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The summer nutrient dynamics of Bosherton lakes,
Pembrokeshire, and the potential impacts of future climate and
policy change

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policy change

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Abstract

Bosherston Lakes, Pembrokeshire have had problems with high nutrient concentrations and algal blooms, particularly in the stream-fed Eastern Arm, leading to the loss of *Chara* within the Eastern Arm. Management in the last 25 years has led to a reduction in external nutrient loading, but the impact of internal loading during the summer has yet to be properly assessed. The potential impacts of climate and policy change on the nutrient dynamics need to be accounted for to be able to efficiently manage the site in the future to preserve the important *Chara* habitat.

The streams and lake water were analysed for both Total Reactive Phosphorus (TRP) and Total Phosphorus (TP) and Nitrate and Total Nitrogen. The sediment in the lakes were analysed for TRP and TP only. Phosphorus release from sediments and the impact of future temperature changes were assessed through laboratory experiments.

It was found that the lakes are still suffering from elevated nutrient levels during the summer. The main source of phosphorus to the lakes in the summer is probably through internal phosphorus release from the lake sediments. The Eastern Arm is the most affected by internal loading. The main sources of nitrates to the lakes are from the streams and groundwater. It was found that phosphorus release increased with increasing temperature.

There are many uncertainties but future climate changes are likely to increase both nutrient and sediment loading and it is unlikely that the water quality in the Eastern Arm will improve sufficiently to accommodate *Chara*. The introduction of an NVZ is unlikely to be counterproductive in terms of reducing N:P ratios and will help decrease nitrate levels in the lakes and streams, some of which are nearing the safe drinking water limits.

Future management should target phosphorus loaded sediment entering the lakes in the winter and contributing to the phosphorus concentration in the lake water during the summer when phosphorus is released. The sediment traps in the catchment should be maintained or enhanced and weed cutting should be continued if it is found to have no adverse ecological effects.

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Abbreviations

EA – Environment Agency

OECD – Organisation for Economic Co-operation and Development

SEPA – Scottish Environmental Protection Agency

DEFRA – Department for Environment, Food and Rural Affairs

UKCIP – United Kingdom Climate Impact Programme

CCW – Countryside Council for Wales

IPCC – Intergovernmental Panel on Climate Change

UKTAG – United Kingdom Technical Advisory Group

NVZ – Nitrate Vulnerable Zone

SAC – Special Area of Conservation

PSU – Practical Salinity Unit

GQA – General Quality Assessment

SOP – Standard Operating Procedure

GPS – Global Positioning System

GIS – Geographical Information Systems

STW - Sewage Treatment Works

DO – Dissolved Oxygen

TN – Total Nitrogen

N – Nitrogen

P - Phosphorus

TRP – Total Reactive Phosphorus

SRP – Soluble Reactive Phosphorus

OrthoP – Orthophosphate

TP/Total P – Total Phosphorus

UE – Upper Eastern Arm

LE – Lower Eastern Arm

WA – Western Arm

CL – Central Lake

CA – Central Arm

TA – Transect sample point A

TB – Transect sample point B

1 INTRODUCTION

1.1 Bosherton Lakes – Site Description

Bosherton Lakes, a shallow marl lake system, are situated in Pembrokeshire in southwest Wales near the villages of Bosherton and Stackpole (Figure 1). The lakes are man-made and were created by the Cawdor family in the late 18th to the mid 19th century with a series of dams along the valley (Dyke and Leach 1979). Bosherton Lakes consist of the Eastern Arm, Central Lake, Central Arm and Western Arm (Figure 2). The lakes are separated from the sea by a dam, and overflow during the winter to spring at the Broadhaven overflow in the southeast corner of Central Lake (Figure 2).

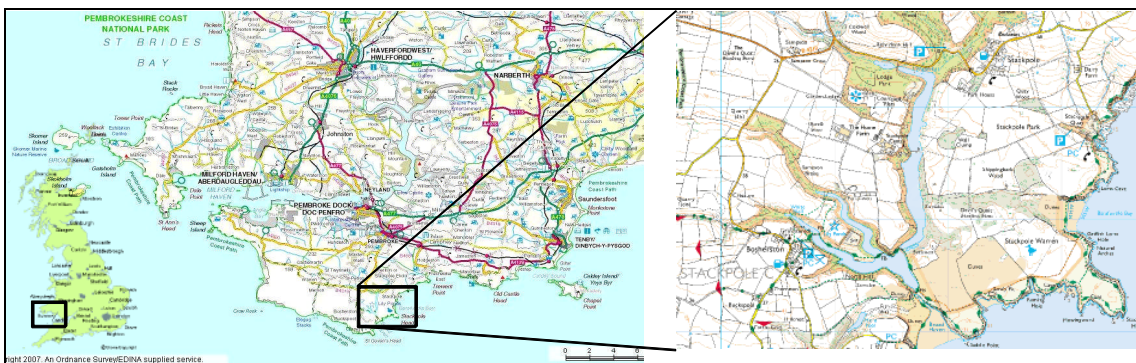


Figure 1: Location of Bosherton Lakes within the UK (Base maps from EDINA Digimap 2008)

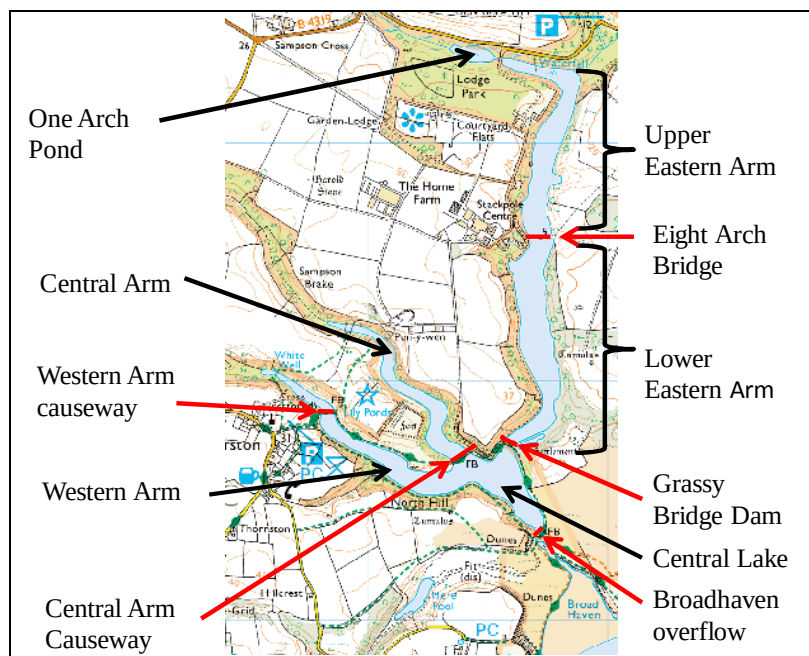


Figure 2: Bosherton Lakes and engineered features (Base map from EDINA Digimap 2008)

The lakes are a Special Area of Conservation (SAC) under the Habitats Directive. This is because of the habitat, which, under Annex 1, is classified as ‘Hard oligo-mesotrophic waters with benthic vegetation of *Chara* species’ and are characterised by low nutrients and very clear water (JNCC 2008). These types of habitat are scarce within the UK and the sites were selected because of good water quality and the rare or local *Chara* species (JNCC 2008).

1.2 Charophytes and eutrophication

Charophytes are sensitive to increased nutrient concentrations and the *Chara* species in Bosherton Lakes are found mainly in the Central and Western arms and to a lesser degree in the Central Lake. Davidson et al (2002) found that the peak diversity of the charophyte community in the Bosherton Lakes was around 1900, with a change to the more nutrient tolerant species occurring in the late 1900s and a loss of charophytes from the Central Lake in the 1940s. *Chara* beds were seen to re-colonise the Central Lake in the late 1980s, though there was little stability between years. These species include *Chara hispida*, the most abundant, with *Chara globularis*, *Chara virgata* and *Chara vulgaris* all present in smaller numbers. The white water lily, *Nymphaea alba* is also abundant in the Central and Western arms, the source of Bosherton Lakes’ other name, the Lily Ponds. The Eastern Arm, however, is characterised by different species of pond weed, including curled pondweed *Potamogeton crispus* and fennel pondweed *Potamogeton pectinatus* (JNCC 2008). There are also reed beds in the top end of the Eastern Arm with an abundance of the common reed *Phragmites australis*, with other species also present in varying amounts.

One of the main reasons why there is a difference in species composition between lakes is high nutrient concentrations leading to eutrophic conditions. Davidson et al (2002) and Rees et al (1991) suggest that an increased inflow of nutrient rich water from the Eastern Arm to the Central Lake was the cause of the decline of *Chara* in the Central Lake in the 1940s. They indicate that nutrient concentrations began to decrease after the 1960s, though they note that there is documentary evidence that suggests eutrophication was evident in the 1970s and 1980s (Haycock and Duigan 1994 cited in Davidson et al 2002). Davidson et al (2002) show that water quality has improved from 1990, with Total Phosphorus concentrations declining since 1981 in the Central Lake coinciding with the re-establishment of *Chara* in the late 1980s.

1.3 Previous management

The lakes are managed by the Countryside Council for Wales (CCW) and the National Trust. The improvement in the water quality in the Bosherton Lakes and re-establishment of *Chara* within the Central Lake has been due to several management techniques implemented since the 1980s. Phosphorus, as the main nutrient controlling eutrophication in shallow freshwater lakes, was targeted for management (Jiang et al in press).

Previous management of the Bosherton Lakes focused initially on external point sources. The Eastern Arm is fed by the Merion, Cheriton Brook and Castle Dock streams, which were thought to be the main inputs of phosphorus to the Bosherton

Lakes, specifically from the Stackpole sewage treatment works on the Cheriton Brook Stream. In the 1980s discharge from the sewage treatment works at Stackpole was diverted away from the lakes to the coast. There were, however, still problems due to storm overflows, and only in the late 1990s was a storage tank installed to reduce the overflow. Therefore the effects of the diversion have only been observed in the last decade (Bob Haycock, personal communication, email 08/08/08). The impacts of the sewage treatment works for the Merrion army camp are unknown and there are also many septic tanks and private sewers. There are also public toilets in the Bosherton car park.

Diffuse sources of phosphorus were then targeted; specifically phosphorus attached to soil that has been eroded from agricultural land. In 1994 silt traps were created at the bottom of the Cheriton Brook and Castle Dock stream to remove some of the sediment entering the lakes (Haycock and Duigan 1994 cited in Davidson et al 2002) and at the same time the lake after the One Arch Bridge was dredged (National Trust 2005).

It is well known that even though external management options have been implemented the recovery of shallow lakes with a history of high nutrient loading may be a long process due to internal sources of phosphorus. The recovery can be aided by management of the lakes internally.

There has been previous and ongoing management of the Bosherton lakes to control the internal release of phosphorus. In 1992 a pipe was installed to divert nutrient rich water from the Eastern Arm away from the Central Lake and directly to the outfall (Haycock and Duigan 1994 cited in Davidson et al 2002). The pipe is no longer in use as it was found that the water levels within the Central Lake were becoming too low without input from the Eastern Arm (Bob Haycock, personal communication, email 08/08/08). Weed harvesting has been undertaken since 1990. Phosphorus can be stored in vegetation and it can be co-precipitated with calcite on the *Chara*, removing this can reduce the deposition of phosphorus from external sources by 30% (Hilt et al 2006, Bob Haycock, personal communication, email 08/08/08). The Western Arm was recently (winter 2007) dredged, though this was to reduce sedimentation rather than nutrient removal (Bob Haycock personal communication – conversation 04/06/08) However, the dredging was successfully implemented and there has been re-colonisation by lake flora, including *Chara* and water lilies, though they may take a few more years to fully re-establish.

1.4 Nutrients

Even with the management of the lakes there are still problems with algal blooms and eutrophication, predominantly within the Eastern Arm. It has been hypothesised that this may be due to the internal loading of phosphorus from the lake sediments as there has been a reduction in external sources entering the lake. Phosphorus has been identified as the limiting factor for eutrophication so will be the focus of this study (Granéli 1998).

However, it is also possible that the N:P ratios have an important role in the process of eutrophication. Downing and McCauley (1992) state that oligotrophic lakes have a high

Nitrate Framework
Nitrate Vulnerable Zones
Focus map 2

Key:
 2006 Eutrophic Waters

1:50,000

0 0.5 1 2 Kilometers

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Figure 3: Proposed NVZ around Bosherton Lakes (Map from the Environment Agency 2007 within Welsh Assembly Government 2007)

1.5 *Climate change*

Carvalho and Kirka (2003) show that there is little knowledge on how climate change interacts with eutrophication pressures and on how climate change will impact on the recovery of eutrophic lakes.

The IPCC (2001) predict that there will be an increase in the net sea level of between 6–16cm (the mean of low and high estimates) in the 2020s and 14–74cm by the 2080s. This increase in sea level raises the risk of salt water intrusion into the Central Lake and Western Arm. *Chara* are sensitive to increases in salinity and therefore there is a need to assess the possibility of creating a freshwater refuge in the Eastern Arm, which has a good freshwater supply from the streams.

Previous research using the UKCIP02 scenarios has indicated that there could be an increase in the maximum summer temperature between 1.7 and 2.7°C, under the low and high 2050s scenarios (Hulme et al 2002). The same research has shown that it is likely that the summer windspeed by the 2050s will increase by up to 0.2m/s and average summer rainfall will decrease significantly. Miller (2007) predicted that during the summer/autumn there would be lower water levels lasting for longer in the Eastern Arm and a greater separation from the other arms. All of these changes could potentially impact on the nutrient dynamics of the Bosherton Lakes and the surrounding catchment during the summer.

1.6 *Aim*

There has been little recent research at Bosherton Lakes on the store of phosphorus within the lake sediments and the effects of internal loading in the summer. It is also recognised that nitrates and the N:P ratios may be important in the process of eutrophication and in causing cyano-bacteria blooms and that these need to be considered when assessing the nutrient status of the lakes. There is also a lot of uncertainty as to the effects of climate change on the nutrient dynamics of shallow lakes and how it may affect both internal and external sources and the *Chara* population in the future.

The aim of this project is to assess the summer nutrient dynamics in Bosherton lakes, Pembrokeshire, and the surrounding catchment, and the potential impacts of climate change in the context of preserving the *Chara* species and future management options.

1.7 *Objectives*

- To assess the phosphorus store within the sediments and therefore the potential for release to the lake water by measurement of the spatial variation of the Total Phosphorus (TP) and Total Reactive Phosphorus (TRP) concentrations within the lake sediments.
- To measure the TP and TRP levels in the streams, springs, and groundwater feeding the lake as well as the lake water to improve the understanding of external and internal sources of phosphorus to the lakes during the summer.

- To assess the impact of future temperature change on phosphorus release from lake sediments through laboratory controlled experiments and modelling.
- To measure the sources and levels of Total Nitrogen (TN) and nitrates within the streams, springs, groundwater and lake water to assess the potential impact of nitrates on the ecology of the lakes and the phosphorus release rates from sediments.
- To assess the impact of future climate and policy change on the lake water quality and the *Chara* population.

All of the objectives will be used to assess any possible problems for the *Chara* population in the future and to assess potential management options to help protect them.

2 LITERATURE REVIEW

The following review provides a more detailed insight into the habitat requirements of charophytes and the species within Bosherton Lakes, the hydrology and geology of the catchment, potential sources of nutrients, previous work on the lakes linked to the nutrient issues, and previous work surrounding climate change and its potential impact on shallow lakes.

2.1 Charophytes

It is important to understand the habitat requirements of charophytes to help to understand their spatial distribution within the Bosherton Lakes.

Bosherton Lakes is designated as a SAC partly due to the presence of charophytes, including *Chara hispida*, *Chara globularis*, *Chara virgata* and *Chara vulgaris*. Charophyte composition can be affected by several factors (Table 1). They are generally found in high alkalinity, shallow, freshwater lakes with low nutrient concentrations (Davidson n.d.). Some species, including *Chara globularis* can tolerate higher salinity, up to 7 PSU (Practical Salinity Units) (Blindow 2000). Some charophyte species can tolerate up to 20 m water depth (*Chara globularis*), whereas some are found only in shallower waters of up to 9 m depth (*Chara vulgaris*), with the optimum depth for most species present in Bosherton lakes being between 0 m and 10 m (Hass 1994 cited in Davidson n.d.). Charophyte growth increases with increasing temperature, with an optimum temperature range of 15–30°C (Andjus et al 1999).

Table 1: Factors affecting Charophytes (Davidson n.d.)

Variable	Effect	Nature of effect
Alkalinity	Direct	Via source of carbon
Salinity	Direct	Affects osmoregulation
Nutrient enrichment	Indirect	Via light climate
Water depth/turbidity	Indirect	Via light climate, wave action or water pressure
Temperature	Direct	On productivity and oospore germination
Sediment structure	Direct	Germination and substrate suitability
Water level change	Indirect	Light Climate, sediment desiccation

It was initially thought that phosphorus may be toxic to some charophytes when levels of Total Phosphorus reached 20 µg/l (Forsberg 1964 cited in Davidson n.d.). However, this has been disputed in recent years. Laboratory experiments have shown that charophytes could tolerate over 40 µg/l of Total Phosphorus (Blindow 1988;1992a in Davidson n.d.). It is now widely accepted that the affects of nutrients on charophytes are through indirect routes, such as the reduction of light due to algal blooms (Simons et al 1994 cited in Davidson n.d.). It is difficult to state a set threshold level of phosphorus above which charophytes are affected. Table 2 shows thresholds according to Blindow et al (1992a) cited in Davidson (n.d.). However, Van de Berg et al (1999) state a

threshold of 300 µg/l of Total Phosphorus when charophytes are lost, and they return when levels fall below 100 µg/l.

Table 2: Total Phosphorus thresholds (from Blindow et al 1992a in Davidson n.d.)

Species	TP (µg/l)	
	Range	Median
<i>Chara hispida</i>	14-98	34
<i>Chara vulgaris</i>	12-270	25
<i>Chara globularis</i>	12-510	47
<i>Chara virgata (delicatula)</i>	12-70	26

2.2 Hydrology and Geology

It is important to understand the geology of the catchment as this can influence the hydrology and, along with the land use, can influence the potential for erosion. The hydrology of the Bosherton Lakes and the catchment is complex and needs to be explored to understand where nutrients may be entering the lakes.

The lakes and most of Merrion Stream are situated on carboniferous limestone, whilst Cheriton Brook and Castle Dock Stream drain predominantly through the Milford Haven sandstone (Figure 4).

The catchment is predominantly rural. Clews (2001) suggests that the predominant land use is pastoral agriculture, followed by arable agriculture and woodland. Clews (2001) also shows the contrast in land use between the three catchments of the Merrion, Cheriton Brook and Castle Dock streams. This land use survey was taken in 2000 and the percentages of arable and pastoral land may have changed in the last seven years. The Castle Dock catchment is predominantly woodland but is also influenced by a mixture of arable and pastoral land, though it has the smallest percentage of pastoral land of the three catchments. The Merrion catchment has the highest percentage of pastoral land and also the higher percentage of housing, roads and public amenity areas. The Cheriton Brook catchment has the highest percentage of arable land of the three catchments and the stream is surrounded by woodland. The headwaters of the Cheriton Brook navigate through the Cheriton or Stackpole Elidor village. The other villages in the catchment are Stackpole, Bosherton and Merrion, where there is an army base. There is also the Stackpole estate to the west of the Eastern Arm of Bosherton Lakes and St Twynells near the headwaters of the Merrion stream.

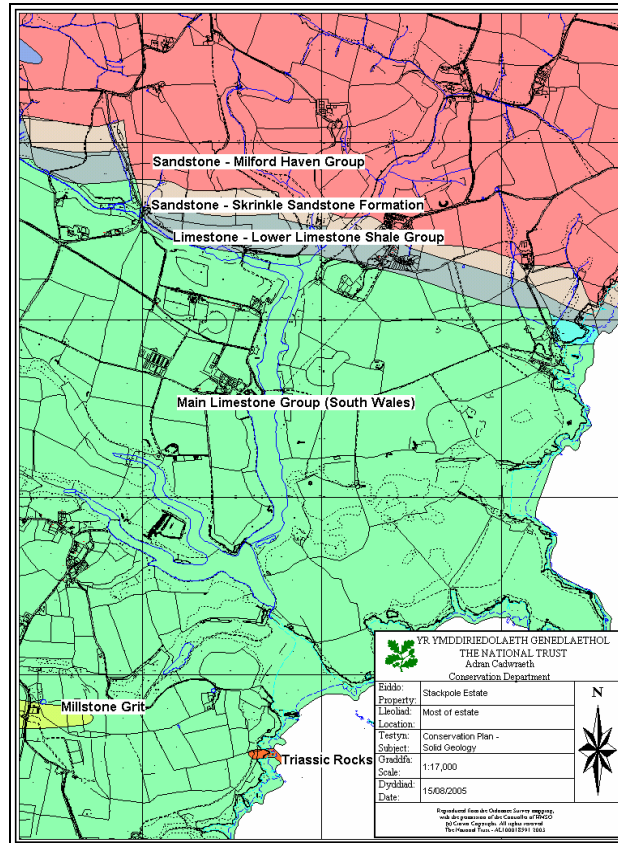


Figure 4: The geology of Bosherton (National Trust 2005)

The hydrology of the catchment is mainly controlled by the underlying geology, predominantly the karstic limestone. The Eastern Arm is fed by the Merrion Stream from the west, which can be dry along part of its course during the summer, and the Cheriton Brook stream, with its tributary, Castle Dock Stream, from the east (National Trust 2005). The Lower Eastern Arm is also influenced by runoff from steep valley sides on the east bank. The other lakes are fed predominantly by calcium-rich springs (Figure 5). According to a report by Howard Humphrey and Sons (1978), the Central Arm has four spring resurgences, the Western Arm has one and there are a couple in the Lower Eastern Arm. The Central Lake is fed with water from the Eastern, Central and Western Arms. All the lakes are well connected with groundwater apart from the Upper Eastern Arm which has an impermeable clay layer on the bottom of the lake (Vale 2007). There is a potential for turbulent and high velocity groundwater flow which has the potential to contain high concentrations of suspended sediment and pollutants (ENSIS Ltd. and DNR 2007). The direction of groundwater flow can be seen in Figure 6. It should also be noted that the groundwater catchment may be significantly different to the surface water catchment (Rees and Hinton 1993)

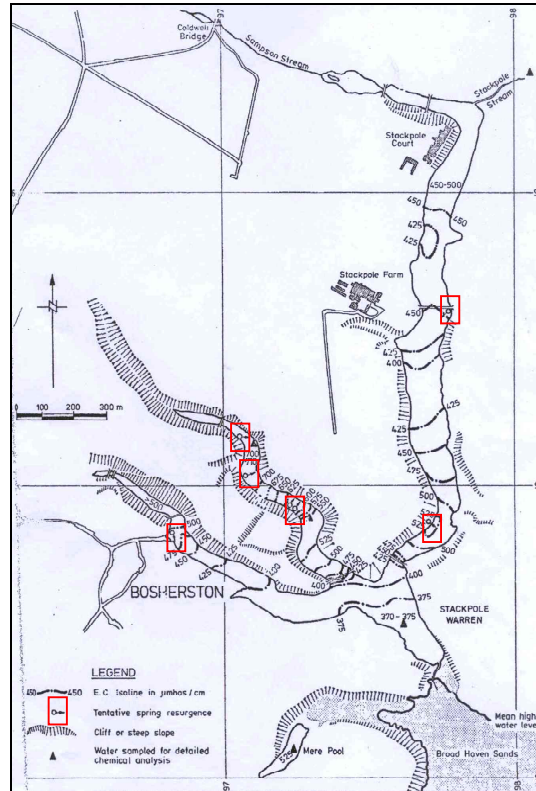


Figure 5: Electrical Conductivity survey (19/7/1978–20/7/1978) showing tentative locations of spring resurgences (red boxes highlight springs). Diagram from Howard Humphrey and Sons (1978)

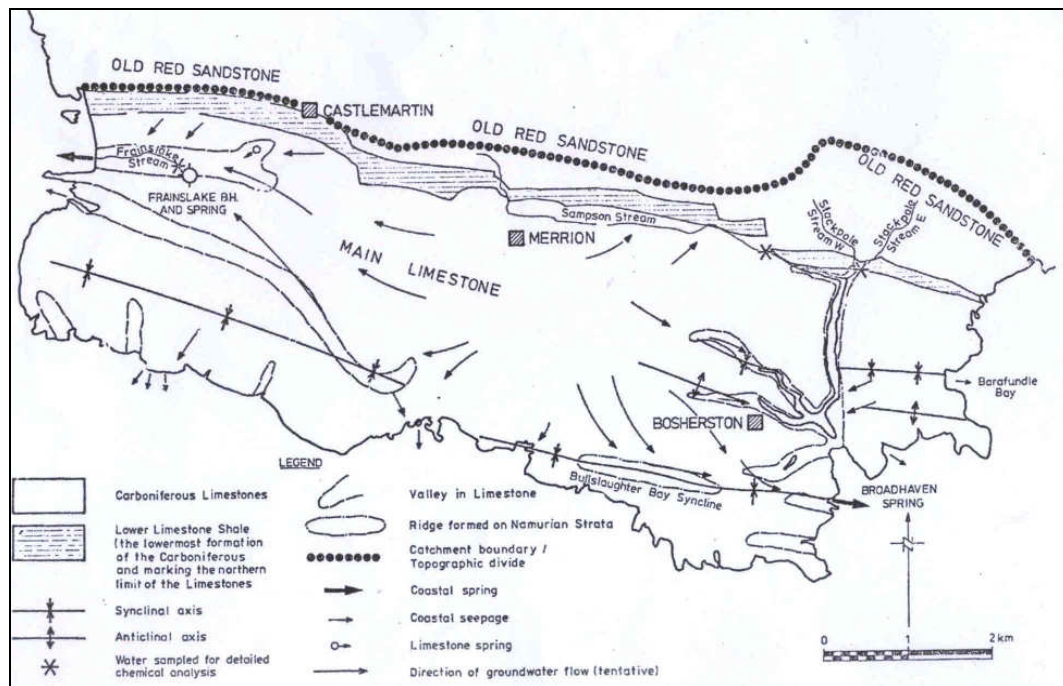


Figure 6: Groundwater flow direction in the Bosherton Lake catchment. Diagram from Howard Humphrey and Sons (1978)

The lakes have a maximum depth of 3.5 m in the winter, though there are large variations during the year, falling by up to 2 m in the summer, due to natural seepage and abstractions from the groundwater (National Trust 2005). There is significant seepage from the bottom of the all lakes apart from the Upper Eastern Arm, due to the impermeable clay layer. During the summer the Eastern Arm becomes separate water bodies as the water level falls below the weirs under the Eight Arch Bridge (Figure 2). It was originally thought that the Lower Eastern Arm and the Central Lake were separated in the summer by the Grassy Bridge Dam as the water fell below the level of the weir in the side of the dam. However, it was discovered that a submerged tunnel was present in the bottom of the dam allowing water to enter the Central Lake even in the summer (Rees and Hinton 1993). However, this has now been shut off. The Central Arm can become separated during the summer from the Central lake by the Central Arm Causeway (Figure 2).

