 times that of the sequencing traps. Consequently the open trap data for Tatton Mere was tripled in an attempt to provide a more representative sedimentation rate. Sediment re-suspension is likely to occur at both Rostherne Mere and Tatton Mere; however there was only a small increase in sequencing trap rates observed after overturn (Figure 3.18; 3.35) suggesting that it does not significantly alter the overall sediment flux data.

4.7 FURTHER RESEARCH

This thesis has made a substantial contribution to furthering the application of metabolic modelling in lake systems but has highlighted some of the key areas that hold potential for further enquiry. These research issues fall into two broad groups: (1) Methodological studies assessing heterogeneity, and (2) Studies that explore and develop better analytical tools for understanding lake metabolism.

(i) **Long-term monitoring**; despite the increase in studies focusing on the metabolism of lakes globally, the majority of this work has utilised short-term (typically less than 4 months), high frequency sonde data to provide yearly C-fixation estimates (Table 4.1). This free-water oxygen approach, as used in this study, has overcome many of the limitations of the bottle and chamber method used extensively before the introduction of automatic water quality sensors, but there is still much to learn about these methods, particularly what sampling regime is necessary to adequately capture ecosystem estimates of processes like metabolism. Without

further evaluation of sensor-based methods, process estimates will suffer ambiguities similar to traditional techniques (Van de Bogert et al., 2005). For example, a single centrally located oxygen sensor may measure some unknown value between pelagic metabolism and whole-lake metabolism. These uncertainties may be reduced with improved sampling designs coupled with models that incorporate spatial heterogeneity in ecosystem processes.

Although it is intuitively clear, and shown in a few lakes, that one sensor is often not sufficient to provide true whole-lake metabolism (Staeher et al., 2011; Coloso et al., 2008; Van de Bogert et al., 2007), further studies are needed on the extent to which this is a general problem, and what to do about it. More precisely, further recommendations of how and when to perform depth-integrated determinations of lake metabolism using automatic profiling systems. Also further recommendations of how and when to perform multiple sonde measurements of lake metabolism using horizontally distributed sondes. In general, by determining lower uncertainties associated with horizontal and vertical heterogeneity, labour intensive and expensive measurement programs could be avoided.

Van de Bogart et al. (2012) have tried to quantify how many sensors are needed to produce more robust estimates. They believe that substantial gains can be made with just a few additional sensors and confidence in metabolism estimates goes up with each additional sensor used, but with diminishing returns. While there is no definite answer to the question, they examined some benchmarks for comparison. Using the partitioned day-to-day variance as a benchmark, an evaluation was undertaken of the number of sensors needed to match the precision of the daily metabolism estimate to the level of precision obtained given the temporal variation over a 10 day deployment. Obtaining estimates that reduce the uncertainty attributable to spatial heterogeneity to the level of uncertainty for a week's worth of values brought the result into a range that many ecologists could accept. At between 10 and 14 sensors were needed to meet GPP and R in Sparkling Lake. However, between 5 and 7 sensors were needed to meet this target for Peter Lake GPP and R. Because estimates of GPP and R are correlated, NEP ($GPP - R$) is somewhat decoupled from the spatial variation. Indeed, for estimates of NEP, just two randomly

placed sensors achieve a level of precision on par with 10 day temporal precision for both lakes.

Although a single-sensor location chosen at random is not likely to represent the lake-wide mean determined by multiple sensor locations for a single day, many researchers are interested in time frames longer than a single day. It is likely that deployments for a week, month, or an entire season at a single site may come closer to the lake-wide mean, and might be adequate if the primary interest is in time frames longer than a single day. While estimates of metabolism can vary greatly from one location within a lake to the next over periods of days, the challenges are not insurmountable. It can no longer be assumed that a single sonde location is an accurate representation of a lake at the daily time scale. Van de Bogart et al. (2012) suggest that using 4 sondes across the lake is necessary to provide reasonable confidence in daily whole-lake estimates and hence longer-term.

(ii) **No. of lakes to study**; typically any upscaling that occurs within studies simplifies the natural environment by mirroring key variable changes across an entire region that may not be reflected in individual lakes. The susceptibility of interconnected lakes to climate change effects is not uniform, and ideally lake districts should be studied as a whole (Cardille et al., 2009). Hanson et al. (2007) believe that sampling lakes across their full size distributions in a variety of regions may prove to be important for characterising lakes at the global scale. Recent work by Downing et al. (2006) estimated that 99% of the world's lakes are smaller than 0.1 km², and that these lakes account for 31% of the total lake surface area, making research on small lakes a vital part of the global picture.