The flushing rate of the lakes can have an important impact on the recovery of the lakes to nutrient loading. Spears et al (2007a) maintain that increased flushing at times of high phosphorus release from the sediment can help lakes to recover from eutrophication. The flushing rates of the Bosherston Lakes are summarised in Table 3.

Table 3: Retention times for Bosherston Lakes (from Rees and Hinton 1993)

Lake	Summer retention time	Winter retention time
Upper Eastern Arm	32-71 days	3-4 days
Lower Eastern Arm	60-72 days	7-9 days
Central Arm	9-15 days	<5 days
Western Arm	-	5 days
Central Lake	-	5 days

2.3 *Nutrient Levels*

There has been previous work on the concentrations of nutrients with the Bosherston Lakes. It is important when looking at the results of these investigations, and for understanding the results of this investigation, that it is clear what are high or low levels of nutrients for the streams and lakes.

Dyke et al (1978) considered an orthophosphate concentration of 0.01 mg/l (10 µg/l) to be normal for a marl lake. The UKTAG standards for a high alkalinity, very shallow lake (<3 m) are shown in Table 4.

Table 4: UKTAG standards for phosphorus in lakes (UKTAG 2008)

Type of Lake	Reference Level of Phosphorus		Class Boundaries			
			High		Good	
	Range	Type*	Range	Type	Range	Type
	Annual (geometric) mean ($\mu\text{g/l}$)					
High Alkalinity, Very Shallow (Northern Atlantic)	12-29	18	15-36	23	21-48	31

*The Type is the median value for that lake type.

The Environment Agency carries out General Quality Assessments (GQA) for rivers and groundwater based on an average of 12 samples per year. The standards for the assessment in terms of nutrients are shown in tables 5 and 6.

Table 5: GQA Total Reactive Phosphorus standards for rivers and groundwater

Classification for phosphate	Grade limit (mgP/l)	Description
1	0.02	Very Low
2	0.06	Low
3	0.1	Moderate
4	0.2	High
5	1.0	Very High
6	>1.0	Excessively High

Table 6: GQA Nitrate standards for rivers and groundwater

Classification for nitrate	Grade limit (mgNO_3/l)	Description
1	5	Very Low
2	10	Low
3	20	Moderately Low
4	30	Moderate
5	40	High
6	>40	Very High

Previous studies on Bosherton lakes, such as by Dyke et al (1978), found the highest concentrations of nitrates were in the top of the Western and Eastern Arms whereas the highest concentrations of orthophosphate were found at the top of the Eastern Arm. Dyke et al (1978) found that the sediment phosphorus levels were highest in the Eastern Arm, then the Central Lake, Western Arm and finally lowest in the Central Arm.

2.4 Nutrient Sources

The potential sources of nutrients to the lakes from the surrounding catchment need to be better understood should future management be required to reduce the levels of nutrients within the lakes. Sources of nutrients to the lakes can be from both external and internal sources, each will be considered separately.

2.4.1 External loading of nutrients to lakes

There are two main sources of nutrients to water bodies, point sources and diffuse sources that can vary in importance temporally and spatially.

➤ Point sources

The Bosherton Lakes catchment is predominantly rural with a few small settlements. Therefore the point sources within this catchment are few and scattered throughout the catchment. The sources include domestic septic tanks, farm drainage/courtyards and small sewage treatment works, in this case at Stackpole and Merriem Army Camp (Edwards and Withers 2007). However, the Stackpole Sewage treatment works is no longer discharging into the Cheriton Brook and should therefore have little impact on the nutrient levels within the lakes. The impacts of the other point sources, such as domestic septic tanks, are harder to control or quantify. Phosphorus from these point sources is generally in dissolved form (Edwards and Withers 2007).

➤ Diffuse sources

Point sources such as sewage treatment works can contribute a more steady input of nutrients. The diffuse sources of nutrients are generally from agricultural land and are influenced more by hydrological events. Diffuse pollution can reach water bodies by overland flow or infiltrate and reach them through groundwater. Agricultural practices can lead to increased runoff and erosion. This runoff can come into contact with faecal matter from animals as well as soil, both of which contain nutrients. Diffuse sources can contribute large amounts of phosphorus through surface runoff events, in both soluble and particulate forms. The main transport route for nitrates is generally within the groundwater.

2.4.2 Internal loading of phosphorus to lakes

It is well documented that internal loading from sediments within a shallow lake can hinder the recovery from eutrophication after the external sources have been targeted (Boström et al 1988; Søndergaard et al 2003). Internal phosphorus release is most important during the summer and is enhanced in shallow lakes by the high 'sediment surface: water column ratio': a high proportion of the water column is in contact with the sediment surface, whereas in deeper lakes there is more water above the surface to dilute the impacts of sediment phosphorus release (Pettersson 1998; Søndergaard et al 2003).

Phosphorus can enter the lake in soluble form in the water and be adsorbed onto the sediment through several mechanisms, such as the uptake onto inorganic molecules, mainly through sorption of inorganic P with iron oxides (Boström et al 1988). The phosphorus concentration within sediments is generally higher towards the surface (Granéli 1998; Pettersson 1998).

The phosphorus can also enter the lake attached to sediment suspended in the water which is deposited on to the lake bottom when the velocity falls as the river enters the lake. Clews (2001) showed that there was sediment suspended in all three streams entering the Upper Eastern Arm. Clews (2001) suggested that the Cheriton Brook contributed the most sediment to the lakes (Table 7), with the least sediment coming from the Merrion stream, even though it had the highest discharge.

Table 7: Sediment Loads (from Clews 2001)

Mean Sediment Load tonnes/Ha/Year		
Merrion Stream	Cheriton Brook	Castle Dock
0.02	0.12	0.06

The author then relates this to the land use, stating that the Cheriton Brook catchment has the highest percentage of arable land.

The amount of loose sediment within the lake can be seen in Figure 7. Holman et al (2007) state that the thickest layer of loose sediment is found within the Lower Eastern Arm, Central Lake and the lower Western Arm. The sediment is shallower in the Central Arm and Upper Eastern Arm. The authors also found thick sediment in areas downstream of the Eight Arch Bridge and Grassy Bridge Dam. There were also areas of thin sediment possibly showing the positions of hydraulically active fissures. Two such areas are towards the east shore of the Central Arm, near the causeway, and in the middle of the Western Arm.

Rees (1989) previously studied the sediments within Bosherton Lakes. The author notes that the TP concentrations were highest in the Lower Eastern Arm, at 1.38 mg/g, decreasing in order of Upper Eastern Arm 1.25 mg/g, Central Lake 1.05 mg/l, Western Arm, 0.61 mg/g and the Central Arm 0.14 mg/g. Rees (1989) goes on to state that the sediment TP concentration in a eutrophic lake is between 0.61 and 3.42 mg/g, with only the Central Arm having a value typical of a mesotrophic lake. This decrease in sediment TP is linked to a matching decrease in detrital clays and iron oxides and an increase in calcium carbonate content. Rees (1989) believes that the sediments in the Eastern Arm and Central Lake are saturated with phosphorus, meaning little is adsorbed onto the sediment and the phosphorus builds up in the pore water and is readily available to be mixed with the water column above. This sediment survey was undertaken before much of the management linked to removing phosphorus from the lakes began.

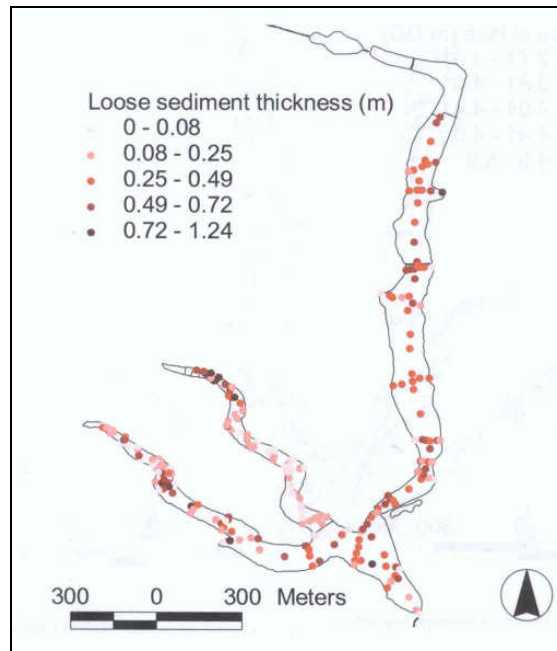


Figure 7: Loose sediment thickness across Bosherton Lakes in March 2007 (Holman et al 2007)

2.5 *Factors affecting phosphorus release from sediment*

It has been established that internal loading of phosphorus from sediments is potentially a large source of phosphorus in the lakes in the summer months. It is therefore important to understand the mechanisms that can cause release of phosphorus from the sediment to the overlying water.

There is a large amount of literature on the factors and processes affecting phosphorus release and retention within lake sediments. Furumai and Ohgaki (1989) state that the reactions controlling the release and uptake of phosphorus are not irreversible and should be considered together. Phosphorus is found in different forms within the sediment and the total amount of phosphorus may not represent the amount that is available for release, it can depend on how it is bound (Holtan et al 1988 cited in Granéli 1998). It is important to note that different factors can influence phosphorus release in different lakes. The shape and size as well as the flushing rate and the history of nutrient loading all have to be considered (Boström et al 1988). For example, Søndergaard et al (1999) found that there was a shorter period of phosphorus release in the summer in lakes with low lake water phosphorus concentrations (<0.1 mg/l), with release occurring only in July and August, and that there was little seasonal variation at levels below 0.05 mg/l. Boström et al (1988) conclude that temperature, pH and redox potential, linked to the iron content of the sediment, are the most important factors.

➤ *Temperature*

Temperature can have an important affect on the release of phosphorus, mainly through indirect effects such as increased biological activity (Boström et al 1988). Spears et al (2007a) concluded that temperature may have played an important role in a mid summer

peak of phosphorus and high phosphorus release rates. They note that temperature increases microbial activity which mineralises the organic phosphorus pool and also decreases oxygen which increases phosphorus release. Jensen and Andersen (1992) found that in a study of four shallow lakes in Denmark temperature explained approximately 70% of the seasonal variation. They also indicate that temperature can have a direct influence through the stimulation of overall mineralisation.

➤ ***Redox/ Iron***

When conditions are anoxic phosphorus can be released when iron (III) is reduced to iron (II) (Søndergaard et al 2003). Shallow lakes can be oxic and inhibit the release of phosphorus, though Lee et al (1977), Boström et al (1988) and Jensen and Anderson (1992) have demonstrated that phosphorus release still occurs in oxic lake water. Kisand and Nõges (2003) found that it made no difference if the sediment conditions were oxic or anoxic in a calcareous and macrophyte dominated lake. Redox potential is related to the presence of iron within the sediment that can encourage release of phosphorus. Søndergaard et al (2003) suggested that there is an iron dependent threshold affecting the ability of phosphorus to bind to the sediment.

➤ ***CaCO₃***

There has been less research into the effects of CaCO₃ on phosphorus release and it has been shown that in areas with hard water, iron is of less importance (Golterman 2001 cited in Søndergaard et al 2003). High pH and temperatures increase co-precipitation of CaCO₃ and phosphorus and can occur constantly if high pH and CaCO₃ content are maintained, decreasing the phosphorus content of the lake water (Boström et al 1988).

➤ ***pH***

High pH can reduce the ability of phosphorus to bind to iron and other compounds, increasing the release of phosphorus, though in lakes with a high CaCO₃ content it can increase co-precipitation of phosphorus with CaCO₃ (Boström et al 1988).

➤ ***Wind***

Wind can cause re-suspension of sediments particularly in shallow lakes and lead to increases in phosphorus concentrations within the water (Koski-Vähälä and Hartikainen 2001). Wind across a lake can lead to an increase in phosphorus release but it may be dependent on the amount of mixing caused and the chemical properties within the lake (Koski-Vähälä and Hartikainen 2001; Søndergaard et al 2003) Wind can also help maintain a gradient for phosphorus release due to mixing (Boström et al 1988; Pettersson 1998).

➤ ***Biological***

Submerged macrophytes can release oxygen from the roots increasing redox uptake of phosphorus onto iron and therefore increasing the retention (Søndergaard et al 2003). Submerged macrophytes remove phosphorus from the sediment and the surrounding

water and release very little throughout the growing season, though they can release phosphorus during senescence (Granéli and Solander 1988).

Charophytes stands decompose slower than other macrophytes and therefore prolong the retention of nutrients within the biomass and can also lower the potential for re-suspension of sediment (Kufel and Kufel 2002). Charophytes use bicarbonate and precipitate calcite bound phosphorus removing this from the water column, they also oxygenate the sediment and can reduce the potential of iron bound phosphorus release (Kufel and Kufel 2002).

Fish and benthic invertebrates can disturb sediment and increase release of phosphorus from the sediment pore water to the lake water column, and bacteria within decomposing organic matter may also influence the release of phosphorus (Boström et al 1988; Søndergaard et al 2003). The lakes are used for recreational fishing, by permit only, and contain roach, pike, tench, perch and eel.

➤ *Nitrates*

There are conflicting views as to whether the presence of nitrates inhibits or stimulates release of phosphorus from the sediments. High nitrate concentrations increase iron bound phosphorus sorption by maintaining a high redox potential, though this conclusion is based on mass balance studies that are not always accurate (Boström et al 1988; Jensen and Andersen 1992). However, Uhlmann and Paul (1994) found through experiment that nitrates can help to reduce phosphate release again by maintaining an oxidized state of iron, they however state that this is only the case in the presence of excess nitrates. It is also possible that nitrates may enhance the release of phosphorus by stimulating bacteria that can reduce iron or microbial activity (Boström et al 1988; Jensen and Andersen 1992).

2.6 *Phosphorus release experiments*

It has been shown that temperature is one of the important factors controlling the release of phosphorus from sediments within the lakes. With increasing temperatures predicted in the future it is important to be able to predict how it will influence the release of phosphorus from sediments. Experiments have generally been used to investigate the impact of temperature on phosphorus release rates.

Spears et al (2007a) used intact cores and overlying lake water with air bubbled through the water to maintain oxic conditions. They took water samples from the water near to the sediment at the beginning of the experiment and at the end of 72 hours, the length they determined was needed to reach equilibrium. They found that the sediment in Loch Leven was still capable of significant phosphorus release and that there was continual release and probably little adsorption during the experiment.

Kim et al (2003) used 6 cm diameter by 45 cm long reactor tubes with air-dried undisturbed sediment samples. They were air-dried to avoid affecting the release rates. They were incubated for a week and were covered to avoid oxygen entering the overlying water. They found that the release of phosphorus increased by five times

between 2 and 25–35°C. They also found that increasing dissolved oxygen decreases the release rates, and release is lowest at pH 8, increasing with more acidic or alkaline waters. The average water depth in the one area studied was 7–9 m and the sediments contained 490–1860 mg/kg of phosphorus.

Kim et al (2004) performed two experiments to study the release rates. The first was forced where they used 200 g of wet sediment with 500 ml of distilled water which were shaken at 20°C for 48 hours. The second method (natural) is the same as in Kim et al (2003). They showed that under natural conditions the release rate is influenced by temperature, keeping the DO at 0.5 mg/l. The release rate increased from 15.8 mg/m² week at 2°C to 115.8 mg/m² week at 35°C.

3 METHODOLOGY

The Bosherton Lakes and surrounding catchment will be assessed in terms of the summer nutrient status, sources of nutrients and in particular on the potential for internal loading of phosphorous from sediments. To do this the streams and lake water will be analysed for phosphorus and nitrogen and the phosphorus concentration in the lake sediment will also be measured. The phosphorus release from sediments and the impact of the temperature changes predicted in the future will be assessed through laboratory experiments

3.1 Lakes

The lakes need to be assessed for their nutrient status both within the water and sediment. The water nutrient status can be compared to the external sources of nutrients in the streams and groundwater and the sediment phosphorus concentration is needed to assess the amount available for internal loading of phosphorus. Due to time and sampling constraints, samples were collected between the 3rd and 5th June at 200 m intervals along a transect down the centre of each arm of the lake, augmented by one random transect across each arm with samples taken equidistant of the centre sample site (Figure 8). All sampling sites can be seen in Figure 9.

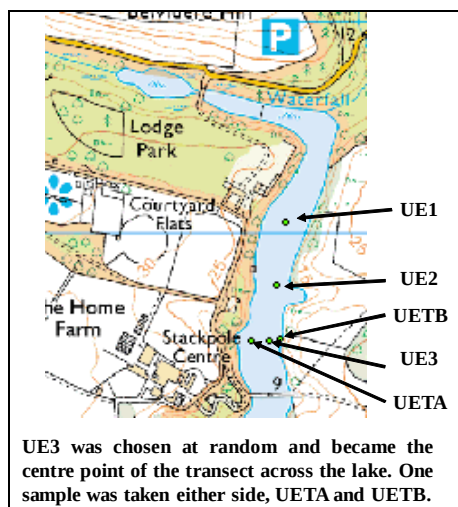


Figure 8: Sampling transects for the lake water and sediment survey on 3rd to 5th June 2008

3.1.1 Collection of sediment samples

Where possible a sediment sample was collected from all sites shown in Figure 9. However, the Central Arm of the lake had a very dense covering of charophytes and it was not possible to retrieve sediment samples in most areas. Instead samples were retrieved from areas of bare sediment (Figure 10). Water samples were collected from two sites above the charophytes for comparison with those over the bare sediment.

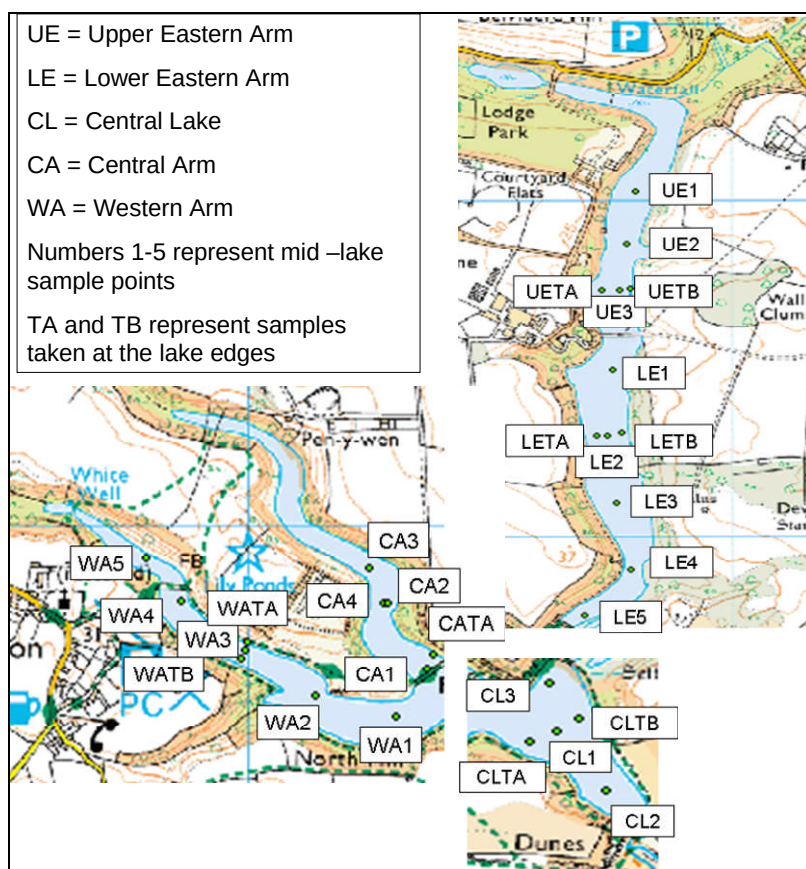


Figure 9: Lake water and sediment sampling points for the survey undertaken between 3rd and 5th June 2008



Figure 10: Bare sediment amongst dense charophytes in the Central Arm

Disturbed sediment samples were collected using a detachable sampler of 20 cm length by 10 cm width with a flap valve (Figure 11). This sample size is believed to be sufficient as the top 20 cm contains the highest concentration of phosphorus which has been shown to decline with depth (Dyke et al 1978). This was connected to a pipe with a valve just above the sampler. The valve is closed when the sampler is pushed into the sediment and opened before the sampler is removed from the sediment. The water in the pipe is released through the valve opening when the sampler is retrieved preventing the water from flushing out the sediment sample. Samples were emptied into labelled plastic bags and stored in a cool box on the boat before being refrigerated.

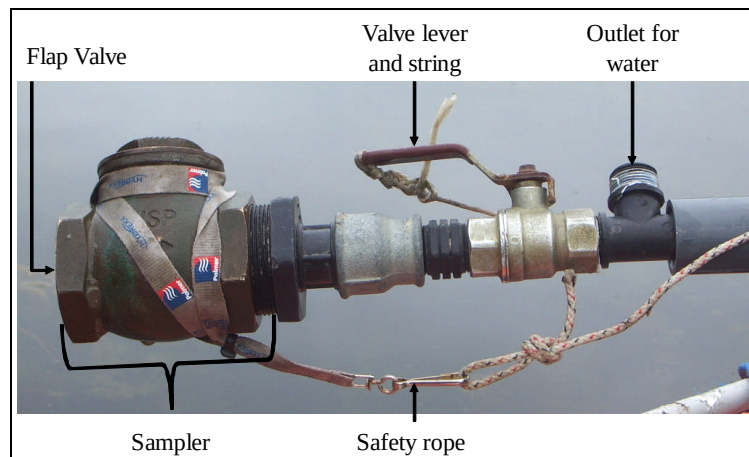


Figure 11: Sediment sampler

3.1.2 Collection of water samples

At each sampling site, one 125 ml water sample was collected from both the surface (10 cm depth) and the bottom of the lake close to the sediment/water interface, to see if there was a difference between the surface water phosphorus concentrations and those near the sediment. Only two small 125 ml water samples and one sediment sample were collected at each site due to the storage capacity of the boat and cool box. A good spatial coverage of sites throughout the lake system was thought to be the highest priority rather than replication of samples, though this will be taken into consideration during the analysis.

3.1.3 Total Phosphorus and TRP

Total Reactive Phosphorus (TRP) was analysed as this is biologically available and is the method used by the EA for their General Quality Assessments, though they record it then as orthophosphate. TRP will be used to avoid confusion with orthophosphate, which is generally used to represent Soluble Reactive Phosphorus (SRP) (Haygarth and Sharpley 2000).

TRP was determined by using ammonium molybdate and sulphuric acid as reagents and measured at 880 nm on a spectrophotometer (Appendix A). The standards used were 4, 8, 12, 16, and 20 $\mu\text{g/l}$. Due to the low amounts of TRP within the samples a 4 cm cell was used in the spectrophotometer to produce a more accurate measurement and the standard amounts of reagents were divided by five to decrease the dilution of the colour in the samples. As there were small amounts of phosphorus within the samples there was still adequate amounts of reagent (5 ml of ammonium molybdate and 1 ml of sulphuric acid) to react with the phosphorus.

Total Phosphorus was chosen to show the total amount of phosphorus within the water and to allow the proportion that is reactive to be determined. Unfiltered samples were used to understand the total amount of phosphorus within the water.

Total Phosphorus was determined using a potassium persulphate microwave digestion, based on a method by Eiseneich et al (1975) and the absorbance was measured at 880 nm using a spectrophotometer (Appendix B). The standards used were 25, 50, 100, 150, 250, 350 and 500 µg/l.

The sediment samples were air-dried before analysis; oven drying was not used as this may affect the phosphorus content of the samples. The standard operating procedure (SOP15), based on the British Standard BS7755: Section 3.6:1995, was used for determining TRP, using sodium hydrogen carbonate solution at a pH of 8.5 (Appendix C). The solution was analysed using a spectrophotometer at an absorbance level of 880 µm using a 1 cm cell and standards of 1, 2, 3, 4, 5, 6 and 7 mg/l.

The samples were analysed for Total Phosphorus using the standard operating procedure (SOP 17), based on the British Standard BS7755: Section 3.13:1998 (Appendix D). The phosphorus is extracted with a hydrochloric/nitric acid mixture and microwave digestion. The solution was analysed on a spectrophotometer at an absorbance of 880 µm with a 1 cm cell and standards of 1, 2, 3, 4, 5, 6, and 7 mg/l.

Replicates were analysed to ensure that any anomalous results due to the equipment or methods are identified. The preparation of sediments for analysis and the limitation of batch size in the microwave and autoclave meant that the sediment samples could only be analysed twice. Total Phosphorus in the lake water samples were only analysed twice and the TRP in the lake water samples were analysed once.

3.1.4 Total Nitrogen and Nitrate

Nitrate and Total Nitrogen were measured in the lake water samples only not in the sediment samples.

Nitrate as NO₃ was measured as this is biologically available. Total nitrogen was measured to allow the proportion of nitrate to be known within the Total Nitrogen present.

Total Nitrogen and nitrate were measured on a Burkard Series 2000 Segmented Flow Analyser using samples filtered through a 0.45 µm filter. The full method for the analysis of nitrates and nitrogen can be found in Appendix E and F.

3.1.5 Water quality data

A Hanna HI-9828 Multi-Parameter meter was used to measure redox potential, electrical conductivity, total dissolved solids, salinity, dissolved oxygen (DO), pH and temperature at the surface and bottom of the lake at each site. A secchi disk was also used to record the turbidity as well as the water depth. However, it was later found that the meter had not been calibrated for measuring redox potential, electrical conductivity, total dissolved solids and salinity, these results were therefore discarded.

3.1.6 GPS

The distance between sampling points on the lake was measured using a Garmin GPSMAP 60C. The positions of the lake sampling sites were recorded using a Trimble Geo Explorer CE Series GPS. Recordings were taken for at least 10 minutes on the carrier mode at one second intervals. The GPS readings were then differentially corrected to give a locational accuracy of around 30-50cm.

3.2 Streams

To understand the external load of nutrients to the lakes during the summer it is important to measure nutrients in streams and groundwater. However, due to time constraints and accessibility to boreholes only stream data could be collected, though available groundwater data were provided by the Environment Agency.

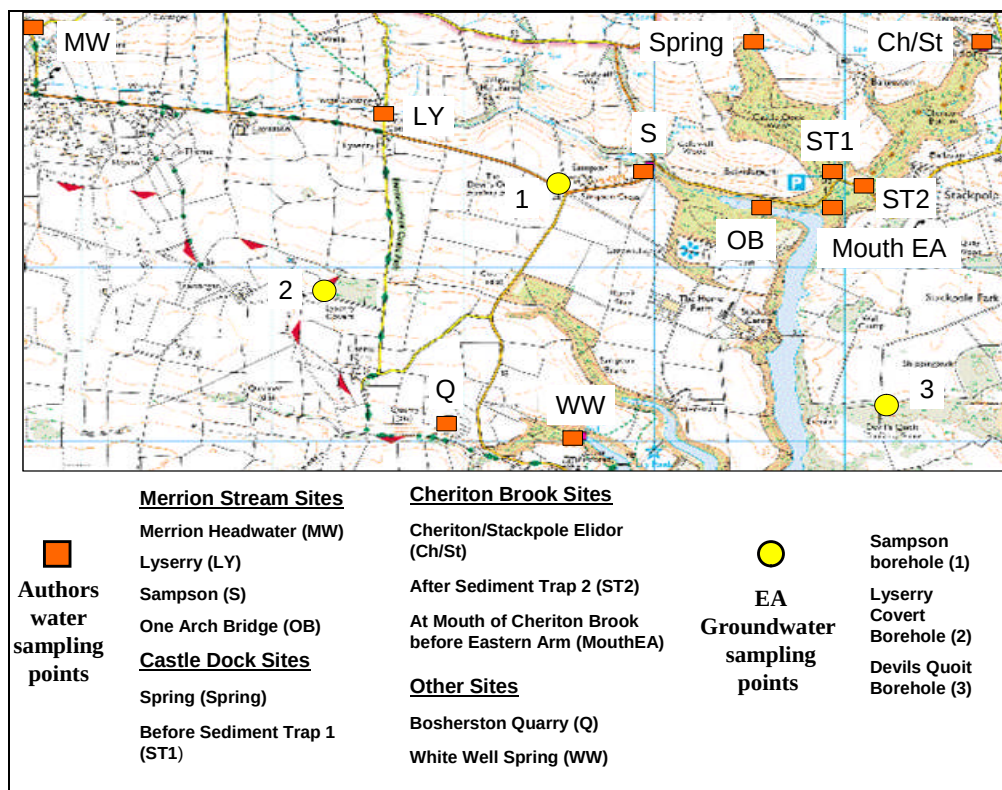


Figure 12: Sampling sites for water samples collected on June 11th and July 8th 2008 and Environment Agency groundwater sampling sites.

The stream sites were chosen to represent the whole catchment (Figure 12) subject to access constraints. The sources of the Merrion (Warren House), Cheriton Brook (near Cheriton church) and Castle Dock (Spring) streams were sampled. Cheriton Brook was sampled just after the sediment trap that is after the Stackpole sewage treatment works. The Castle Dock stream was sampled just before the sediment trap. The stream was sampled again after the confluence with Cheriton Brook where it enters the Upper Eastern Arm. The Merrion stream was sampled at the One Arch Bridge at the entrance to the Eastern Arm after the One Arch Pond. There were also samples at the bridge near

Sampson Cottage and Forge Cottage. It was planned to take a sample downstream from the Merrion sewage treatment works but the stream was running dry. The white well at the top of the Western Arm was sampled as well as Bosherton Quarry as this is primarily groundwater fed so could give an indication of the groundwater quality.

3.2.1 Collection of water samples

Triplicate water samples were collected from each site on the 11th June and 8th July 2008 to assess spatial and temporal differences. The water samples were collected in one litre plastic bottles to minimise the surface area of plastic in contact with the water sample to prevent reaction with any phosphorus within the sample. The samples were collected with as little sediment disturbance as possible. The samples were refrigerated and analysed within a week of collection. Triplicate samples were collected at each site so it was considered to be unnecessary to analyse replicates of these samples as a mean could be determined from the triplicates.

3.2.2 Total Phosphorus and TRP analysis

The stream water samples were analysed for Total Phosphorus and TRP using the same methods as for the lake water samples (section 3.1.3)

3.2.3 Total Nitrogen and Nitrate analysis

Total Nitrogen and nitrate were determined for the stream water samples, using the same method as for the lake water samples (Section 3.1.4). Three replicates were analysed for total nitrogen and nitrates.

3.2.4 Discharge and phosphorus load

To calculate the discharge of the stream sites, the width, depth and velocity were recorded at each site. Depth profiles were created by taking measurements every 10 or 20 cm across the stream depending on its width. Velocity measurements were taken at the same places as the depth measurements using a Kant LEA Miniflow-Probe 265-3 at all but one of the stream sites. The discharge at these sites was calculated using the mean velocity-area method. At the One Arch Bridge site a weir was used to calculate the discharge. This was calculated using the equation for a v-notch weir with a constant of 0.6 and where H is the head over the weir:

$$Q = 0.6(8/15)\tan(\theta/2)\sqrt{2g}(H^{5/2})$$

(Howden 2008 personal communication, conversation, 28/07/08, adapted from Shaw 1994, p124)

The bucket method was used to measure the discharge at the spring site at the headwaters of Cheriton Brook.

3.3 *Phosphorus Release Experiments*

Three experiments were set up in order to assess whether future predicted temperature changes may influence the amount of phosphorus that is released from the sediment. Two experiments had still water conditions and one disturbed conditions, to simulate any possible disturbance of the sediment by wind or through bioturbation.

Eighteen sediment samples were collected from one area in the Central Lake (CL3 on Figure 5). These samples were air-dried and then blended to produce one sample to use in the experiments. Acrylic cylinders of 11 cm by 6 cm were filled with 30 g of the blended sediment sample and 100 ml of deionised water was carefully added over the sediment with minimal disturbance. Deionised water was used to produce a good gradient for release and to keep the pH consistent as this is known to affect release rates. The tubes were sealed to reduce evaporation and to restrict the amount of oxygen in the tubes to simulate the anoxic conditions of the sediment in the lakes (Rees 1989). Three tubes were set up for three different temperatures, 5°C, 12°C and 20°C and placed on shakers and left for 48 hours. For comparison three tubes at each temperature were also left undisturbed for 48 hours. A further three tubes for each temperature were set up and left for two weeks to assess whether further phosphorus has been released. Due to time constraints and the limited amount of sediment collected it was decided that it was not possible to take samples from the tubes at regular intervals but only at the end of the time frames. Further to this, taking samples at regular intervals would also mean that the water level would have to be topped up each time affecting the concentration of phosphorus.

At the end of each experiment water samples were syringed from the bottom of the water column without disturbing the sediment. They were filtered through a 0.45 µm filter to ensure little sediment was in the sample as it is important to only record the concentration of the phosphorus that has transferred to the water column, thereby sampling only the Soluble Reactive Phosphorus (SRP). The samples were then analysed for both Total Phosphorus and SRP using the same methods as for the lake water samples previously. Total Phosphorus was analysed to see if there were larger fractions of inorganic or organic phosphorus being released, SRP is dissolved inorganic phosphorus.

4 RESULTS AND ANALYSIS

The results will be separated into five main sections. The first two are the results for phosphorus and nitrogen from the current study. In each section the lake results, from samples collected on the 3rd-5th June, will be discussed first followed by the stream results, from samples collected on the 11th June and July 8th. The third section will explore the results of the TN:TP ratios calculated from the data collected during 3rd–5th June. The fourth section shows results of further water quality data collected during the same period. The last section will analyse Environment Agency data from 1979 to see if any noticeable trends are apparent in terms of nutrient loading to the lakes.

4.1 *Phosphorus*

4.1.1 *Phosphorus in the Bosherton Lakes sediments*

The results for the Total Reactive Phosphorus (TRP) and Total Phosphorus (TP) are shown as the mean of two analyses of the same sediment sample to allow for errors within the method and equipment. The top 20 cm of the sediment within Bosherton Lakes will contain phosphorus that entered the lake before many of the management techniques were installed to reduce phosphorus loading. The results data can be found in Appendix G. The prefixes to sample locations indicate the ‘arm’ of the lake, e.g. CA is Central Arm. The number indicates the location on the transects down the middle of the lake, the suffixes TA or TB refer to the samples at the edges of the lakes. Sample locations can be seen in Figure 9; Section 3.1.1

The results show that there is a store of phosphorus within the sediment of varying concentrations throughout the lake system. Generally the phosphorus content within the sediments decreases with increasing distance from the stream inflows. The highest concentrations of both TP and TRP are found in the Upper Eastern Arm and the lowest concentrations are found in the Central Arm (CA2 and CA3) and upper Western Arm (WA4) (Figures 13 and 14). Looking at just the transects that move down the middle of the lakes the TP concentrations within the Upper Eastern Arm decrease down the lake towards the Lower Eastern Arm (Figure 15). Only UE1 and UE2 have concentrations above 0.61 mg/g, which are typical for a eutrophic lake as defined by Rees (1989). The highest TP concentration in the Lower Eastern Arm is LE1, the first site below the Upper Eastern Arm. The second highest concentration is LE5 at the bottom of the Lower Eastern Arm before the Grassy Bridge Dam. The lowest TP concentration is at LE4. The TP concentrations within the sediment in Central Lake decrease towards the Broadhaven overflow, with the highest concentration at CL3 and the lowest at CL2. The Central Arm sediment TP concentrations decrease with increasing distance from the Central Arm Causeway. The same is true for the Western Arm with increasing distance from the Central Lake up to the causeway, apart from WA3 that is slightly higher than WA2. The highest TP concentration in the Western Arm is at WA5 above the causeway. The top of the Western Arm (WA5) has a much higher concentration of TP than the rest of the Western Arm (Figure 13).

The Lower Eastern Arm has a high concentration of TP within the sediment although TRP concentrations are a lot lower than the Upper Eastern Arm. The Western and

Central Arms have the lowest concentration of TRP within the sediment, apart from the CATA sampling point, which is in a much deeper area near the right bank just beyond the causeway, which has a high concentration compared with the rest of the lakes excluding the Upper Eastern Arm (Figure 14).

The sediments taken from near the edges of the lake, on the transects across the width of the lake, contain higher amounts of TP than those from the middle of the lake in the Lower Eastern, Western and Central Arms (Figure 15). In the Central Lake and Upper Eastern Arm the sediments from the edges contained slightly lower TP concentrations.

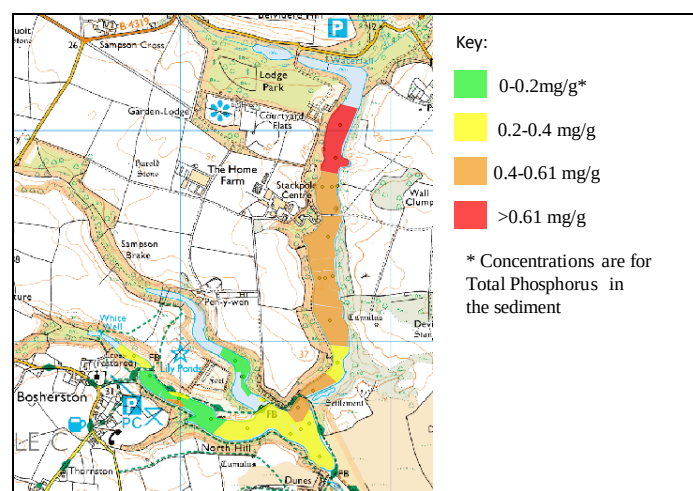


Figure 13: Total Phosphorus in the lake sediment. The red areas indicate sediment concentrations typical of eutrophic lakes (Rees 1989). The samples are an average of the top 20 cm of sediment and were collected between 3rd and 5th June 2008

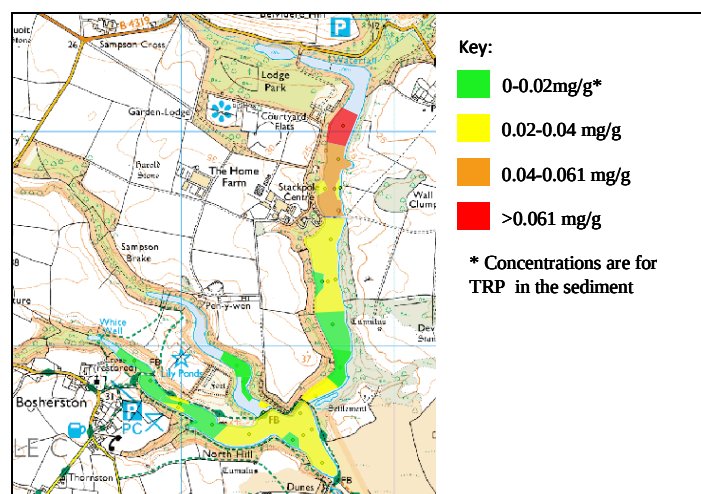


Figure 14: Total Reactive Phosphorus in the lake sediment. The samples are an average of the top 20 cm of sediment and were collected between 3rd and 5th June 2008)

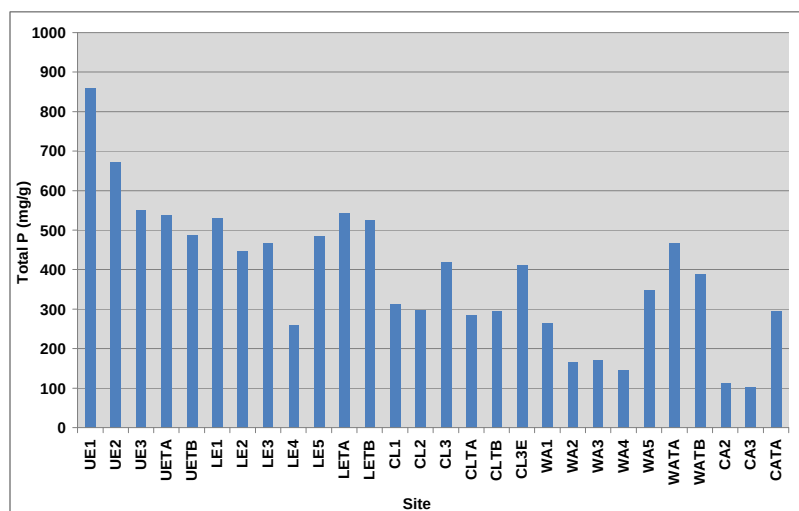


Figure 15: Total Phosphorus in the lake sediments ordered from the Upper Eastern Arm, down to the Central Lake, into the Western Arm and finally the Central Arm, including both middle and edge of lake samples. Samples were collected on 3rd to 5th June 2008 and are the average of the top 20 cm.

4.1.2 Phosphorus release experiments from lake sediment

Of the four experiments only the two week undisturbed samples produced results that had similar phosphorus levels within all three replicates. The 48 hour results may not have had enough time to reach equilibrium. As sediment from the lakes was used it was not possible to make sure that all samples had the same amount of phosphorus, or the same fractions, e.g. inorganically or organically bound phosphorus. This may explain why there was little replication between samples in the experiment. The following analysis will focus on these results.

Table 8 shows that there seems to be a trend of increasing phosphorus release with increasing temperature. The lowest concentration of both SRP and TP (<0.45) is at 5°C and the highest at 20°C.

Table 8: Average phosphorus concentrations of triplicate samples at each temperature from disturbed sediment samples after two weeks under still conditions.

Temperature °C	SRP µg/l	Total P (<0.45) µg/l
5	12	52
12	135	227
20	199	349

However, Figure 16 shows that the variation between the triplicate samples at each temperature increases as the temperature gets higher, as shown by the larger standard error. Figure 16 shows that the changes in Total Phosphorus release are statistically significant but that the increase in SRP release between 12°C and 20°C is not statistically significant.

Overall the SRP concentration increases by a factor of 16 from its original concentration between 5°C to 20°C. Overall the TP (<0.45) concentration increases 7 times its original concentration from 5°C to 20°C.

At the lower temperature (5°C), only 24% of the TP (<0.45) is SRP; however, this percentage rises to 60% at 12°C and 57% at 20°C. Therefore, whilst there is an increase in the amount of SRP released, it seems that the proportion of SRP to TP stays reasonably steady as the temperature increases from 12°C to 20°C. The increase in the proportion of SRP released between 5°C and 12°C may be showing the effect of temperature on the release of iron-bound phosphorus that is influenced by temperature increases (Spears et al 2007a).

Looking at the change in TP (<0.45) concentrations between 12°C and 20°C, as this is closer to the range of water temperatures recorded in the lake and is statistically significant compared to the SRP concentrations, it can be shown that there is an increase of 15 µg/l with every 1°C increase.

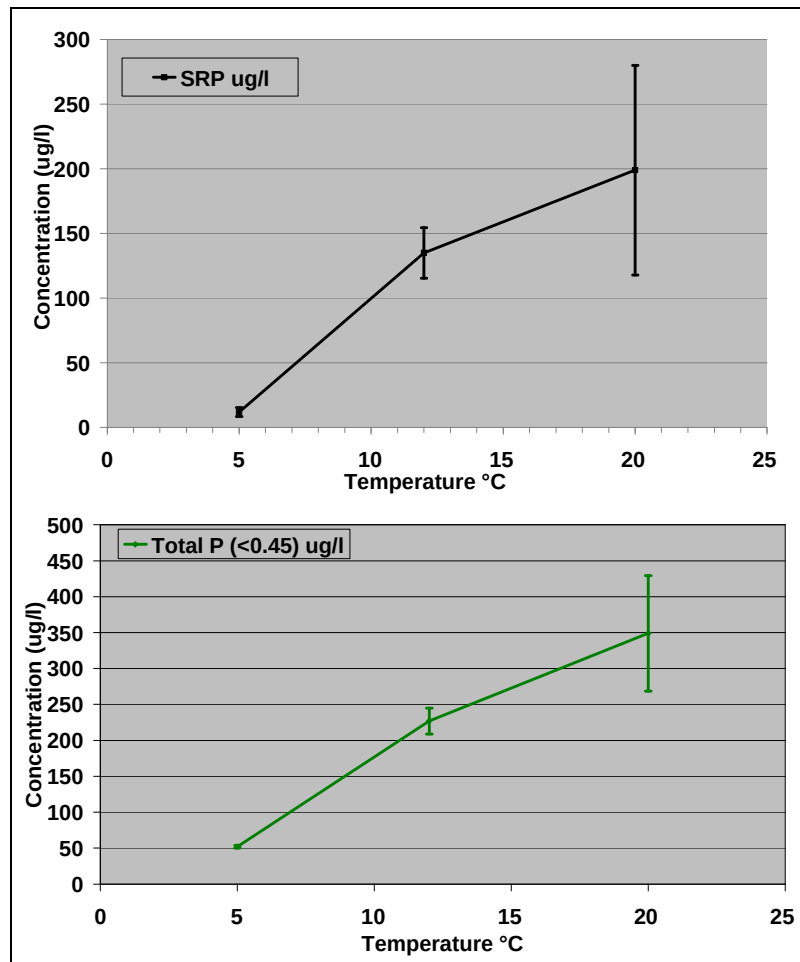


Figure 16: Average SRP and TP release with increasing temperature from disturbed sediment samples after two weeks under still water conditions. Error bars show the standard error.

4.1.3 *Phosphorus in Bosherton Lakes water*

It was found that at the time of sampling there was no TRP within the lake water, both at the bottom and surface of the lake. The only sites to register any TRP were in the Upper Eastern Arm (Surface and Bottom UE1 and Bottom UETA) and the Lower Eastern Arm (Bottom LE4 and Surface LE1), as well as one Central Lake site (Surface CLTA). These sites only registered between 1 and 5 µg TRP/l (0.001-0.005 mgTRP/l). These small amounts may indicate that there is more TRP within the Eastern Arm than elsewhere in the lake. However, these are very small amounts, there is an error of about 0.3µg/l from the spectrophotometer and the results are far below the lowest standard used of 40µg/l. Results data for both TRP and TP in the surface and bottom water samples can be found in Appendix H.

There were, however, adequate amounts of Total Phosphorus within the water and it is these results that will be further analysed. It can be seen from figures 17 and 18 that there is little difference between the TP concentrations in the bottom and surface water samples. Within the bottom samples there were a couple more sites (six sites bottom; four sites surface) that had above 45 µgTP/l, therefore there is little indication that there are higher levels within the bottom than surface samples. For both the bottom and surface samples the highest concentrations were found within the Upper and Lower Eastern Arms and the Central Lake, with the lowest concentrations within the Central and Western Arms. This may indicate that the Eastern Arm is more affected by inflow of TRP from the streams, shown by higher surface levels, and higher phosphorus release, shown by the highest bottom concentrations.

To get an overall picture of the TP concentrations within the lake (during the sampling period between 3rd and 5th June) the average of the surface and bottom samples was calculated. Figure 19 shows that the highest concentrations (>45 µgTP/l), as with the sediment TP concentrations, are found in the Upper Eastern Arm and the Lower Eastern Arm. The majority of sites within the Upper Eastern Arm, Lower Eastern Arm and Central Lake have TP concentrations above 30 µgTP/l, with only three sites below 30 µgTP/l, the UKTAG 'good' standard. The lowest concentrations are at the top of the Western Arm and in the Central Arm. There is an isolated spot in the Central Arm at site CATA, where the concentration is above 30 µgTP/l, coinciding with the higher sediment phosphorus levels at this site.

Looking at only the transects that progress down the middle of the individual arms of the Bosherton Lakes it can be seen that the highest concentration within the Upper Eastern Arm is at the top, at UE1, decreasing to UE2 and then rising again at UE3. Moving into the Lower Eastern Arm the concentration of TP continues to fall until LE4 where it doubles and then falls again to LE5, though not as low as the TP concentration at the top of the Lower Eastern Arm (LE1). The other side of Grassy Bridge Dam, in the Central Lake, the TP concentration increases very slightly, and then falls minimally as you move towards Broadhaven outflow. The concentration within the Central Lakes is the most uniform of all the sections of Bosherton Lakes. The lake continues unimpeded into the Western Arm where the TP concentration stays at a similar level to the Central Lake until WA2 where it falls and continues to fall with the lowest concentration at WA5, though there is a slight increase at WA4 (Figure 20). Within the Central Arm two

water samples were collected over the *Chara* beds, CA1 and CA4, and two were collected over bare sediment, CA2 and CA3. There is a decrease in the concentration of TP as you move away from the Central Arm Causeway, from CA1 to CA4. The two samples over the sediment have lower concentrations than CA1 but higher than CA4.