(iii) **Lake sensitivity**; there are many analytical considerations to be made when estimating lake metabolism from high-frequency sonde data as these measurements, particularly dissolved oxygen, are often noisy (Figures 3.8 & 3.25). Although there is a basic understanding of what controls this variability over multiple timescales within the literature (e.g. Hanson et al., 2006), there is a need for analytical solutions to help separate variation caused by physical and chemical processes from biological processes that affect metabolism (Staeher et al., 2010). An assumption central to calculating metabolism from O₂ diel is that respiration

measured during night-time is used to represent respiration during daylight hours, which is masked by the signal for primary productivity. However, small-scale studies investigating respiration in ponds with dense phytoplankton communities indicated higher respiration during daylight hours (Sadro et al., 2011; Karakaya, 2011). This implies that the current method using a 1:1 ratio may be underestimating daytime respiration and thus affect primary productivity measurements. The extent to which this occurs in the context of lakes and what to do about it needs consideration. Other issues of data sensitivity concern uncertainties associated with calculating the air-water exchange term. Most literature uses wind speed as a proxy of turbulence on the lake surface to calculate piston velocity (k) and state that a relationship between wind and k should be established for each lake due to local conditions, but this is often difficult to achieve due to lack of local, established meteorological stations. Ideally, analytical methods and/or techniques should be made that enable continuous estimation of k (Staeher et al., 2010).

Despite the assumptions and uncertainties associated with using a sonde based 'free-water' approach to determining metabolic rates in lakes, its relative ease of application, data quality and high temporal resolution will continue to make the technique a suitable method for determining the magnitude and variability in metabolic rates in lakes. Application of a common protocol on measurements and data analysis will hopefully improve our ability to compare metabolic rates, understand the importance of different drivers, and the importance of lakes for carbon storage and release globally (Cole et al., 2010; Staeher et al., 2010; Hanson et al., 2008; Van de Bogert et al., 2007).

4.8 CONCLUSIONS

There is significant progress being made each year to better our understanding of lake metabolism, especially as technology for measuring lake metabolic processes continues to develop. This is the case for lakes such as Rostherne Mere and Tatton Mere, where unattended monitoring has enabled lake productivity to be measured, near uninterrupted, for ~18 months, for the first time. Previous research at these meres has been mainly limited to nutrient studies examining their eutrophic history through sediment cores, diatom analysis and short term enclosure studies (e.g. Moss et al., 2005; Carvalho, 1993; Walker, 1987; Davison et al., 1985; Nelms, 1984).

However despite the greater recognition of the importance of lake water quality in regions such as Europe through the EU Water Framework Directive, which can have a major impact on the C-dynamics of a lake, the majority of studies into lake metabolism are focused on boreal zone lakes (e.g. Sobek et al., 2003, 2006; Algesten et al., 2004). This trend is beginning to change, however, as although the overall C-storage potential of temperate, eutrophic lakes may not be as high as in the boreal zone (typically as a result of the sheer abundance of lakes in many regions) there is a growing shift towards understanding the metabolism of lake regions or lake groups as the global climate begins to change. As a result, regionally integrated carbon budgets are becoming more widely investigated (e.g. Anderson et al., 2013; Buffam et al., 2011) and high-resolution monitoring projects have been formed with collaboration between numerous research institutions creating networks from national to continental and global scale (e.g. GLEON <http://www.gleon.org>, GLOBOLAKES <http://www.globolakes.ac.uk>, NETLAKE <https://www.dkit.ie/netlake> and UKLEON http://www.ceh.ac.uk/sci_programmes/water/uk-lake-ecological-observatory-network).

This study has highlighted that intensive, unattended lake monitoring is achievable, but to succeed on a larger scale requires investment in people and technology. The UKLEON (UK Lake Ecological Observatory Network) project has begun to connect 11 lakes, of various trophic status and mixing regimes, across Northern Ireland, north Wales, NW England and central Scotland through standardised equipment, both in-lake and meteorological, and the data collection method in an attempt to forecast lake behaviour, the effect of meteorology on the fate of carbon within lakes and understand the level of regional coherence in lake response on sub-seasonal timescales. Advancements within the UKLEON projects on the methods employed in this study include permanent surface water pCO₂ sensors and the installation of an automatic winch system for sonde measurements through the entire water column at regular intervals (i.e. every hour). Although projects such as UKLEON and others are data intensive, they provide the prospect of significantly furthering our knowledge of lake functioning and the potential impacts of a changing climate.

The awareness of the importance of lakes within the terrestrial landscape has increased significantly over recent decades; mostly as a result of our improved

understanding of lake function. When compared to other components of the C cycle, lakes can be efficient at both processing and storing allochthonous and autochthonous OC in a long term sink (Tranvik et al., 2009; Cole et al., 2007; Downing et al., 2006). However estimates of their current levels of productivity and storage potential are varied, often spatially and temporally constrained and difficult to upscale to larger lake regions. To date the majority of lake research has been focused on arctic and boreal lakes, which tend to be DOC-loaded and net heterotrophic. In particular eutrophic and hypertrophic lake systems are often overlooked, despite their abundance and importance across Europe and other temperate zones.

This project has attempted to address this research gap by showing that eutrophic lakes are an important component of the C-cycle. Stratifying, eutrophic lakes in particular bury a high percentage of C assimilated within the water column, due to persistent anoxia within the hypolimnion, as a result of strong stratification. As a result, C mineralisation rates in such systems are typically lower than those experienced in more oxygenated, generally better mixed shallow lakes. This assertion is based upon an intensive, high frequency approach that provides data on C-fixation, loss and burial for over 18 months, in an attempt to reduce the errors associated with calculating a lake C balance based on extrapolation of seasonal data. This project has not only shown that this method of high-intensity monitoring provides a valid and robust dataset, but has enabled two eutrophic lakes to be assessed in near unparalleled detail.

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