Looking at the transects that move across the width of the lake it should be noted that there seems to be higher concentrations of TP in the water at the edges of the lakes than at the corresponding sites within the middle of the lake (Figure 20), apart from in the Upper Eastern Arm and one site at the edge of the Central Lake that have lower concentrations. This generally agrees with the findings of higher sediment concentrations at the edges of the lakes compared to the middle, apart from in the Upper Eastern Arm and Central Lake.

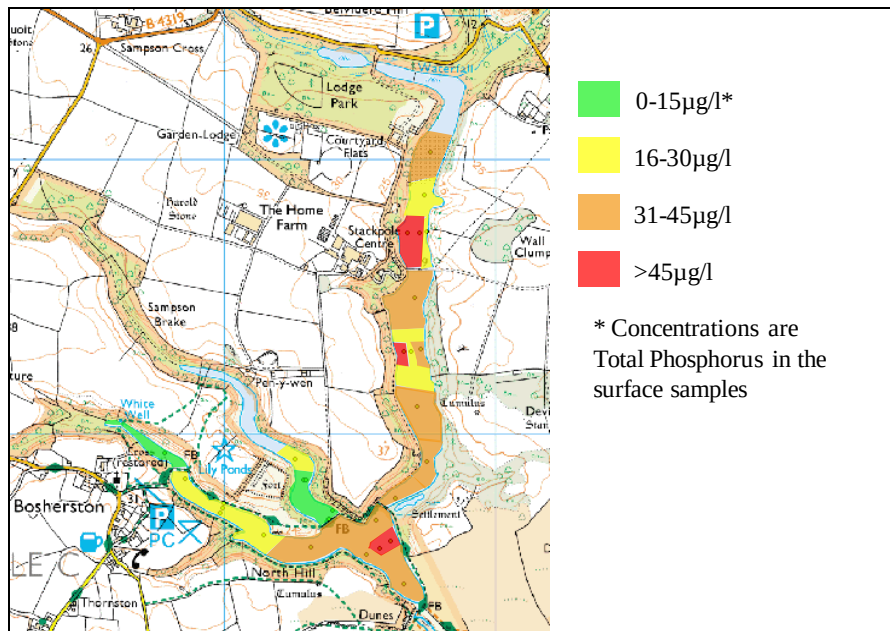


Figure 17: Total Phosphorus in the surface lake water samples taken between 3rd and 5th June 2008.

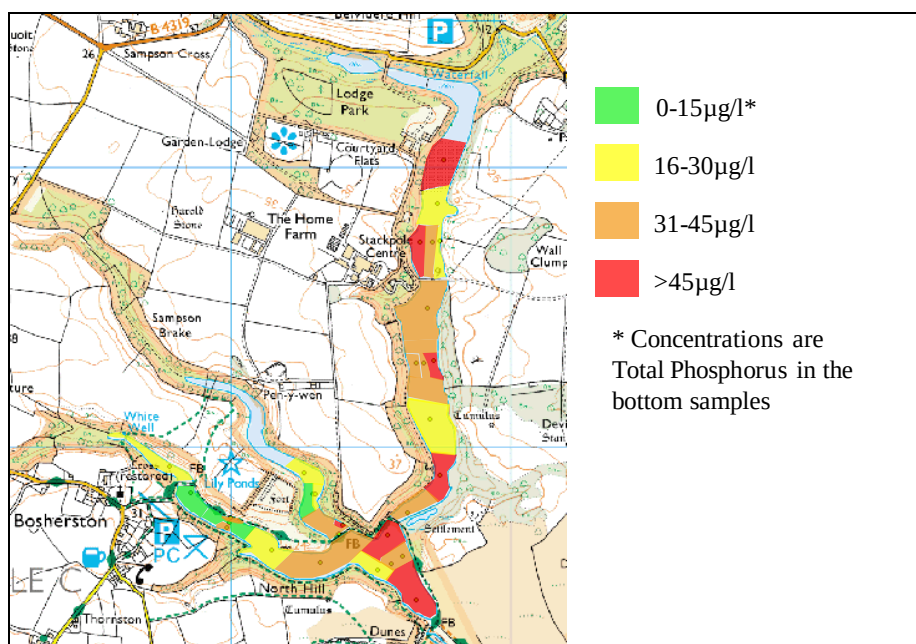


Figure 18: Total Phosphorus in bottom lake water samples taken between 3rd and 5th June 2008.

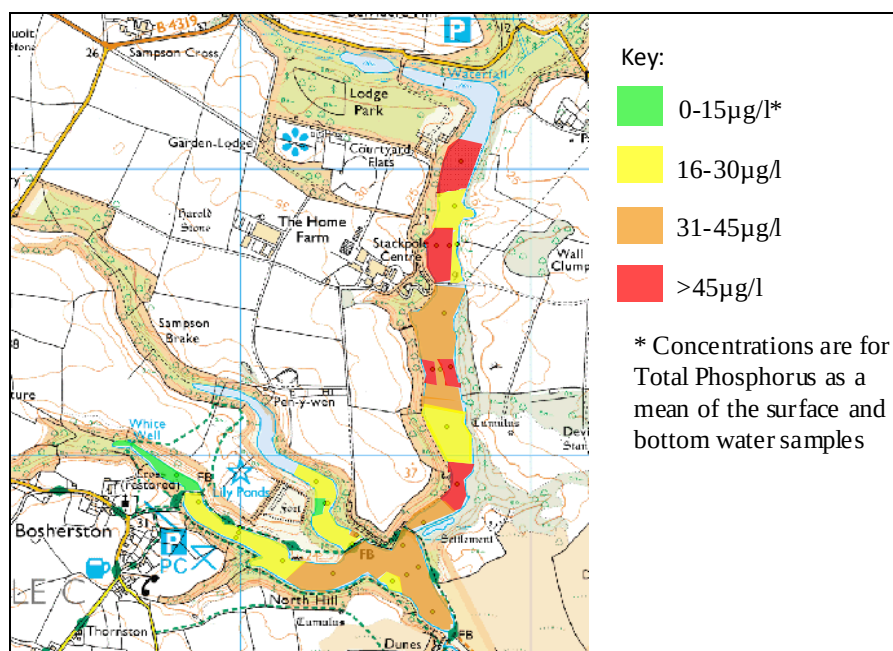


Figure 19: Mean of Total Phosphorus concentrations in the surface and bottom lake water taken between 3rd and 5th June 2008.

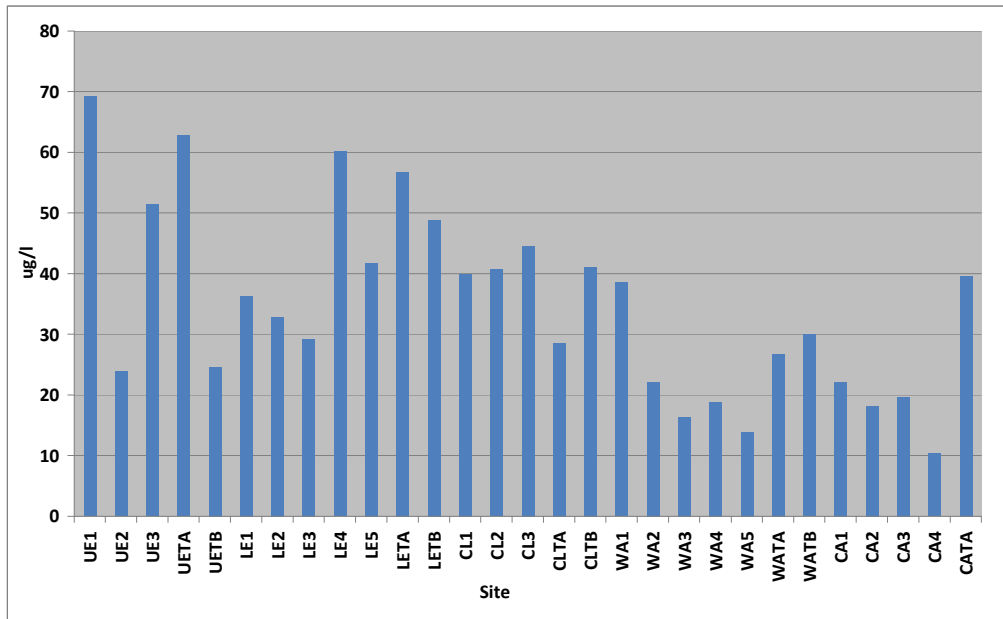


Figure 20: Mean of Total Phosphorus concentrations in the surface and bottom lake water, ordered from the Upper Eastern Arm, down to the Central Lake, into the Western Arm and finally the Central Arm, including both middle and edge of lake samples. Samples were collected between 3rd and 5th June 2008.

4.1.4 Phosphorus in the surrounding catchment - streams and groundwater

Unlike the lake water, there was enough TRP within the streams and groundwater to record. This analysis will focus on the TRP levels in the streams as this is what is used for the Environment Agency General Quality Assessments (GQA). However, the full results for both the TRP and TP levels within the streams can be found in Appendix I.

There were higher concentrations of TRP and TP in the samples taken on the 8th July 2008 than those taken on the 11th June 2008. This may be because there was a period of rainfall before the July samples were collected. The site at the headwaters of the Merrion (MW) had a large increase in TRP and TP on 8th July 2008 compared to the 11th June 2008 (Figures 21 and 22). Overall the general spatial pattern of TRP and TP concentration is the same apart from at the mouth of Cheriton Brook (Mouth EA) which on 11th June 2008 had a lower concentration than sites ST1 and ST2, at the mouths of Castle Dock stream and Cheriton Brook respectively, but a higher concentration on 8th July 2008. There were also higher concentrations at the headwaters of Castle Dock stream and at Lyserry on the Merrion stream.

However, to get a general idea of the TRP concentration for the summer of 2008 based on the two sets of data from the 11th June and 8th July 2008, a mean was calculated (Figure 23). The mean was then used to analyse the TRP levels using the Environment Agency General Quality Assessment standards (GQA). There is a Very High concentration of TRP found towards the headwaters of the Merrion stream at point MW (0.49 mg/l), this is before the Merrion sewage treatment works. The TRP concentration in the Merrion stream decreased to a Low level by the next sampling point downstream (Lyserry /Ly), and remains low before entering the Upper Eastern Arm. There is a High

concentration near the headwaters of the Cheriton Brook at point Ch/St (0.12 mg/l). The concentration along the Cheriton Brook decreases as with the Merrion, though to a Moderate, rather than Low level, by the next sampling point (ST2), with a concentration of 0.07 mg/l. The Castle Dock stream TRP concentration is Low at the headwaters, at 0.04 mg/l, but increases in concentration downstream, registering 0.06 mg/l just before the sediment trap (ST1). The level remains Moderate as the two streams (Castle Dock and Cheriton Brook) converge before entering the Upper Eastern Arm, with a concentration of 0.07 mg/l. The groundwater concentrations of orthophosphates from the Environment Agency data are Low or Very Low as are the TRP concentrations within the Bosherton Quarry, which is groundwater and rain fed, and at the White Well spring at the top of the Western Arm. The lowest concentrations of phosphates within the groundwater are at Lyerry Covert (0.009 mg/l), and in the Bosherton Quarry (0.007 mg/l) and White Well spring (0.01mg/l).

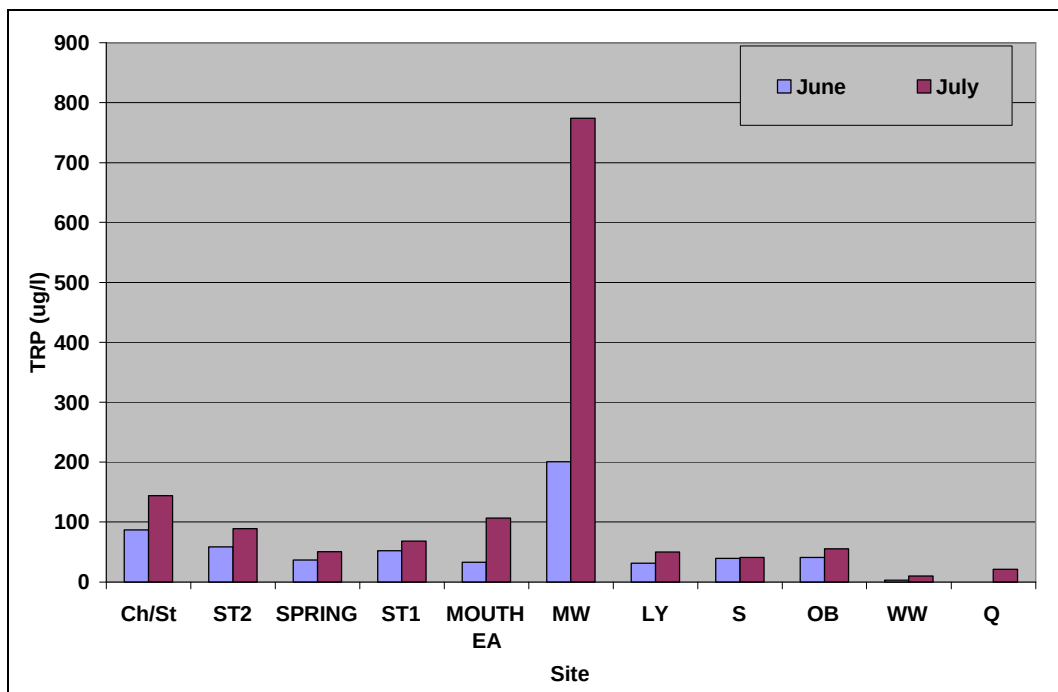


Figure 21: TRP concentrations in the streams. Samples were collected on the 11th June and 8th July 2008

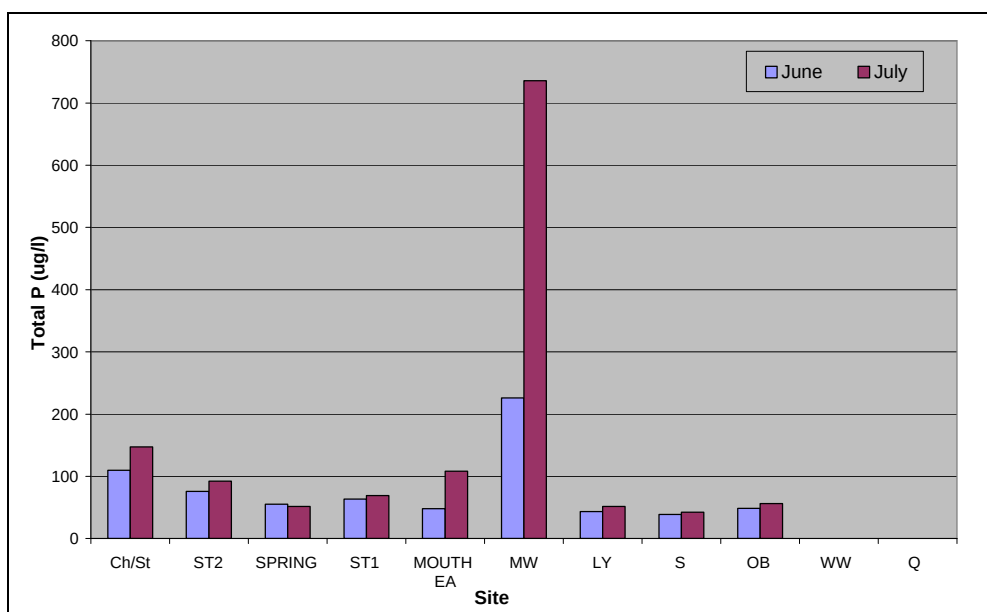


Figure 22: Total Phosphorus concentrations in streams. Samples were collected on the 11th June and 8th July.

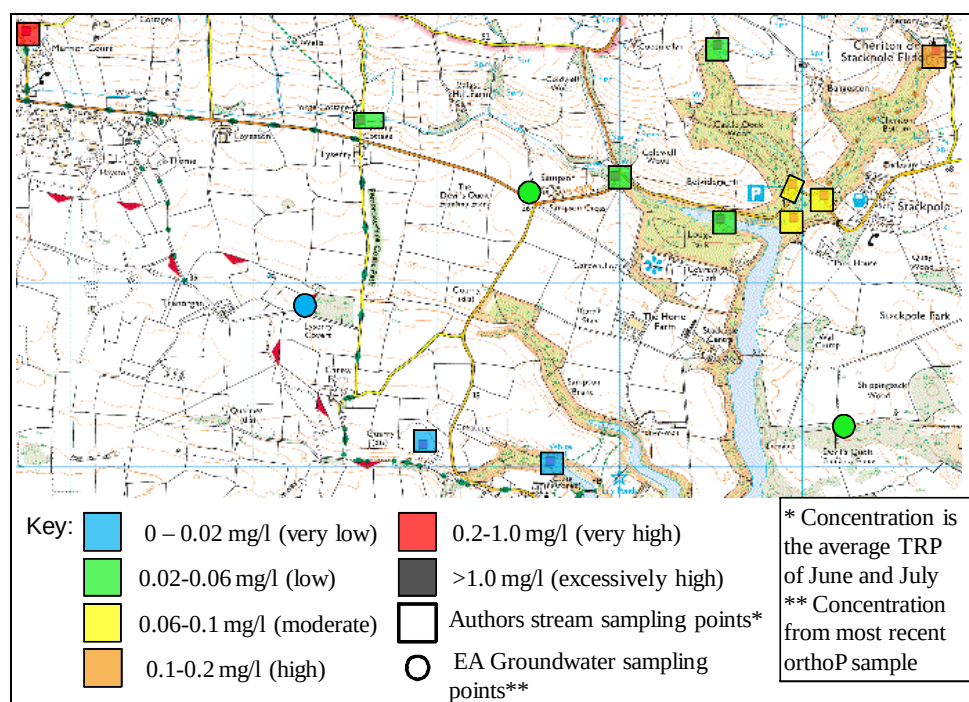


Figure 23: Mean TRP concentrations of stream samples collected on June 11th and July 8th 2008. The groundwater concentrations are the most recent orthophosphate concentrations from Environment Agency data, Lyserry Covert (13/11/02), Devils Quoit (29/11/06), Sampson (03/05/07).

4.1.4.1 *Phosphorus Loads*

Just considering the concentrations at certain stream locations, however, does not necessarily indicate the overall impact of the stream on the lake. The discharge needs to be accounted for as a section with low discharge but high TRP concentration may affect the river water quality less than a site with a lower TRP concentration but a higher discharge.

Table 9: Stream discharges calculated using the mean area-velocity method with spot velocity, width and depth measurements taken on the 11th June and 8th July 2008

Site	June (l/s)	July (l/s)
Ch/St	1.1	1.3
ST2	1.7	1.3
Spring	0.076	0.001
ST1	1.1	0.9
MouthEA	0.6	0.5
Sampson	8.6	4.9
Lyerry	0.3	0.2
Warren House	0.9	0.4
White Well	1.1	1
OB (One Arch Bridge)	16.9	11.3

Table 9 shows the discharge at the sites for 11th June and 8th July 2008. There is no outlet at the Bosherton Quarry so no discharge could be calculated. There are likely to be large errors in the velocity readings as the velocity was very low and it was difficult to generate a reading in many areas. Therefore, some areas may have lower velocities than in reality. The Castle Dock stream discharge increases downstream, which would be expected as the first reading was from a spring and the last from in-stream. The Cheriton Brook discharge increases or stays the same from the headwaters to the point before the confluence with the Castle Dock stream. The most obvious error within the results is the discharge at the mouth of the Cheriton Brook, after the confluence with Castle Dock stream. Here you would expect the discharge to increase, but it is lower than both the Castle Dock and Cheriton Brook discharges. The velocity is likely to be higher than was recorded at this site. The discharge generally increases downstream in the Merrion stream, apart from at Lyerry, but this may be because this point is just after the stretch of the stream that runs dry during the summer. There may be higher inaccuracies in the discharge measured at the mouth of the Merrion stream under the One Arch Bridge (OB) as a weir was used to calculate the discharge. There are errors in this as the constant used was for an average 90° v-notch weir and not for that specific weir. However, from personal observations, this site did have the largest discharge of all the sites and certainly had a larger discharge than the mouth of the Cheriton Brook.

Loads for TRP and TP were calculated by multiplying the discharge by the TRP or TP concentration. In detail TRP and TP loads for each site can be found in Appendix J. Figures 24 and 25 show the TRP and TP loads for 11th June and 8th July 2008. The loads are different between June and July but the overall spatial pattern is the same, therefore mean 'summer' 2008 loads were calculated from the data collected on the

11th June and 8th July 2008. The highest mean ‘summer’ loads are on the Merrion Stream at the One Arch Bridge (OB), Sampson (S) and Warren House (MW) sites (Figure 26). The lowest loads are at the White Well at the top of the Western Arm, the spring and at Lyserry. The Cheriton Brook stream contributes a larger phosphorus load than the Castle Dock Stream. Even though there is a low concentration of TRP and TP at the mouth of the Merrion stream, at One Arch Bridge, because there is a high discharge the contribution to the lake is higher than that from the Cheriton Brook and Castle Dock streams which have lower discharges but higher concentrations. Alternatively, the high load at Warren House at the headwaters of the Merrion stream is due to high phosphorus concentrations rather than a high velocity.

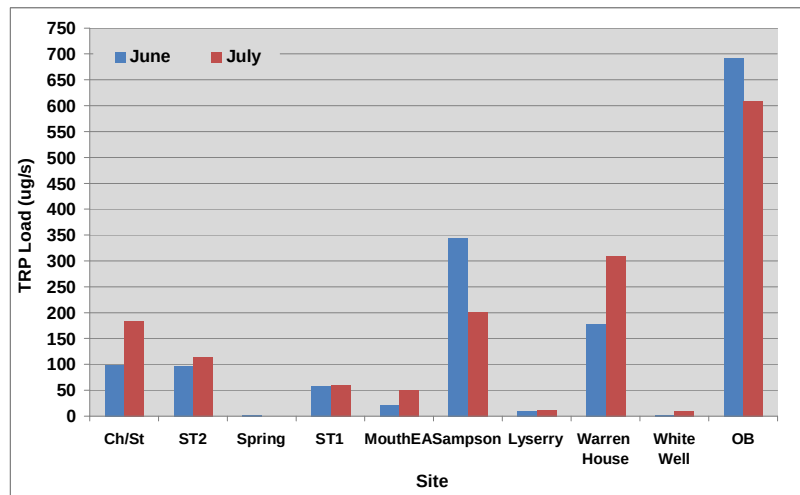


Figure 24: TRP loads calculated using samples and discharge readings on the 11th June and 8th July 2008

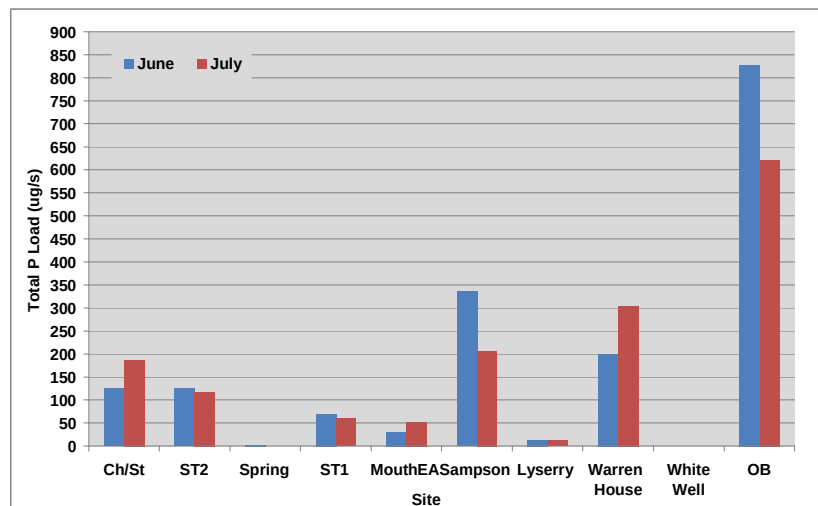


Figure 25: TP loads calculated using samples and discharge readings on the 11th June and 8th July 2008

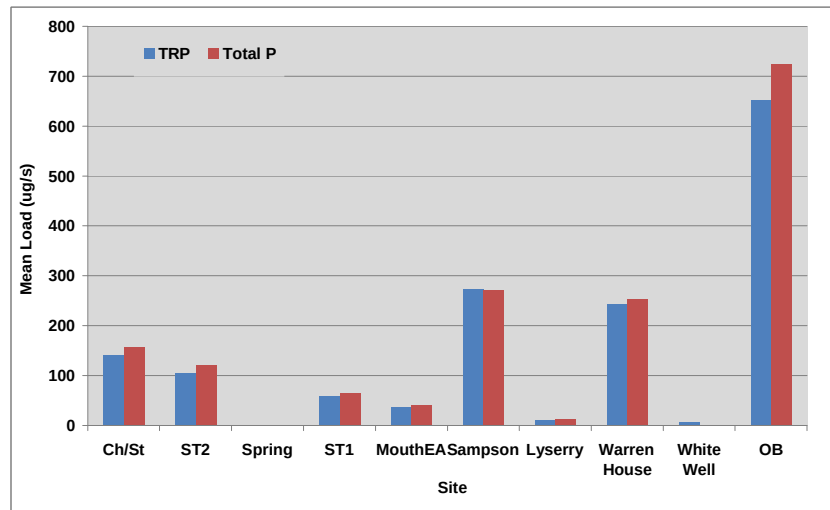


Figure 26: Mean 'summer' TRP and TP loads in the streams calculated from samples and spot discharge readings taken on the 11th June and 8th July 2008.

4.2 Nitrogen

4.2.1 Nitrogen in Bosherton Lakes water

The spatial pattern is the same for both nitrate and Total Nitrogen, (Figure 27), and the Total Nitrogen within the samples consists mainly of nitrates. Therefore, the following analysis will be based on the nitrate concentrations within the lakes. Appendix K contains the results for both nitrates and Total Nitrogen.

There is very little difference in the nitrate concentration of the surface and bottom water samples. There is slightly more nitrate within the majority of the bottom samples than the surface samples though the overall spatial pattern is the same as between the two samples as well as with the mean concentration.

The overall view of the nitrate status of the lakes at the time of sampling (3rd–5th June 2008) can be seen by using the mean of the surface and bottom water samples (Figure 28). The Upper Eastern, Western and Central Arms contain the most nitrates, with very little in the Lower Eastern Arm and Central Lake. The highest concentrations are in the Central Arm, CA3, the Western Arm, WA5, and the Upper Eastern Arm, UE1, all of which are in the upper parts of the respective 'arms' of the lakes, the area furthest from the Central Lake (Figure 27).

Within the transects that move down the middle of the lakes there is a clear pattern in the Upper Eastern and Western Arms where the nitrate concentration is higher in the upper points and decreases steadily down the lakes (Figure 27). In the Central Arm the pattern is similar, with the lowest concentration nearest the Central Arm Causeway. The two samples that are above *Chara* beds, CA1 and CA4 are lower than those above bare sediment, CA2 and CA3, probably due to higher nitrate uptake by the *Chara*.

The nitrate concentrations at the sites at the edge of the lakes, on the transects running across the width of the lakes, are roughly the same as the corresponding sites in the middle of the lake.

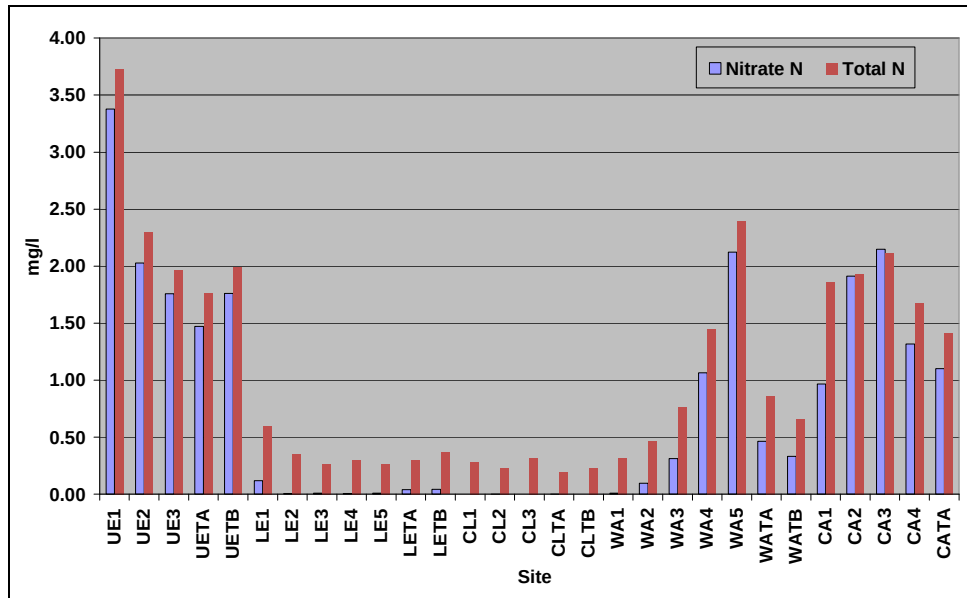


Figure 27: Mean Nitrate-N and Total Nitrogen concentrations in Bosherton Lake water calculated from bottom and surface water samples collected between 3rd and 5th June 2008. The samples are ordered from the Upper Eastern Arm, down to the Central Lake, into the Western Arm and finally the Central Arm, including both middle and edge of lake samples.

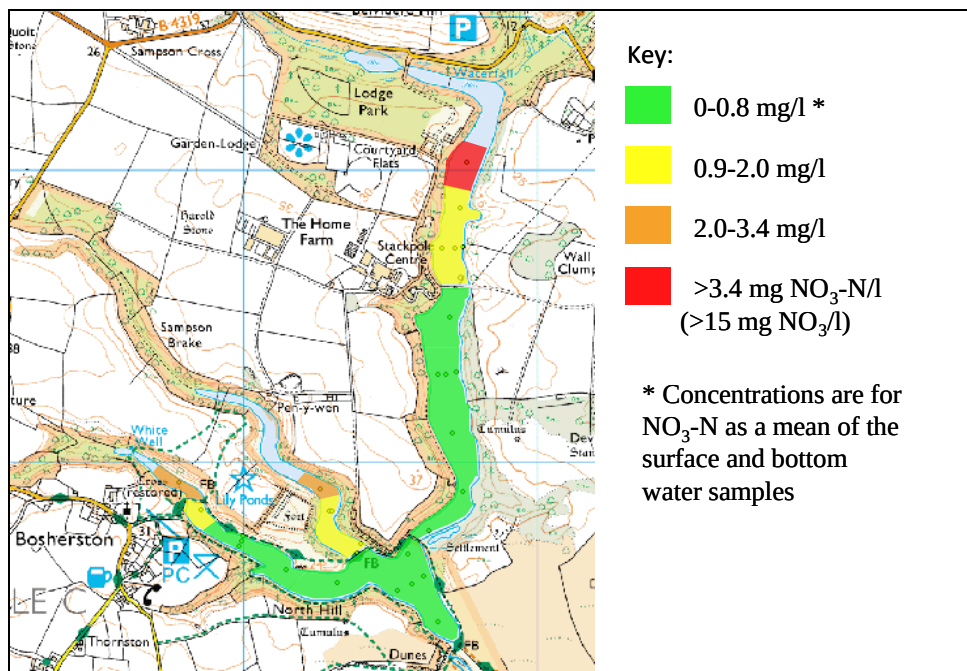


Figure 28: Mean Nitrate (NO₃) concentration calculated from bottom and surface water samples collected between 3rd and 5th June 2008.

4.2.2 Nitrogen in the surrounding catchment – streams and groundwater

The following analysis will again be based upon the nitrate concentrations for the reasons explained at the beginning of section 4.2.1. The concentrations at individual sites for both Total Nitrogen and nitrates can be found in Appendix L.

The nitrate (NO_3) levels within the streams are lower in the samples taken on 8th July 2008 than on 11th June 2008, but the spatial pattern is the same (Figure 29). Therefore, mean ‘summer 2008’ stream nitrate (NO_3) concentrations were calculated using the data from these two sampling dates (Figure 30). It should be noted that the only record for groundwater at the Devils Quoit borehole and Lyserry Covert borehole were from November 2006 and November 2002 respectively, outside the summer period. The Sampson borehole concentration is an average of summer concentrations from 1998, 2003/04/05 and 2007. The highest concentrations of nitrates are found at the headwaters of the Cheriton Brook (40.1 mg/l) and in the groundwater at Devils Quoit (54.0 mg/l) to the east of the Lower Eastern Arm. The lowest concentrations are found at the Bosherton Quarry (0.83 mg/l) and in the groundwater at Lyserry Covert (9.2 mg/l).

The headwaters of the Merrion stream (MW) have a High level of nitrates which decrease downstream to Moderate levels and remain at this level apart from at Sampson (S), where a small tributary enters the river and the level increases to High concentrations. The nitrate concentration decreases from Excessively High levels at the headwaters of the Cheriton Brook (Ch/St) but they remain Very High at ST2. The Castle Dock stream has a Very High concentration both at its headwaters and just before the confluence with Cheriton Brook. After the confluence just before the stream enters the Upper Eastern Arm the concentration decreases slightly but the remains High (26.5 mg/l). There are Moderate levels of nitrates at the White Well (19.2 mg/l) at the top of the Western Arm.

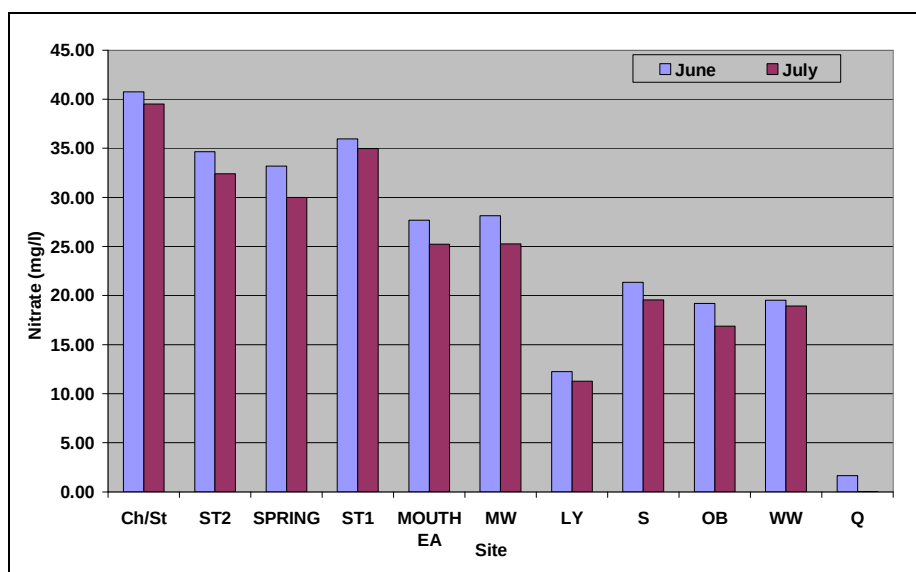


Figure 29: Nitrate (NO_3) concentrations in the streams on the 11th June and 8th July 2008

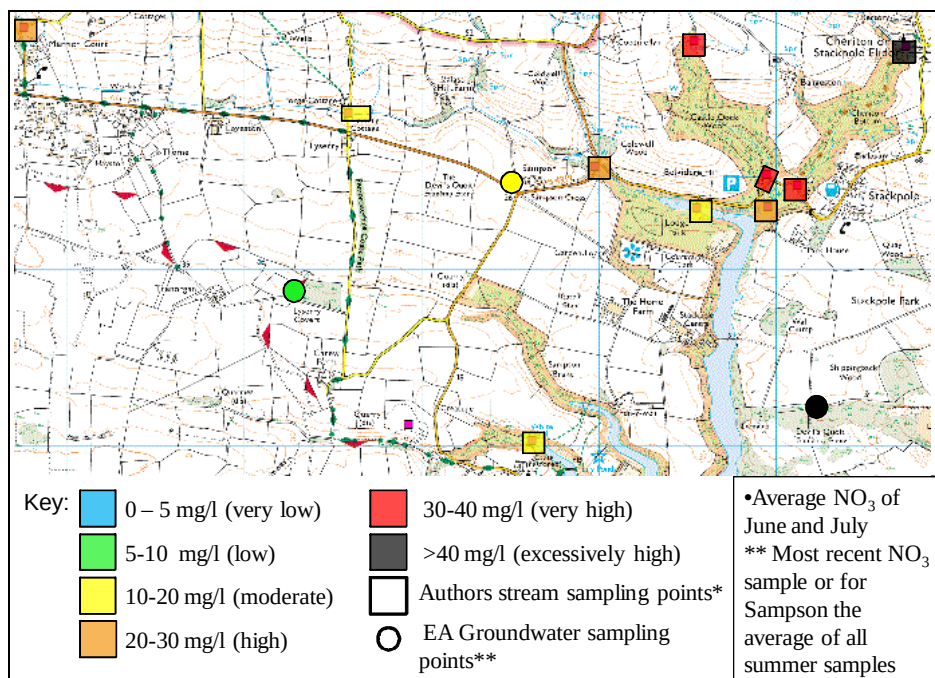


Figure 30: Mean ('Summer 2008') nitrate (NO₃) concentrations in the streams calculated from samples taken on 11th June and 8th July 2008. Groundwater concentrations are from Environment Agency data. The samples from the Devils Quoit and Lyserry Covert boreholes were from November 2006 and November 2002 respectively; the concentration at the Sampson borehole is an average of summer samples from 1998, 2003/04/05 and 2007.

4.2.2.1 Nitrogen Loads

The nitrogen loads were calculated using the discharges in Table 9 (Section 4.1.4) multiplied by the Nitrate (NO₃) or Total Nitrogen concentrations, the in detail loads for all sampling sites can be found in Appendix M. Figure 31 shows the Nitrate (NO₃) loads on 11th June and 8th July 2008. The highest load entering the lakes is from the Merrion Stream, at One Arch Bridge (OB). This is consistent with the phosphorus loads and is again due to a higher discharge at this site than at the mouth of Cheriton Brook, confirmed by observations at the two sites. The White Well, at the top of the Western Arm, has a similar nitrate load to the mouth of the Cheriton Brook. The loads are lower in the samples collected on 8th July 2008 compared to those collected on 11th June 2008.

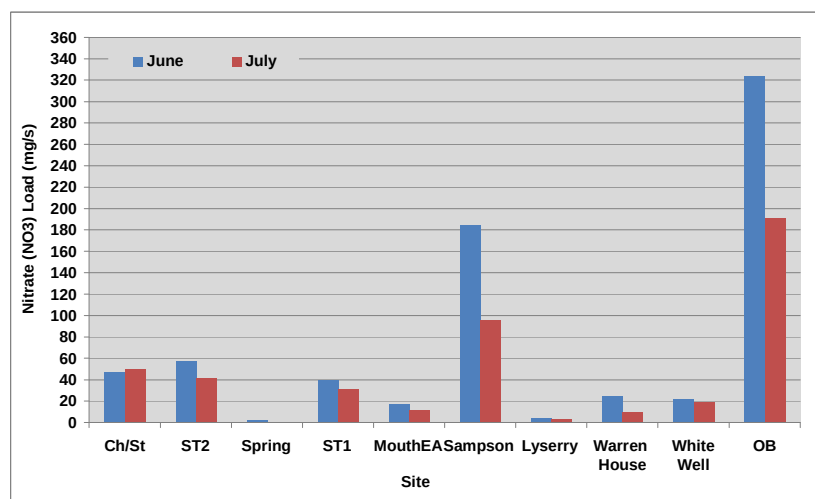


Figure 31: Nitrate (NO_3) loads calculated using samples and discharge readings on 11th June and 8th July 2008

4.3 N:P ratios

The N:P ratios were calculated for Total Phosphorus and Total Nitrogen as there was no TRP present within the lakes. Figure 32 shows the TN:TP ratios within Bosherton Lakes. The highest ratios are found in the Central Arm and Upper Western Arm, and less so in the Upper Eastern Arm. The lowest TN:TP ratios are found in the Lower Eastern Arm, Central Lake and the Lower Western Arm.

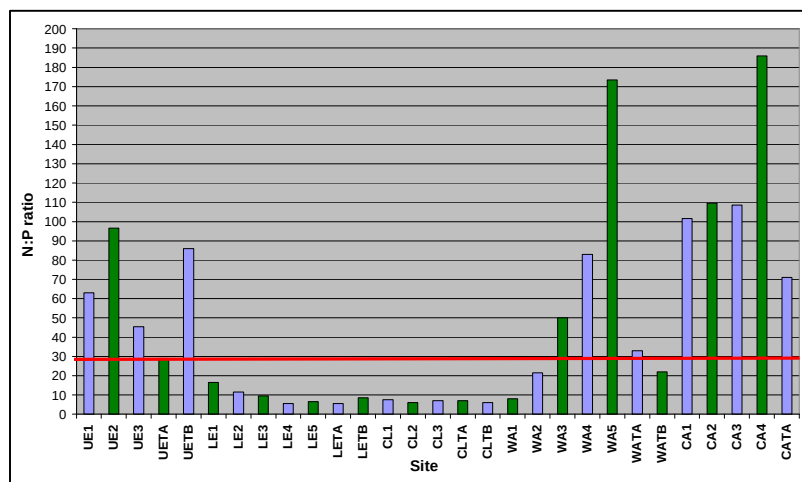


Figure 32: N:P ratios for Bosherton Lakes. (Red line is tentative threshold below which there is a higher risk of cyano-bacteria blooms. The threshold is taken from the higher end of those stated in the literature).

Downing and McCauley (1992) state that a low TN:TP ratio will only increase the chance of cyano-bacteria blooms if there is a higher level of phosphorus within the water, above $30 \mu\text{gTP/l}$. Figure 33 shows that the Lower Eastern Arm and Central Lake are most at risk from cyano-bacteria blooms as they contain TP concentrations above $30 \mu\text{g/l}$ and have a TN:TP ratio below 30:1. The orange sections in Figure 33 show areas that have a low TN:TP ratio but have TP concentrations below $30 \mu\text{g/l}$, those areas at

risk should the TP concentration increase. The green areas show low risk areas where the TN:TP ratio is high.

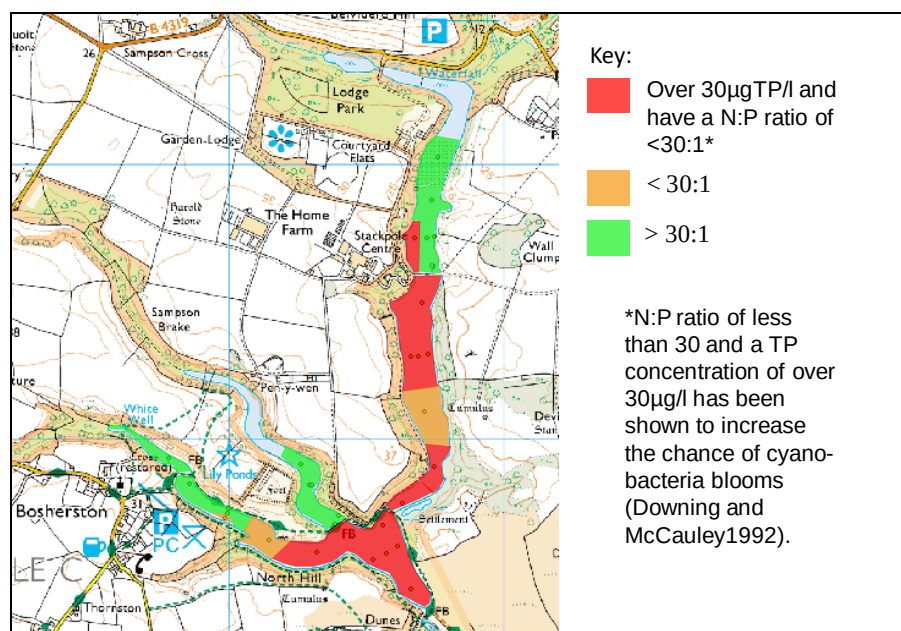


Figure 33: Areas at risk of cyano-bacteria blooms based on TN:TP ratios calculated from the mean of surface and water samples collected between 3rd and 5th June

4.4 Other water quality indicators

4.4.1 Turbidity

In general the secchi was visible to the bottom of the lake, shown by the secchi depth being equal to the water depth (Figure 34). From observations on the lake these sites were slightly murkier than the other sites, but in the Upper Eastern Arm this was generally due to the thick pondweed (Figure 35). The clearest water was in the Central Arm. The upper part of the Western Arm is similar to the Central Arm, and the lower part similar to the Central Lake.

4.4.2 Temperature

The temperature on the surface of the lake, during the sampling period of 3rd to 5th June 2008, stays above 17°C. The highest temperatures were found in the Upper Eastern Arm, though these were taken at the end of a very hot day and the lowest temperatures in the Central Lake were recorded on a cooler and overcast day.

The bottom temperatures of the lake were consistently lower than those on the surface and ranges between 19.58°C at WA2 in the Western Arm and 15.36°C at UE3 in the Upper Eastern Arm (Figure 36).

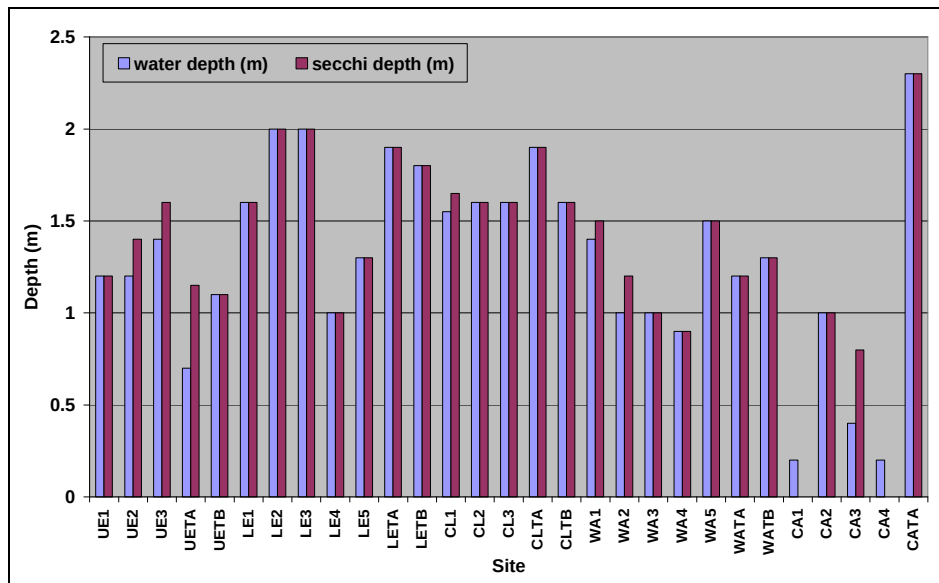


Figure 34: Secchi and Water depth in the Bosherton Lakes for the period between 3rd and 5th June 2008. The data is ordered from the Upper Eastern Arm, down to the Central Lake, into the Western Arm and finally the Central Arm, including both middle and edge of lake samples.

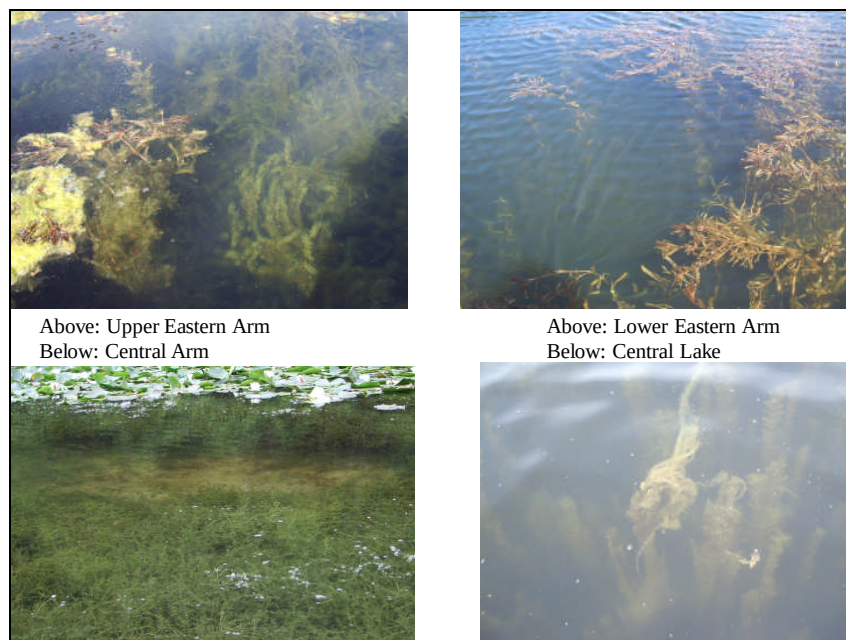


Figure 35: Photos showing water clarity and vegetation in the Bosherton Lakes between 3rd and 5th September 2008

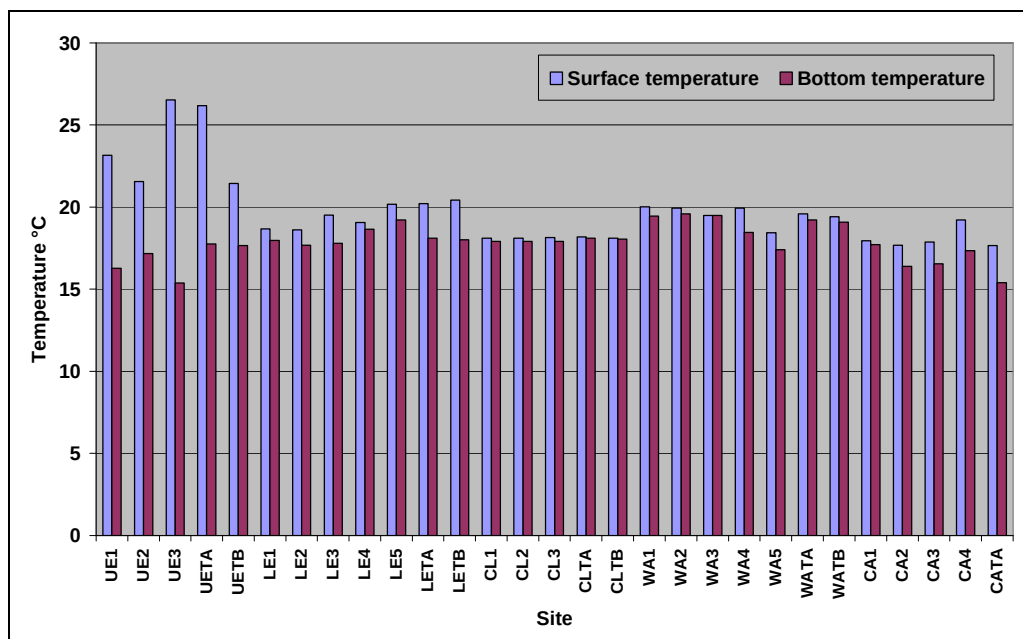


Figure 36: Surface and bottom water temperatures recorded between 3rd and 5th June 2008. The Eastern Arm records were taken on 3rd June, the Western and Central Arms on 4th June and the Central Lake on 5th June.

4.4.3 Dissolved Oxygen

Figure 37 shows that the lakes are saturated with Dissolved Oxygen (DO). The highest percentage of DO was found in the Upper Eastern Arm with the lowest in the Central Lake and Central Arm.

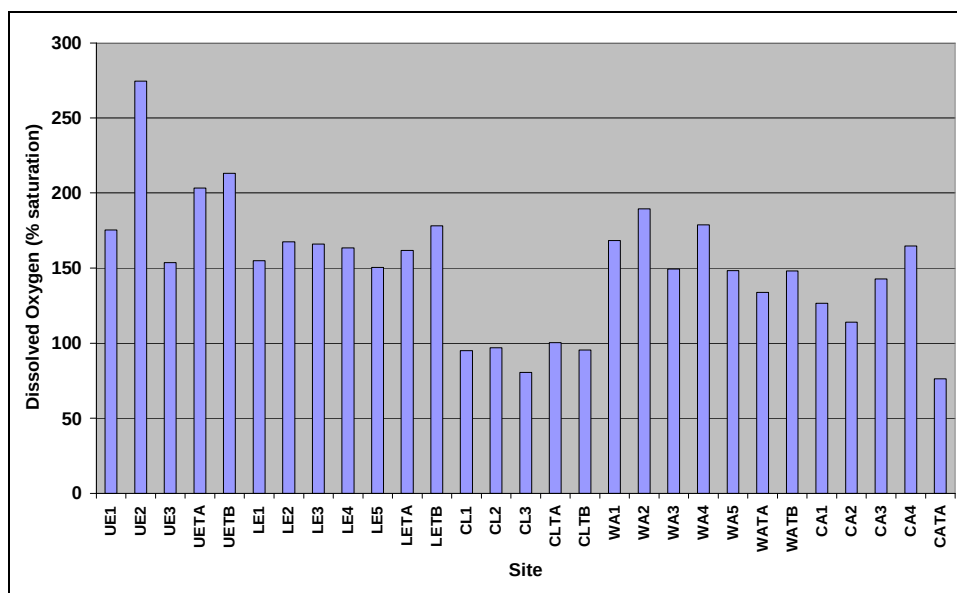


Figure 37: Mean DO concentrations for the Bosherton Lakes, calculated from bottom and surface water data in recorded between 3rd and 5th June 2008.

4.4.4 pH

The pH is lowest in the Central Arm and upper Western Arm and highest in the Lower Eastern Arm (Figure 38). The pH ranges from 7.5 at WATA in the upper part of the Western Arm to 9.5 in at LE5 in the Lower Eastern Arm, just before the Grassy Bridge Dam.

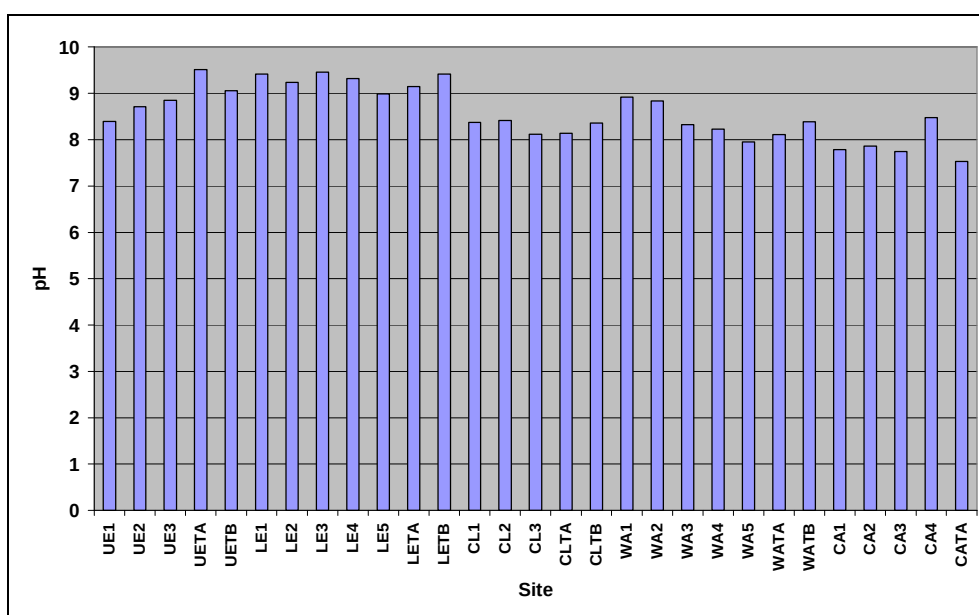


Figure 38: Mean pH concentrations for the Bosherton Lakes, calculated from bottom and surface water data in recorded between 3rd and 5th June 2008.

4.5 Temporal change

4.5.1 Phosphorus

The following analysis is based data from the Environment Agency (EA). The fixed sampling points can be seen in Figure 39 from 1979 to 2005. The EA sample orthophosphate and it is unknown whether this is SRP or TRP. Therefore, it will be referred to still as orthophosphate (orthoP).

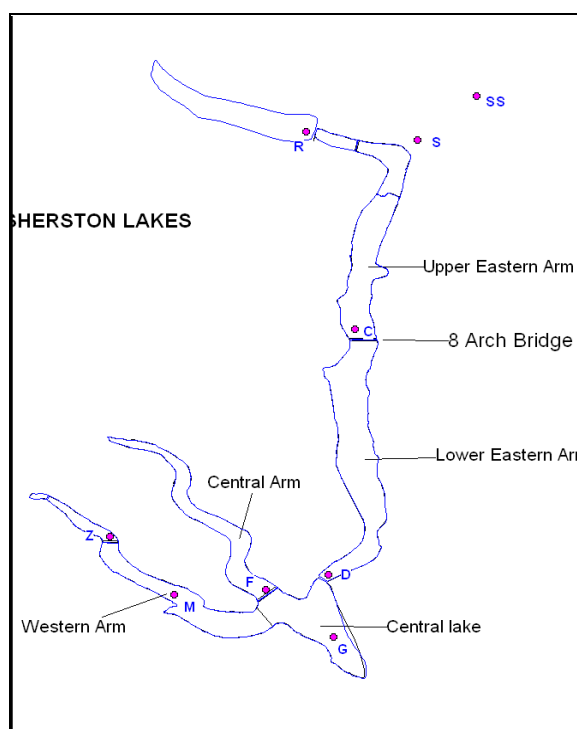


Figure 39: EA routine chemical sampling points

There is an obvious inconsistency in the way the data was recorded or analysed. Between 1979 and 1994 the results are all rounded to the nearest ten, and as the concentrations of orthoP are low in some 'arms' of the lake it makes a large difference in the concentration. From 1994 to 2005 the results were recorded without rounding and the differences between months can be seen more clearly.

This may be due to the introduction of more accurate lab analysis techniques in 1994, or just a change in the way the data was recorded. The discrepancies in the data are especially apparent in the Central Lake (site G) and the Central and Western Arms (sites F, M and Z) where the orthoP concentrations are lower (Figure 40). Only in the Eastern Arm is it obvious that there are more higher peaks in the time before the Stackpole STW was diverted in 1984 as the orthoP concentrations were much higher in the Eastern Arm than the rest of the lakes. However, the second half of the data, from 1994, can give an indication as to the levels of orthoP within the lakes. This is useful as there was no TRP recorded in the lakes during the current survey (between 3rd and 5th June 2008).

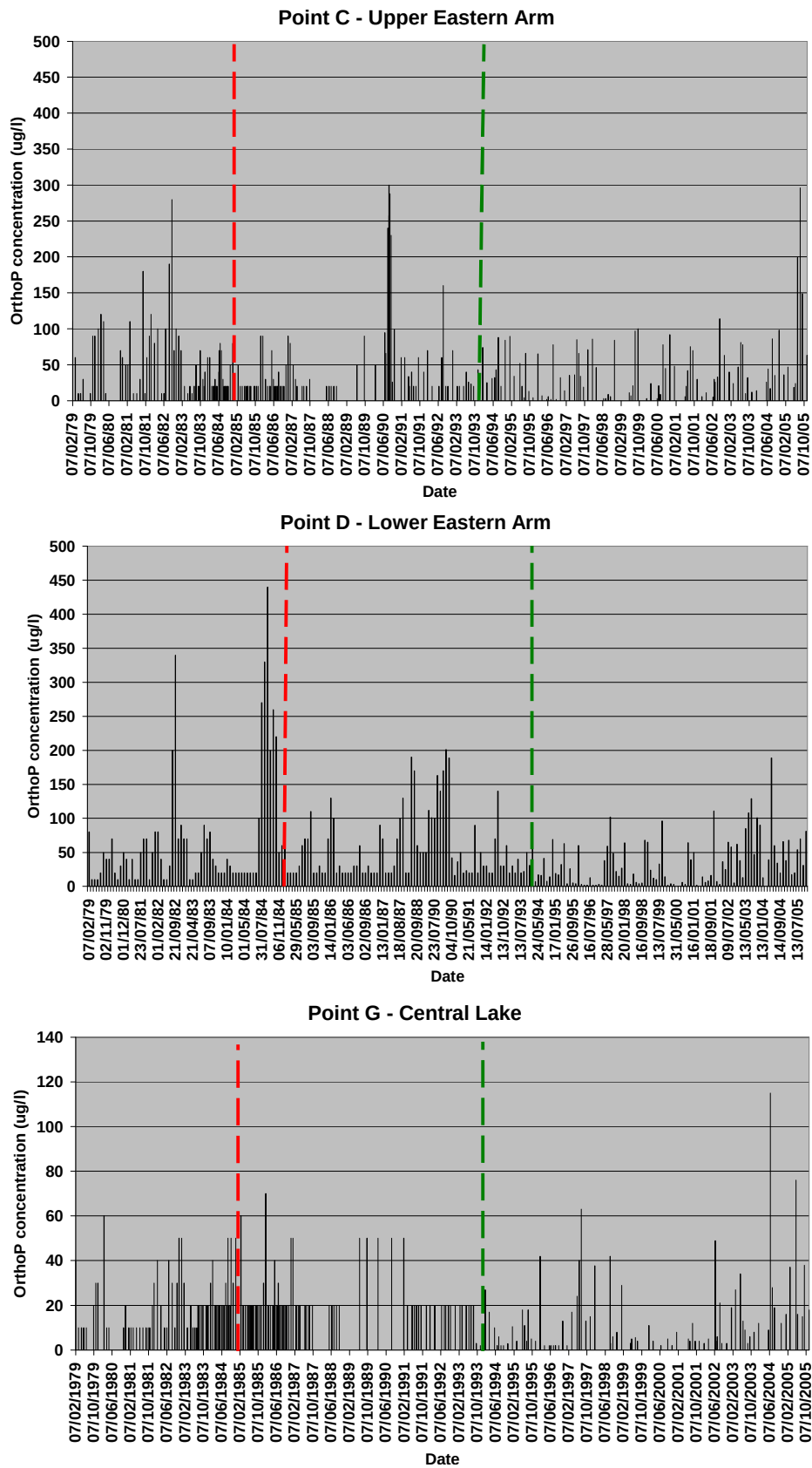


Figure 40: Environment Agency orthophosphate data 1979–2005. The red dashed line indicates the diversion of the Stackpole STW, the green dashed line indicates the change in the recording or analysis of the data.

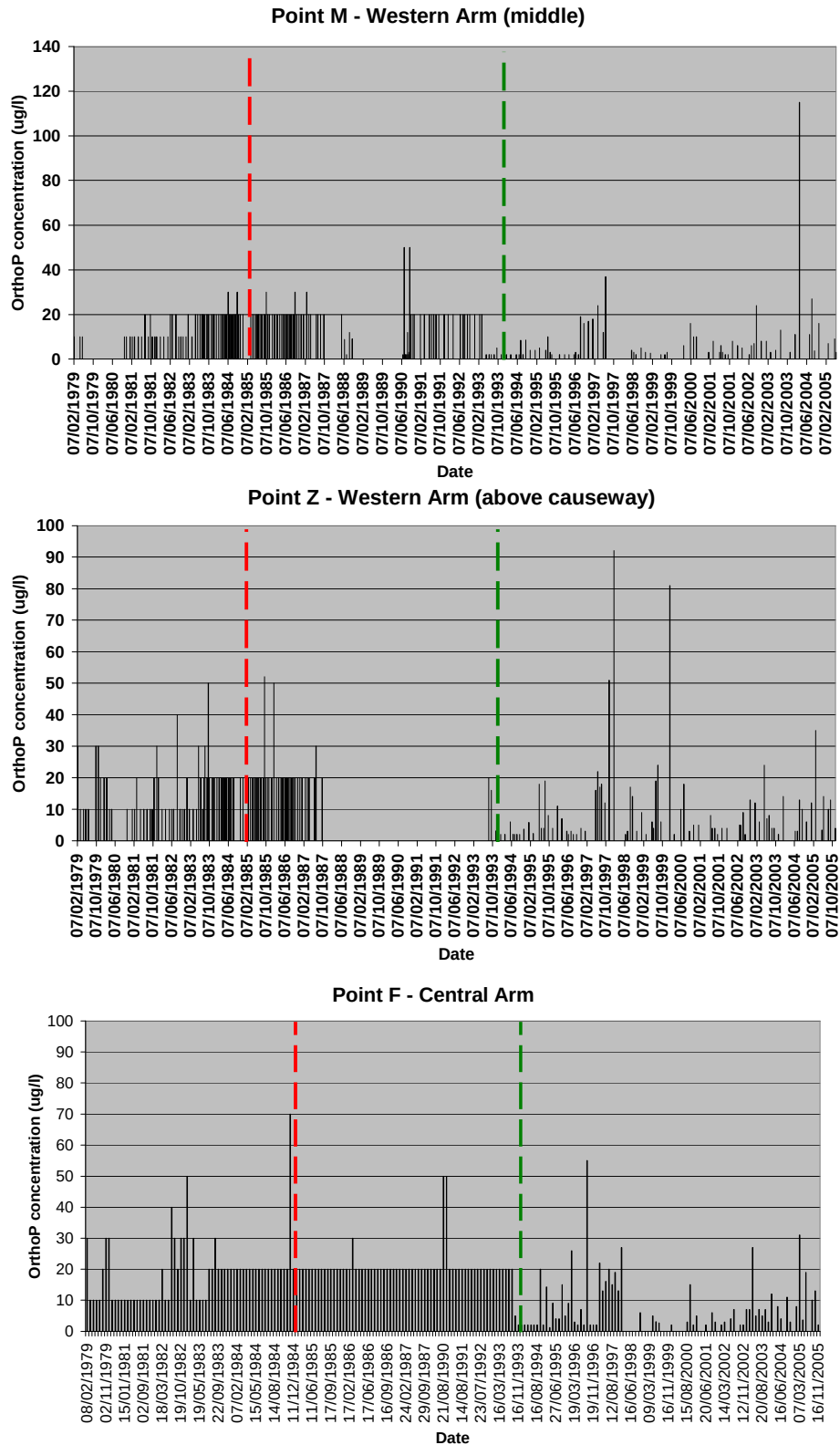


Figure 40 cont: Environment Agency orthophosphate data 1979–2005. The red dashed line indicates the diversion of the Stackpole STW, the green dashed line indicates the change in the recording or analysis of the data.

Spears et al (2007b) show the average seasonal variation in SRP for Loch Leven (Figure 41). They discover that there is a late-summer peak that, in the absence of external sources, is most likely due to internal loading of SRP due to the release of redox-sensitive sediment phosphorus in the Loch.

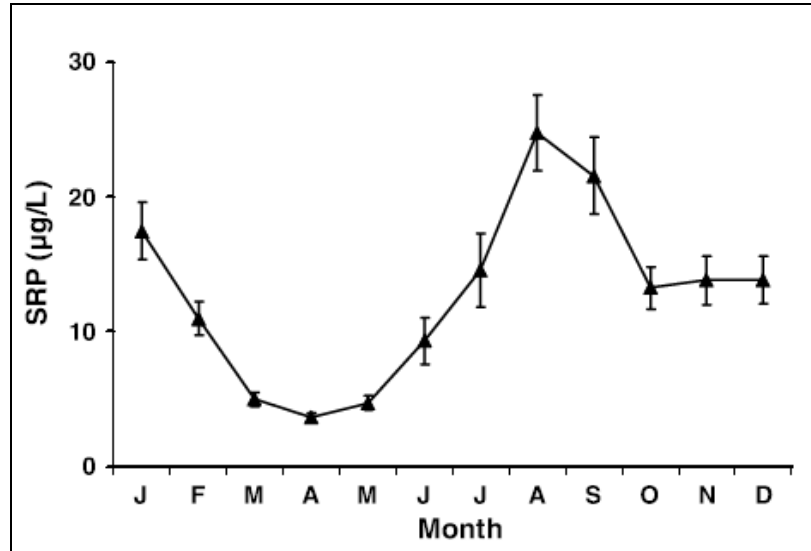


Figure 41: Average (1968–2004) monthly water-column SRP concentrations in Loch Leven (with standard error bars). From Spears et al (2007b).

To help understand whether there is internal loading in the summer months in Bosherton Lakes in the absence of external sources, the averages of orthoP need to be calculated after 1984, when the main external source of phosphorus, the Stackpole STW, was diverted. However, due to the recording discrepancies in the data, only the years after 1994 were used to calculate the averages. There were four months (Feb, Apr, Oct and Dec) where there was insufficient data available after 1994 so an average was calculated using records after 1985. The orthoP seasonal averages for the different ‘arms’ of the lake show a late summer peak in the Eastern Arm but not in any of the other ‘arms’ of the lake (Figure 42). Unlike the SRP concentrations in Loch Leven that stay roughly the same between October and January, there is a noticeable peak in winter OrthoP in the Eastern Arm and Central Lake (Figures 41 and 42).

The average (1994–2005) orthoP concentrations in August show that the highest concentrations are found within the Upper and Lower Eastern Arm (79 µg/l and 65 µg/l). The concentrations decrease in the Central Lake and Central Arm to 17 µg/l and 18 µg/l. They decrease further in the Western Arm to 14 µg/l in the middle and 10 µg/l above the causeway (Figure 41). There is, however, more of a range in concentrations recorded in the Eastern Arm shown by the larger standard error, though even if the mean was at the lowest end of the error the concentrations in the Eastern Arm are still much higher than in the any of the other ‘arms’.

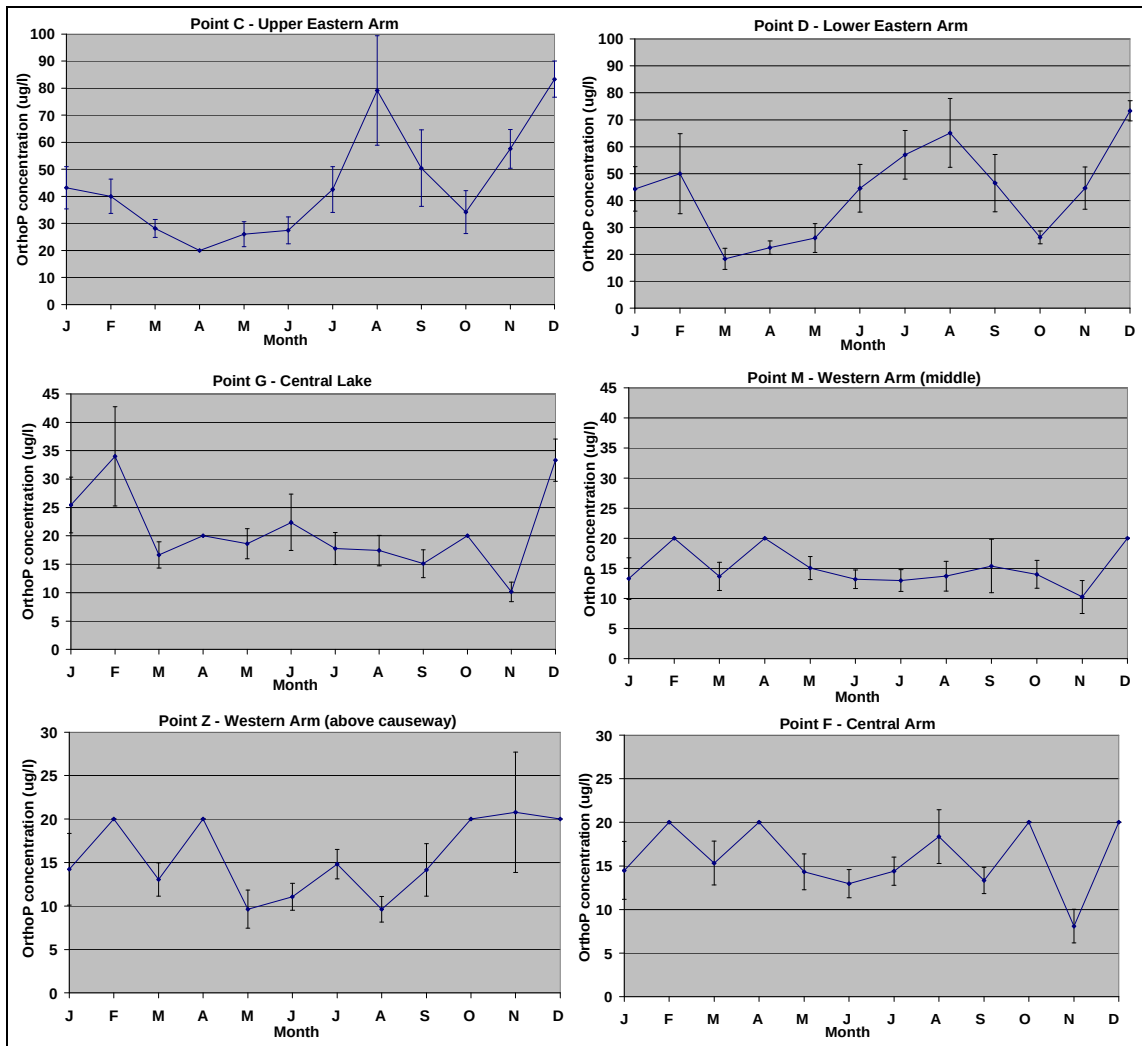


Figure 42: Average (1994–2005 or 1985–2005) monthly water-column ortho-P concentrations in Bosherton Lakes (with standard error bars).

The differences in the EA data due to rounding are less obvious in the TP records as the concentrations are much higher and therefore the differences in rounding to the nearest ten are less obvious in the Eastern Arm and Central Lake. There is an obvious reduction in TP concentrations the Eastern Arm and Central Lake after the diversion of the Stackpole STW in 1984 (Figure 43). The Western and Central Arm records are more useful after 1994, as the discrepancies in the data are more noticeable in these records, especially in the Central Arm as the TP concentrations are lower. The average (1994–2005) TP concentrations in August show that the highest concentrations are in the Upper and Lower Eastern Arm (135 µg/l and 111 µg/l) and then decrease again in the Central Lake and Central Arm to 36 µg/l and 32 µg/l. The concentration in the middle of the Western Arm is 36 µg/l and above the causeway is 22 µg/l. This confirms the trend seen in the TP concentrations of the current survey (3rd–5th June 2008).

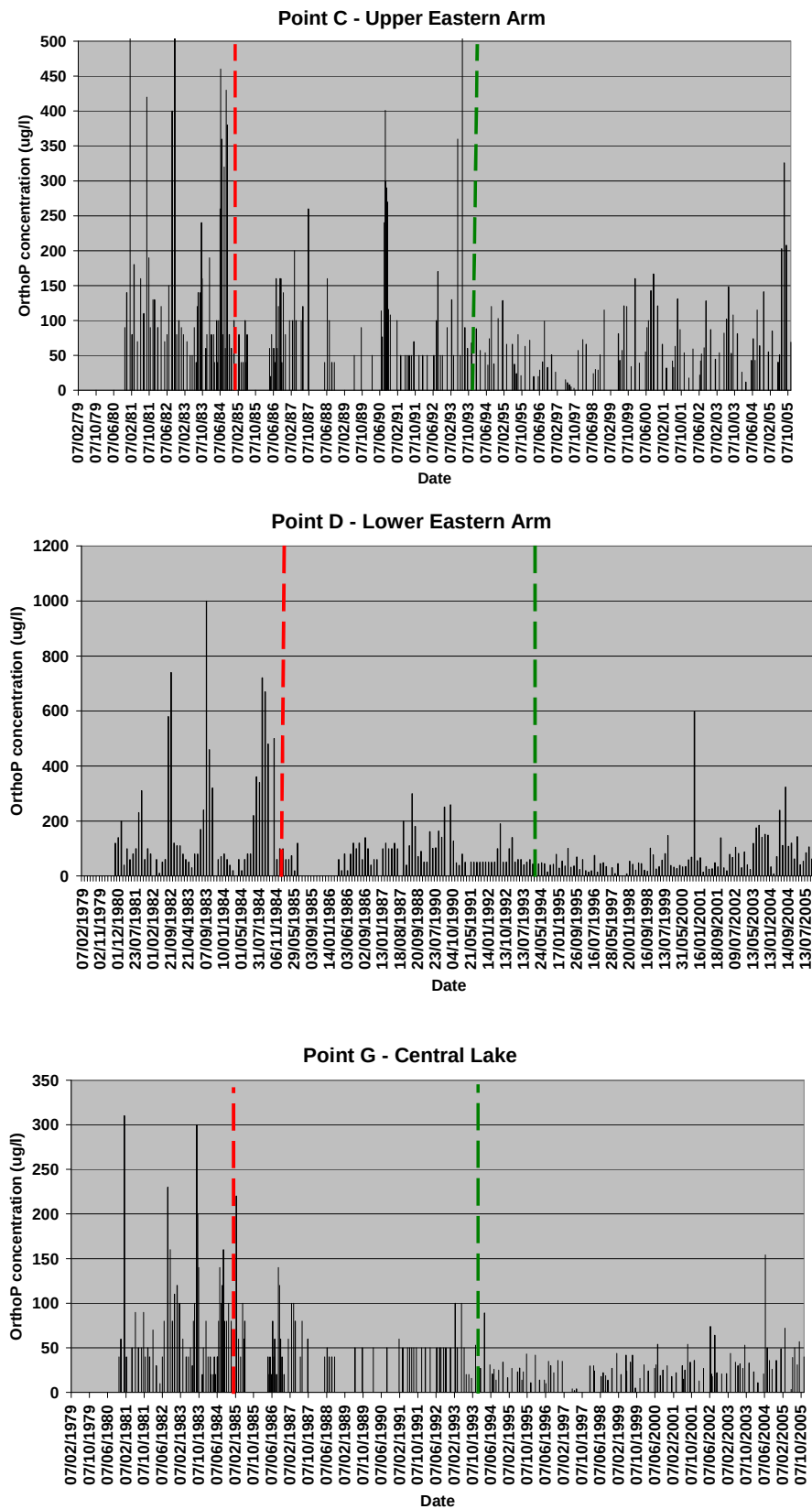


Figure 43: Environment Agency Total Phosphorus data 1979–2005. The red dashed line indicates the diversion of the Stackpole STW, the green dashed line indicates the change in the recording or analysis of the data.

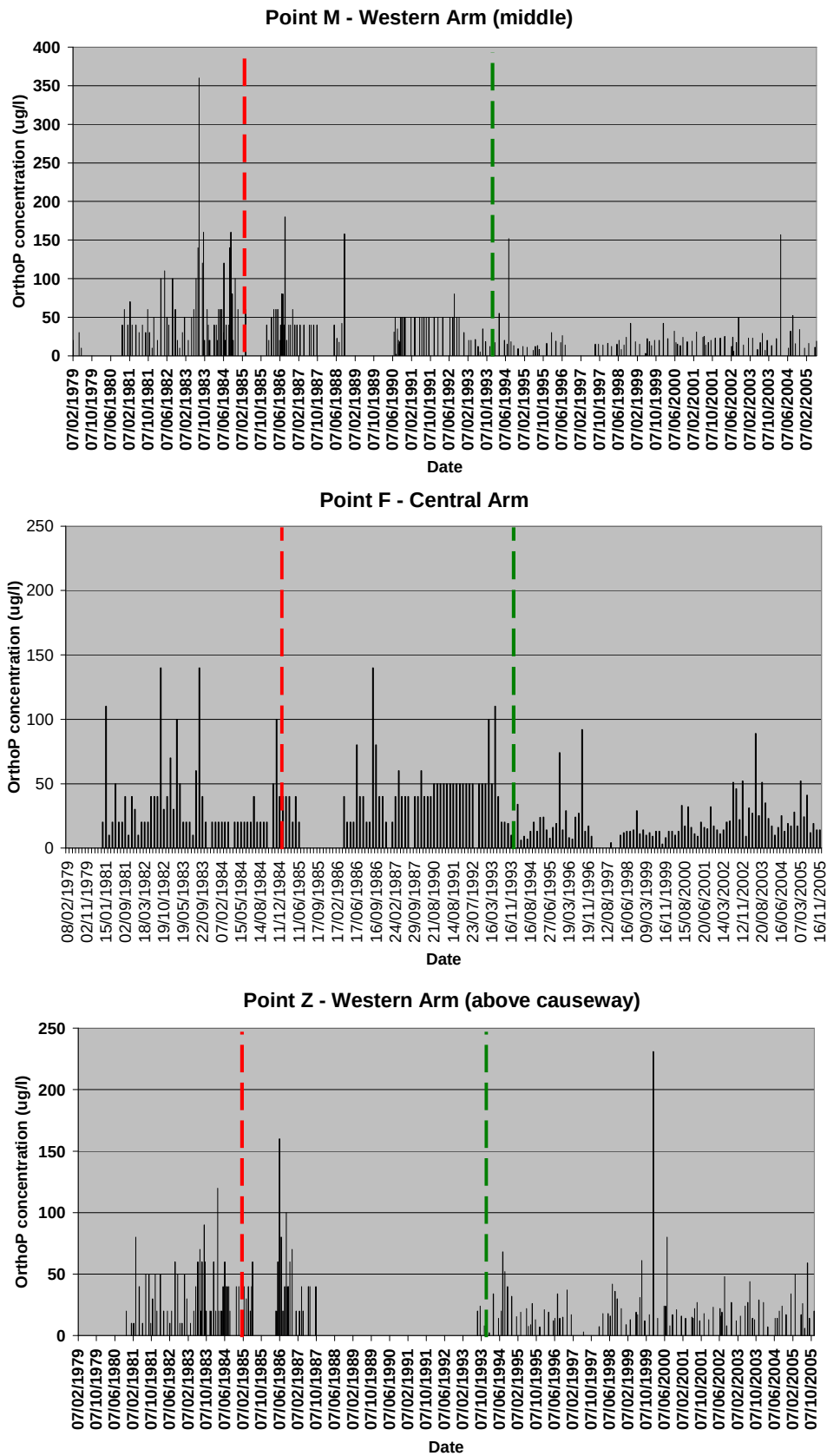


Figure 43 cont: Environment Agency Total Phosphorus data 1979–2005. The red dashed line indicates the diversion of the Stackpole STW, the green dashed line indicates the change in the recording or analysis of the data.

4.5.2 Stream Phosphorus

There is less consistent monitoring of the streams than there is in the lakes. There are only three sites available and these are at the mouths of the Cheriton Brook and Merrion Streams and the after the sediment trap near the Stackpole STW on Cheriton Brook.

The highest concentrations of orthoP and Total Phosphorus seem to be found after the sediment trap on Cheriton Brook, though the differences between this site and the others are not always statistically significant (Figure 44 and 45). The concentrations of both orthoP and Total Phosphorus in the Merrion stream seem to be lower than the Cheriton Brook, and this is supported by the results from the current surveys undertaken on the 11th June and 8th July 2008. There seems to have been a decrease in orthoP and Total Phosphorus concentrations at the mouth of the Cheriton Brook, with concentrations from the mid – 1990s onwards more like the levels in the Merrion stream. Unfortunately there is no data available for before 1984 at the site after the STW, therefore the impact of the diversion cannot be seen.

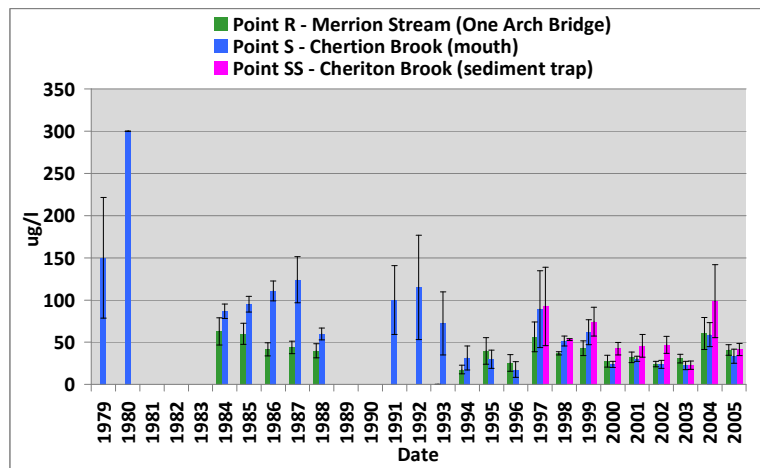


Figure 44: Average summer (April to September) ortho-P concentrations in the streams using EA data. Black bars indicate standard error around the mean.

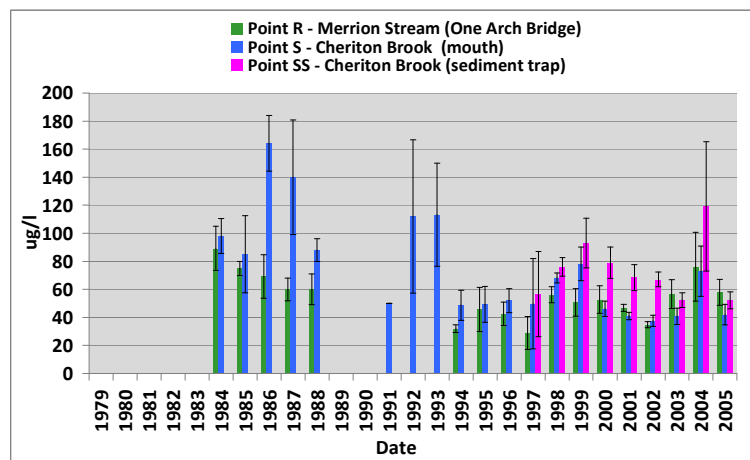


Figure 45: Average summer (April to September) TP concentrations in the streams using EA data. Black bars indicate standard error around the mean.

4.5.3 Lake Nitrates

To confirm that the spatial pattern of nitrates in the Bosherston Lakes in the current survey (3rd -5th June 2008) was not just a one-off occurrence the average summer (April – September) nitrate concentrations from 1979-2005 were calculated. Figure 46 shows that there are no clear temporal patterns as the error bars show a large spread in the data, therefore it is possible that the nitrate levels have remained much the same over the time series. There does seem to be one significant trend in the temporal data of the Upper Western Arm, it shows that there seems to be an increase in nitrates after 1993. The highest nitrate concentrations are within the Western Arm (above the causeway, point Z), Central Arm and Upper Eastern Arm (Figure 47). The lowest concentrations are in the Lower Eastern Arm, Central Lake and mid Western Arm. This confirms the spatial pattern observed during the current survey. Figure 47 shows that there seems to be more of a difference between the levels in the Central Arm and Upper Western Arm and the other parts of the lakes after 1993. There does not seem to be any obvious discrepancies in the data as with the phosphorus data, however the change does occur after the same date, so it is possible that this may also be due to differences in how the nitrate concentrations were measured or recorded.

4.5.4 Stream Nitrates

The nitrate concentrations are higher in the Cheriton Brook compared to the Merrion stream (Figure 48). This confirms the findings from the current surveys undertaken on the 11th June and 8th July.

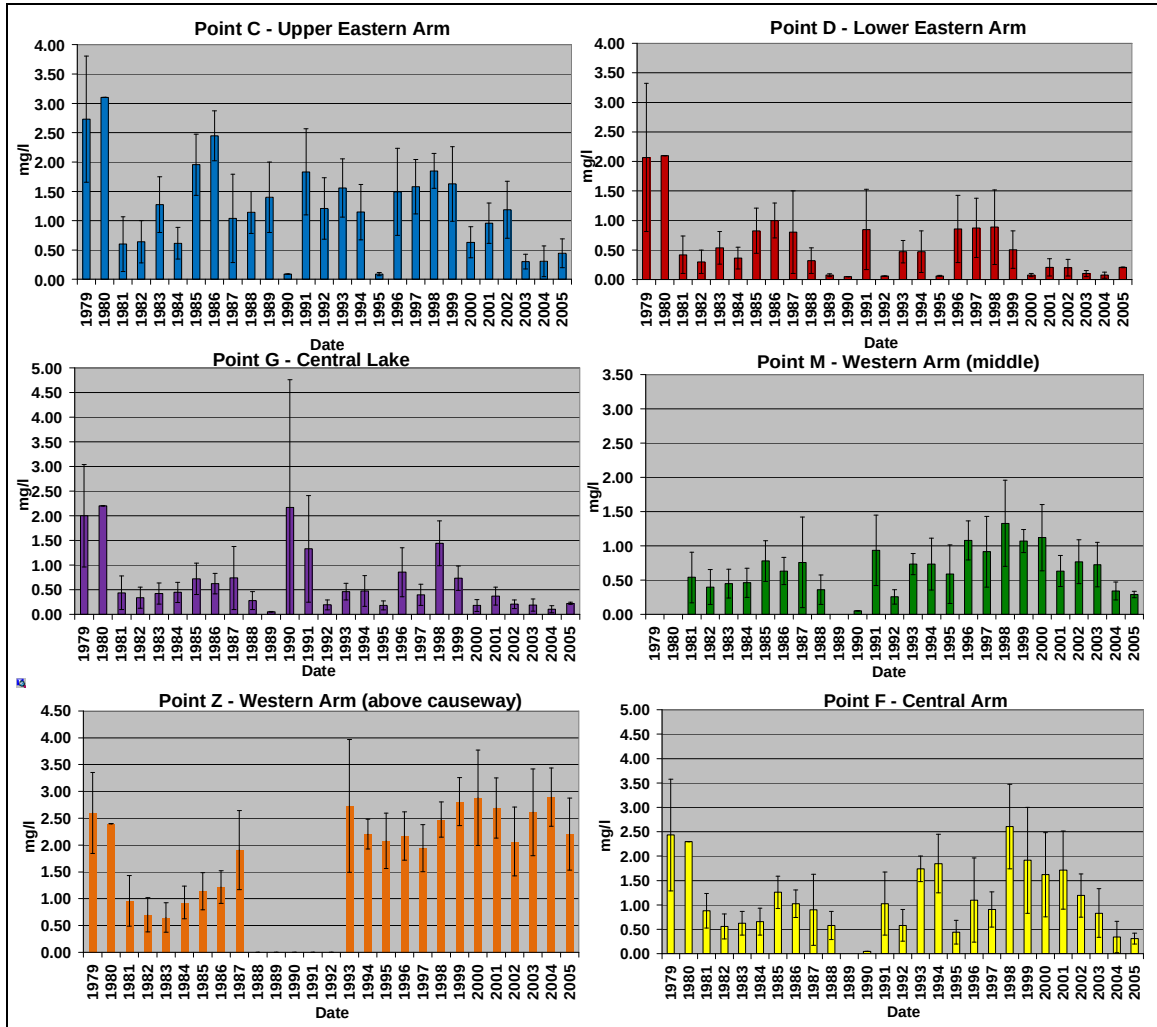


Figure 46: Average summer (April-September) Nitrate-N concentrations in each 'arm' of Bosherton Lakes calculated from EA data. Black bars indicate standard error of the mean.

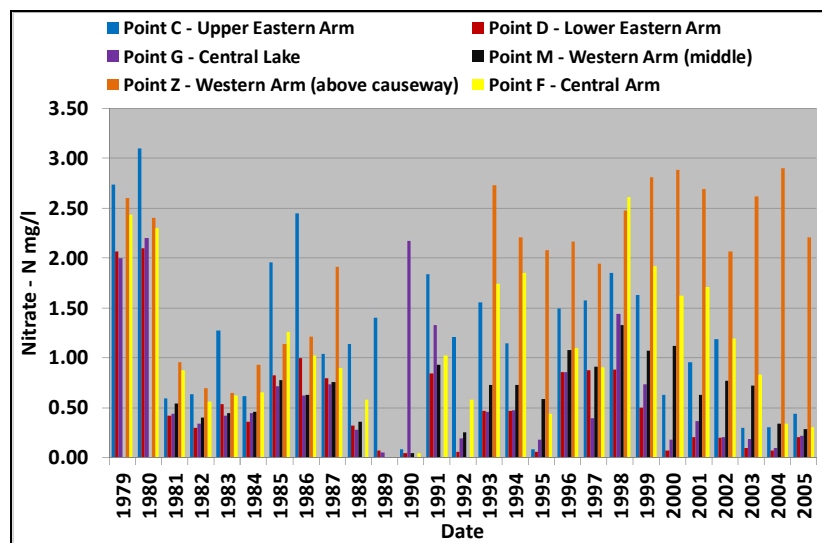


Figure 47: Average summer (April-September) Nitrate-N concentrations for all EA sites.

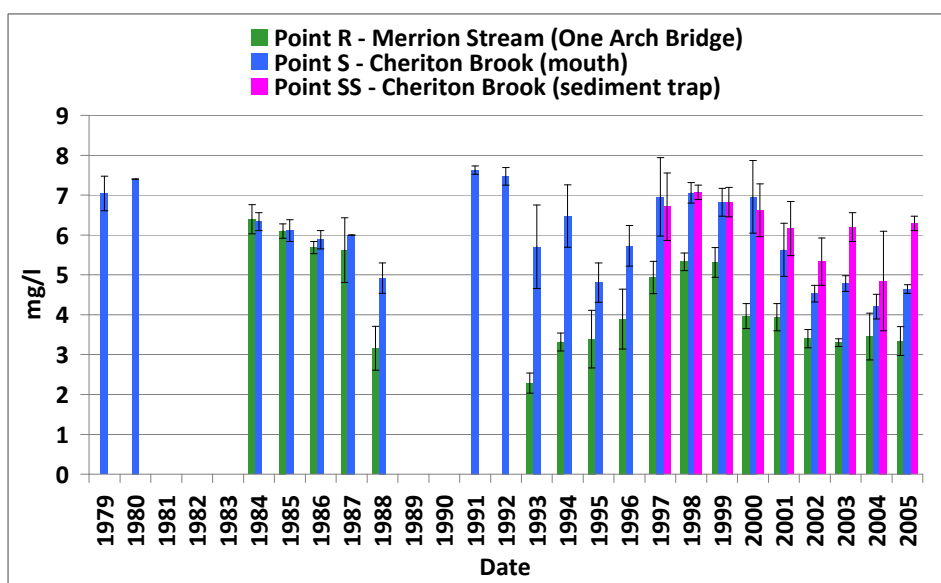


Figure 48: Average summer (April to September) Nitrate-N concentrations in the streams using EA data. Black bars indicate standard error around the mean.

5 DISCUSSION

5.1 *Nutrient dynamics*

5.1.1 *Lake trophic status*

During the summer months under baseflow conditions there are still possible problems with elevated nutrient levels in Bosherton Lakes. Figures 49, 50 and 51 show the lakes trophic status based upon thresholds of TP defined by OECD (1982) fixed boundary system and TN levels defined by Nürnberg (1996). It is apparent that different parts of the lake are affected by different issues, either elevated phosphorus levels and/or nitrate levels.

The lake water in the Upper Eastern Arm, Lower Eastern Arm, Central Lake and the very lower end of the Western Arm all have Total Phosphorus levels indicative of eutrophic conditions as defined by the OECD fixed boundary system and are above the targets of 25 and 50 $\mu\text{gTP/l}$ set by the Countryside Council for Wales (CCW) (OECD 1982, CCW 2008). The Central Arm and upper Western Arm have lower levels of phosphorus typical of a mesotrophic lake (Figure 49). There are high levels of Total Nitrogen within the Upper Eastern Arm, the upper part of the Western Arm and the Central Arm. All these areas have levels above the 1 mgN/l target set by CCW. Figure 50 shows that based just on the nitrogen levels, these areas are hyper-eutrophic according to the levels set by Nürnberg (1996). The Lower Eastern Arm, Central Lake and lower Western Arm have nitrogen levels typical of an oligo-mesotrophic lake.

The sediment Total Phosphorus concentrations are possibly less than were found in the last survey in 1989 by Rees. In 1989 the levels for the Upper and Lower Eastern Arms and Central Lake all contained levels of phosphorus typical for a eutrophic lake, as defined by Rees (1989) as 0.61–3.42 mgTP/g . The levels recorded are the average of the top 1 cm of sediment. The results showed the Upper Eastern Arm had 1.26 mgTP/g , the Lower Eastern Arm, 1.38 mgTP/g and the Central Lake 1.05 mgTP/g . However, these levels were based on the top 1 cm of sediment, the layer that is most phosphorus rich, compared to an average sample from the top 20 cm of sediment in the current survey, which is likely to show lower concentrations. Also the sediment cores in 1989 were taken in November when the sediment phosphorus levels are likely to be higher than in June, after there has been a likely phosphorus release from the sediment (Søndergaard et al 1999). Taking this into account it is possible that current survey shows decreased levels of phosphorus as only the TP sediment concentrations at the top of the Upper Eastern Arm are above 0.61 mg/g , with levels of 0.86 mg/g and 0.67 mg/g recorded (Figure 51). These levels are much lower than those in 1989 and are at the very lower end of the levels for a eutrophic lake. The Lower Eastern Arm and Central Lake have maximum TP levels of 0.54 mg/g and 0.42 mg/g , respectively. These are again much lower than the previous levels in Rees (1989) and are below the levels for eutrophic lakes. The Central Arm and the middle of the Western Arm have levels typical of mesotrophic lakes, at around 0.14 mg/g .

Overall it seems that the Upper Eastern Arm is eutrophic due to high phosphorus and nitrate levels both in the sediment and water column. The main problem in the Lower

Eastern Arm, Central Lake and lower Western Arm is elevated Total Phosphorus levels in the water column, whilst the Central Arm and upper Western Arm are mainly affected by elevated Total Nitrogen levels in the water column. The current trophic status of Bosherton Lakes is based on one survey between the 2nd and 4th of June 2008 and therefore may not be representative of the overall trophic status for the whole summer; several surveys would be needed to confirm these results.

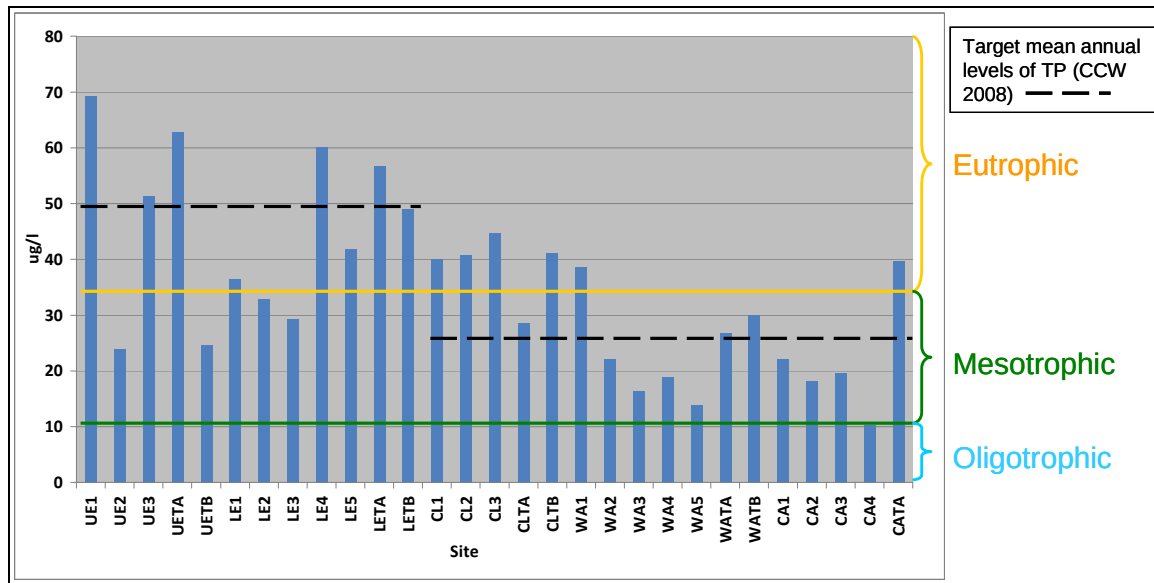


Figure 49: Lake trophic levels based on levels of Total Phosphorus in Bosherton lakes on June 2nd–4th 2008. The TP trophic boundaries are from the OECD (1982) fixed boundary scheme.

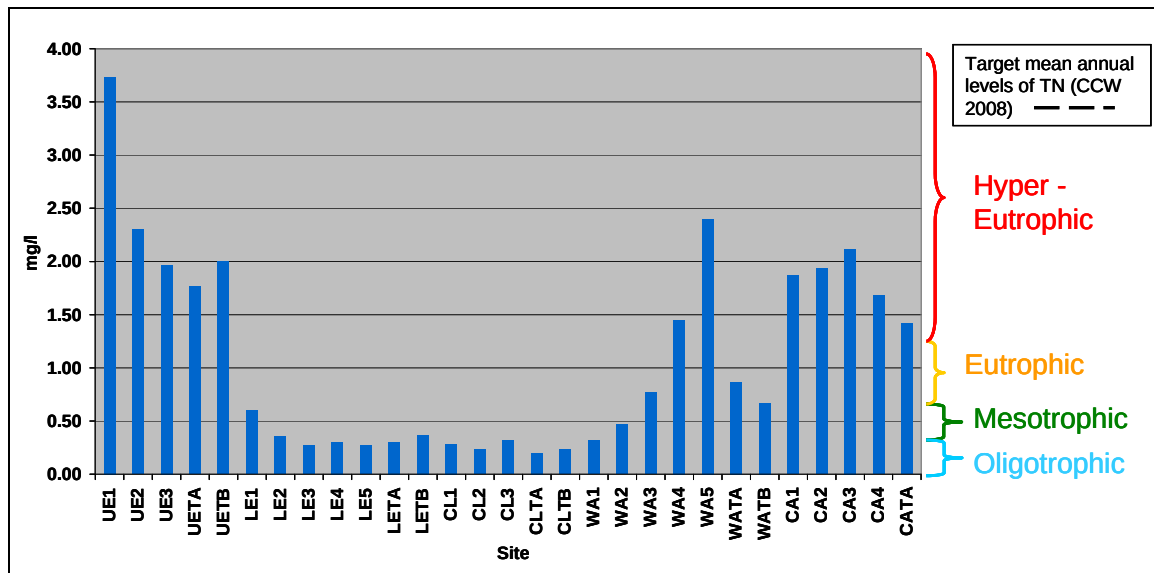


Figure 50: Lake trophic levels based on water Total Nitrogen in Bosherton Lakes on June 2nd–4th 2008. The TN trophic boundaries are the levels defined by Nürnberg (1996).

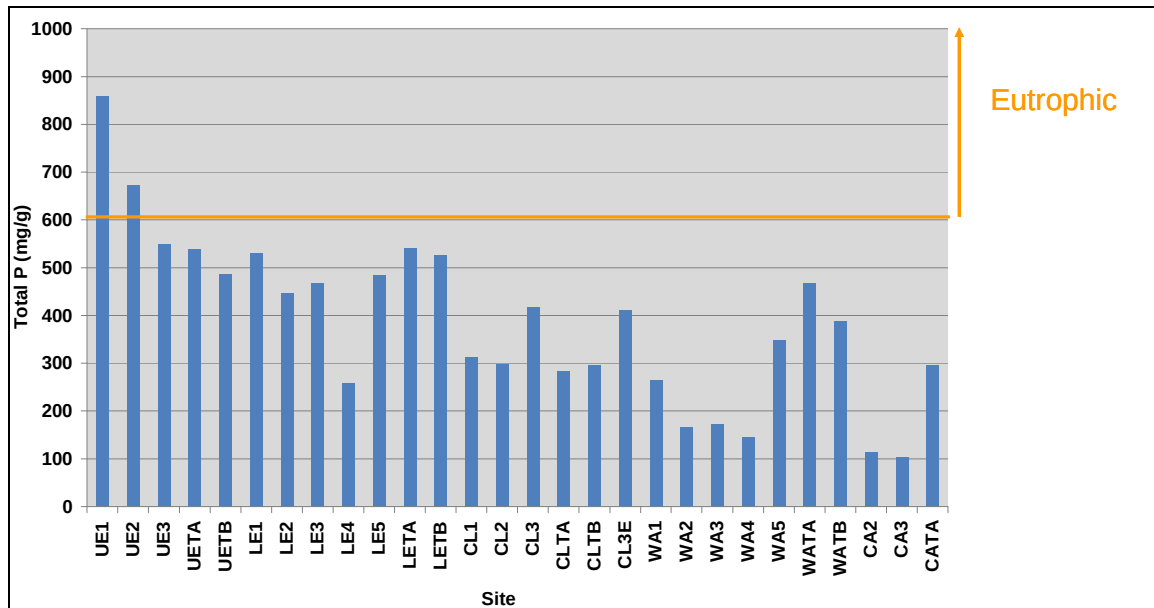


Figure 51: Lake trophic levels based on sediment Total Phosphorus in Bosherton Lakes on June 2nd–4th 2008. The level of eutrophication is taken from Rees (1989).

5.1.2 Source of nutrients to Bosherton Lakes

Given the differences in the nutrient levels in the sediment and water columns of the different water bodies, it is important to identify the sources of the nutrients to Bosherton Lakes during the summer baseflow period for future management of the lakes. Phosphorus will be addressed first followed by nitrogen.

5.1.2.1 Phosphorus

Internal phosphorus loading has been shown to be an important source of phosphorus to shallow lakes recovering from external loading during the summer, as shown in the Norfolk Broads and Loch Leven (Phillips et al 1999, Spears et al 2007b). The current survey between 3rd and 5th June 2008 show elevated Total Phosphorus levels within the Eastern Arm and Central Lake. This is likely to be mostly unreactive organic phosphorus, as the TRP, which consists mainly of inorganic reactive fractions, was found to be absent throughout the Bosherton Lakes at the time of sampling. This is possibly due to high biological uptake. Labile organic phosphorus is often loosely bound and is potentially available for release from sediments (Søndergaard et al 2003). However, the EA temporal data show elevated amounts of average (1994–2005) orthoP concentrations in August (79 $\mu\text{g/l}$ and 65 $\mu\text{g/l}$) within the Eastern Arm, showing that there is potentially inorganic phosphorus release from the sediments within at least the Eastern Arm. The higher orthoP levels in the summer/late summer are characteristic of internal phosphorus release and are most noticeable in the late summer as there is less uptake by plants (Granéli 1999; Søndergaard et al 1999; Spears et al 2007b). Spears et al (2007b) link these late summer peaks with redox-sensitive release from the sediment, possibly triggered by higher water temperatures in the late summer. This shows that it is probable that phosphorus release from sediments is occurring during the summer in the Eastern Arm, but not necessarily in the other ‘arms’.

It has been proposed that there is little seasonal difference in phosphorus release in lakes with phosphorus levels below 0.05 mg/l and only a short period in the summer where there is release in lakes with levels below 0.1 mg/l (Søndergaard et al 1999). The Eastern Arm average August (1994–2005) TP levels during the summer, shown by the EA data, are above 0.1 mg/l, whereas the other ‘arms’ are under 0.05 mg/l during the summer. This may help explain the more obvious seasonal differences in phosphorus levels in the Eastern Arm. The current data from samples taken between the 3rd and 5th June 2008, also suggests that there would be higher phosphorus release from the sediments in the Eastern Arm as there is a correlation between sediment TP loads and the mean TP concentrations in the lake water column. They both decrease in order of the Upper Eastern Arm, Lower Eastern Arm, Central Lake, Western Arm and Central Arm. A Spearman's Rank Correlation test also shows that there is less than a 5% chance that the correlation between the water and sediment phosphorus levels occurred by chance (Appendix N). The higher phosphorus levels in the Eastern Arm sediment may therefore indicate that there would be higher release rates.

Another likely reason as to why there is higher phosphorus content in the sediment and higher release in the Eastern Arm is the differing CaCO_3 and iron oxide contents within the sediment. These were not analysed within this study but Rees (1989) showed that the CaCO_3 content increased and the iron oxide content decreased in the following order: Upper Eastern Arm, Lower Eastern Arm, Central Lake, Western Arm and Central Arm. The streams entering the lake carry a relatively high content of clays and iron oxides which can increase the adsorption of phosphates onto the sediment in the Eastern Arm (Rees 1989). Rees (1989) proposes that it is the iron content rather than the CaCO_3 content that is the most important factor in lakes dominated by calcareous sediments. The higher iron content in the Eastern Arm will mean that the sediment is more susceptible to phosphorus release from iron bound fractions under redox conditions. The late summer peaks in orthoP in the Eastern Arm shown by the EA data have been associated with redox-sensitive release from sediments, which is linked to the iron content, and as there is a higher iron content in the Eastern Arm it may explain why the peaks in orthoP are visible here but not in the rest of the lake (Spears et al 2007b). Rees (1989) suggests that the Bosherton lake sediments are anoxic and therefore the conditions are favourable for phosphorus release from iron oxides (Søndergaard et al 2003). The absence of late summer peaks in the EA data for the Central Arm and upper Western Arm may possibly be due to co-precipitation of phosphorus with calcite on the *Chara*, removing any phosphorus from the water column that may have been released from the sediment (Hilt et al 2006). Through weed harvesting this is also removed from the system, and so reduces the amount within the sediment.

Nitrate levels are very high in the upper Western Arm and Central Arm and the Upper Eastern Arms. There are conflicting views as to whether nitrates inhibit or increase the release of phosphorus from sediments. It is difficult to assess the affect of nitrates on phosphorus release in the Bosherton Lakes. There are areas of high Total Phosphorus in the lake water and low nitrates, but there are also areas of high Total Phosphorus and high nitrates as well as areas of low Total Phosphorus and high nitrates. It may be linked to the iron content within the sediment. Boström et al (1988) state that excess nitrates can increase the growth of bacteria that reduce iron and release phosphorus,

therefore the high nitrates in the Upper Eastern Arm may increase the release of phosphorus more than in the Western and Central Arms, another possible explanation of the late summer orthoP peaks in the Upper Eastern Arm shown by the EA data.

Three further factors that are important for phosphorus release from sediments are pH, dissolved oxygen (DO) and temperature. The following discussion is based on readings taken between 2nd and 4th June 2008, and is therefore only based on a snapshot in time and may not be consistent for the whole of the summer period. There is slightly higher pH in the Eastern Arm, which can increase the potential of phosphorus release as it reduces the ability of phosphorous to bind to iron. This would also affect the Eastern Arm more due to the higher levels of iron in the sediment (Boström et al 1988). The water throughout the lake is well aerated, with saturation levels above 100% recorded (Figure 37 Section 4.4.3). This may be due to the high photosynthetic activity of the vegetation during the day (Brönmark and Hansson 2005). Boström et al (1988) explain that phosphorous release rates in shallow lakes that are oxic can be of the same magnitude as those from anoxic bottom waters of deeper, stratified lakes. The temperature is quite consistent throughout the lake and is less likely to explain any differences in release rates. However, overall, because the lakes are shallow the water temperature near the sediment changes seasonally with the air temperature, and there is generally only a few degrees difference between the surface and bottom water temperature in the lakes (Figure 36, Section 4.4.2). Jensen and Andersen (1992) found that in a study of four shallow lakes in Denmark temperature explained approximately 70% of the seasonal variation in phosphorus. In the summer the higher water temperatures will increase the rates of release of phosphorus compared to deeper stratified lakes. Spears et al (2007b) concluded that temperature may have played an important role in a mid summer peak of phosphorous and in areas where there were high phosphorous release rates. They note that temperature increases microbial activity which mineralises the organic phosphorous pool. Retention times can also be important in explaining high levels of TP and orthoP during the summer in the Eastern Arm. The retention times in the Eastern Arm are up to 72 days, compared to 15 days in the Central Arm, which means that less of the phosphorus is flushed from the system, contributing to the higher concentrations in the Eastern Arm.

The current survey (3rd–5th June 2008) also indicates that there are elevated levels of phosphorus within the Central Lake and the very lower end of the Western Arm, though not in the Central Arm and most of the Western Arm. The most probable explanation for this, rather than high release rates, though there may be some release, is the influx of phosphorus rich water from the Lower Eastern Arm, which is due to internal loading rather than stream water inputs. At the time of the survey there was still water entering the Central Lake via the weir in the Grassy Bridge Dam. The higher concentrations in the Eastern Arm may be due to additional phosphorus entering from the streams during the summer; the other ‘arms’ are less likely to be affected by the stream water as the hydrological connectivity between ‘arms’ is reduced during the summer. Within this study there seem to be higher concentrations of both TRP and TP within the stream water than the lake water. This indicates that the streams may still be an important source of phosphorus to the lakes even under baseflow conditions. However, this is only based on two sampling dates from the streams (June 11th 2008 and July 8th 2008) and only one period of sampling on the lakes (June 2nd–4th 2008).

The phosphorus within the sediment can enter the lake as dissolved phosphate and be adsorbed onto the sediment in the lake, can enter the lake already attached to sediment and settle to the bottom of the lake, or can be contained in vegetative material within the lake that then dies and settles on the bottom of the lake.

The first two processes would normally be important during the winter when there are higher rainfall events bringing phosphorus into the lakes from external sources. The EA data shows that there is a possible increase in orthoP in the winter in the lake water column, after a fall in autumn, most noticeable in the Eastern Arm and Central Lake. This may indicate that there are still external sources of phosphorus entering the lake in dissolved forms during the winter. The average monthly (1997–2005) EA data for the stream inflows shows that there may be an increase of orthoP in the winter but the standard error shows that there is a large scatter in the data and that this increase is not statistically significant. It is believed that point sources within the catchment have been managed sufficiently since the diversion of the Stackpole STW (Ellis 2008). It is possible though that unidentified sources of dissolved phosphorus, such as septic tanks are still a problem (see Section 5.2) and the effect of the Merrion STW is still unknown.

The issues of sediment input from the streams and the decomposition of in-lake vegetation were partly addressed in the early 1990s, with the introduction of annual weed cutting to remove this source of phosphorus, and in 1994 silt traps were dug in the streams feeding the lakes. It is known from Clews (2001), however, that the sediment traps are not as effective as was hoped, and that there is still sediment entering the lake during winter rainfall events. Therefore, the current high phosphorus content of the Eastern Arm sediment is probably due to phosphorus entering the lakes during the winter attached to sediment and then settling in the Eastern Arms. Holman et al (2007) have shown that the sediment thickness is higher in the Lower Eastern Arm, Central Lake and Lower Western Arm, and below the Eight Arch Bridge and Grassy Bridge Dam, which shows that the sediment is generally settling in the Lower Eastern Arm and Central Lake, which also have some of the highest sediment loads. There are increased levels of phosphorus in the sediment below the Eight Arch Bridge and before and after the Grassy Bridge Dam, supporting the fact that areas where sediment is trapped and settles have increased phosphorus loads. The increased connectivity of the lakes during the winter when water levels are higher allows the sediment to be transported further down the lake system. The main sources and processes affecting the phosphorus concentrations in the lake water during the summer and winter are summarised in Figure 52.

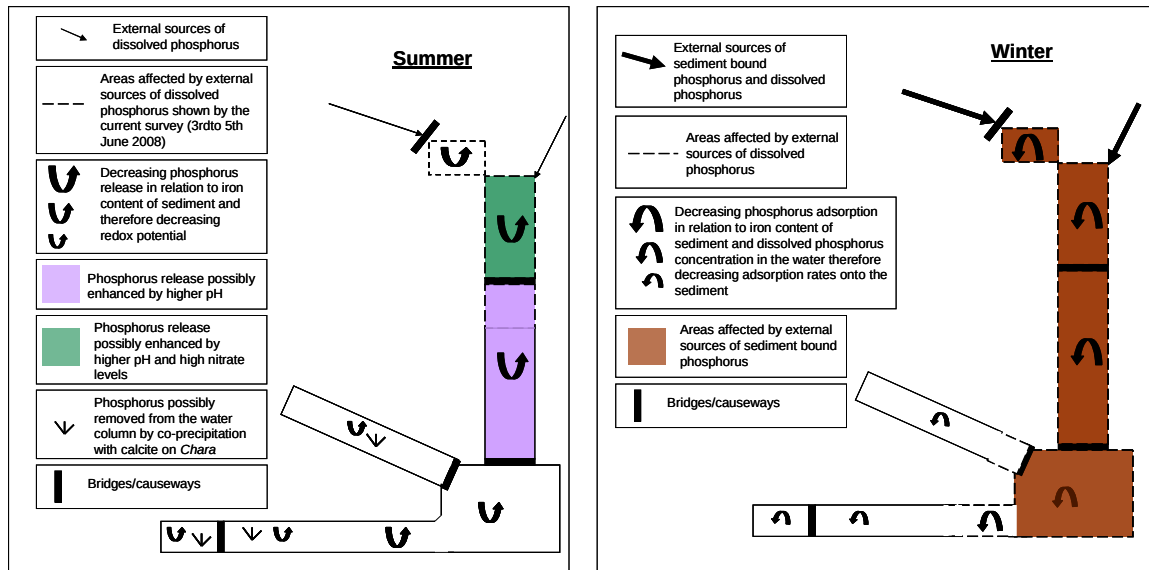


Figure 52: Schematic of Bosherton Lakes showing the main sources and processes that may explain the differing phosphorus concentrations during the summer based on current and previous surveys of the lakes (Rees 1989). The winter diagram is based on predicted phosphorus dynamics in the winter and previous research on sediment inputs and levels in the lakes (Clews 2001; Holman et al 2007).

5.1.2.2 Nitrates

There are elevated nitrate concentrations within the lake in the summer in the upper parts of the Central Western and Lower Eastern Arms and the Upper Eastern Arm, as shown in this study and confirmed mostly by the EA data (Figure 47 Section 4.5.3). The source of the elevated nitrate levels within the Upper Eastern Arm are most likely to be from the stream water. There are high nitrate concentrations entering from Cheriton Brook and also moderate levels from the Merrion Stream, with the higher discharges of the latter contributing more to the nitrate load to the lakes than Cheriton Brook. However, the velocity readings are possibly inaccurate in many places due to the difficulty of recording the low velocities. In the current survey the nitrates seem to be carried throughout the Upper Eastern Arm and into the upper part of the Lower Eastern Arm, as there was still a small amount of flow over the weirs under the Eight Arch Bridge. There is little nitrate within the rest of the Eastern Arm, Central Lake and Lower Western Arm. This may be due to little movement of water in the summer between the 'arms.' This therefore increases the likelihood that the phosphorus in the lake water of the Lower Eastern Arm and Central Lakes is due to release from the sediment, rather than the transfer of dissolved phosphorus between the lakes. The elevated nitrate levels within the Central Arm and Upper Western Arm are more likely to be due to elevated levels within the groundwater and springs that feed these lakes. The direction of the groundwater can be seen in Figure 6 (section 2.2). This shows that there is groundwater feeding the Central and Western Arms, from predominantly agricultural land to the west of the lakes, as well as into the downstream end of the Lower Eastern Arm from the east of the lake.

The groundwater concentration at the Devils Quoit borehole of 54 mgNO₃/l is just one result from November 2006. Therefore, this does not show summer concentrations and may have been after a large rainfall event. However, it does show that the groundwater can be susceptible to extremely high concentrations. If there was a high nitrate concentration in this area in the summer it would be expected to be reflected in the Lower Eastern Arm nitrate concentrations. There is little nitrate in the lower part of the Eastern Arm that is thought to be influenced by the groundwater but it is possible that it might feed the upper part of the Lower Eastern Arm and help to explain the nitrate concentrations in this area. It is of course possible that the nitrate levels during the summer in the groundwater in this area are low, or that the groundwater flow into the lakes is low. The Sampson borehole, with a concentration of 18 mgNO₃/l, is based on five years of summer data; therefore it has the most accurate average level of nitrate in the groundwater of all three boreholes and shows that there are high levels within the groundwater from the land to the west of the lakes. These levels are supported by the result from the White Well that feeds into the top of the Western Arm, with a nitrate concentration of 19.23 mg/l. This shows that there are nitrates entering the Central and Western Arm, from the groundwater. The main sources and areas affected by nitrates in the summer and winter are summarised in Figure 53.

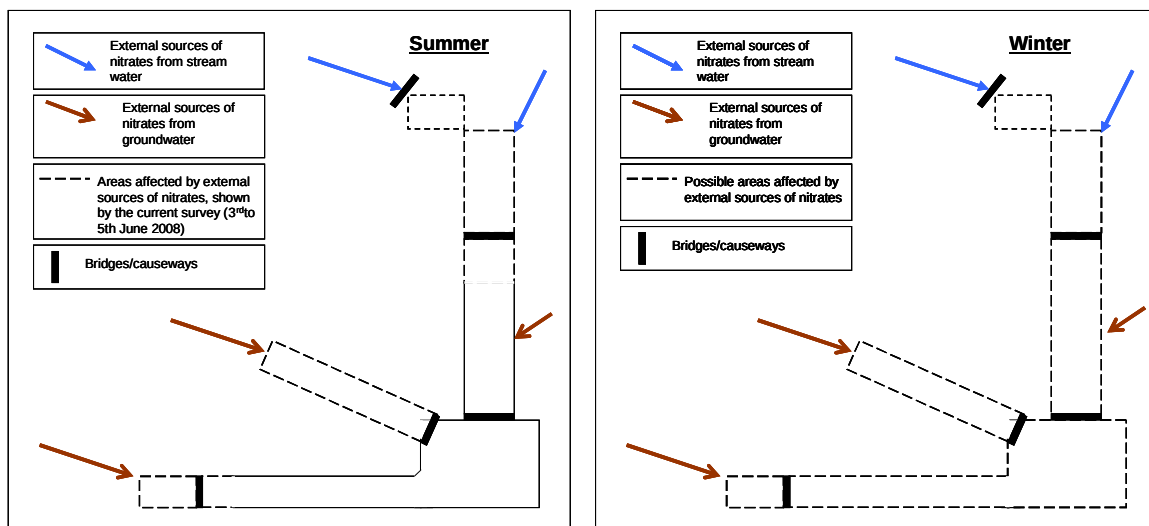


Figure 53: Schematic of Bosherton Lakes showing the main sources and processes that may explain the differing nitrate concentrations during the summer based on the current survey (3rd to 5th June 2008). The winter diagram is based on predicted higher nitrate concentrations and rainfall in the winter and increased hydrological connection of the lakes.

5.1.3 Source of nutrients to the streams and groundwater

It seems that even under baseflow conditions there are still nitrates and to a lesser extent phosphates entering the lakes from the surrounding catchment through the streams and groundwater. Therefore, it is important to identify the possible sources of the nutrients to allow for future management options to be considered. The EA has limited temporal data on the stream nutrient levels, with only two sites at the mouths of the Merrion Stream and Cheriton Brook and one below the sediment trap on the Cheriton Brook. These sites are useful to see the concentration of nutrients entering the lake but do not

help to identify possible sources of the phosphates. The following discussion on the possible sources of nutrients to the streams and groundwater is based on two sampling dates, one in July and one in June. This may not be representative of every summer; therefore, further monitoring of the sites is required to confirm that this is a persistent problem.

The highest concentrations for phosphates are found towards the headwaters of the Merrion Stream (site MW) and the Cheriton Brook (site Ch/St). These sites also have high levels of nitrates, as has an additional site at the headwaters of the Castle Dock Stream. The sources of these nutrients may be from fertilisers, for example high phosphates near the Merrion and Cheriton Brook headwaters may be from slurry or manure applied in these areas but not near the Castle Dock headwaters. Clews (2001) shows that the Castle Dock catchment has the lowest percentage of pastoral land and therefore probably lower livestock numbers, though it is unknown whether these areas are improved or unimproved grassland which have different nutrient inputs. The Merrion Stream has the highest concentration of pastoral land and therefore probably higher livestock, most likely cattle as the area is dominated by dairy farming. However, diffuse sources of nutrients from agriculture, particularly phosphorus, are generally worse in the winter during runoff events. There does seem to be an increase in phosphorus in the July samples that were taken after heavy rain, though there is not a coinciding increase in nitrate levels. This may be expected if the runoff was mostly surface flow as it would possibly carry more sediment bound phosphorus rather than soluble nitrates that may be lost to the groundwater or sub-surface flow rather than being carried in surface runoff.

It is maybe more likely that the source of the high phosphates in the headwaters of the Merrion Stream and Cheriton Brook is due to sewage effluent, possibly from private sewers or septic tanks. These sources are generally independent of hydrological events and therefore would give a more constant source of phosphorus to the streams during the summer. A study into septic tanks in the Loch Leven catchment area showed that only 10% of properties found to have septic tanks were registered with the Scottish Environment Protection Agency (SEPA) and that a large number are not maintained properly (Dudley and May 2007). The sampling points are both near built up areas: the MW site is next to a large private home and near the village of St Twynnels, whereas the Ch/St site is situated near the church in the village of Cheriton/Stackpole. This may also help explain the low levels of phosphorus in the Castle Dock stream which is surrounded by fields rather than an urban area. There seems to be little phosphorus being added by the Merrion STW as the levels do not increase downstream, though it was not possible to sample soon after the STW as the stream in this area was dry.

Inorganic fertilisers may have been applied to the land near the headwaters of all the streams and could explain the elevated nitrate levels. The streams in the summer are more likely to be dominated by groundwater than surface runoff and it is known that there can be high concentrations of nitrates transported within the groundwater. High levels of nitrates in the groundwater are indicated by the high nitrate levels but low phosphorus levels in the spring at the headwaters of the Castle Dock stream, indicating that this may be groundwater fed. According to Clews (2001) the Cheriton Brook catchment has the highest percentage of arable land and could contribute high levels of

nitrates, whereas the Merrion catchment has the lowest percentage of arable land. DEFRA (2007) state that 60% of nitrates in English waters come from diffuse pollution from agricultural sources. Nitrates are generally highest in areas of arable farming due to higher fertiliser inputs to the land (DEFRA 2008a). The elevated level of nitrates near Sampson (site S) on the Merrion Stream may be due to elevated levels of nitrates in the small tributary feeding this part of the Merrion Stream. There is an excessively high nitrate concentration at the Ch/St site at the headwaters of the Cheriton Brook of 40.14 mg/l which is nearing the 50 mg/l safe drinking water limit set out in the EU Nitrates Directive (91/676/EC). There is also a possibility that nitrates within sewage effluent from septic tanks/private sewers in the village are contributing to the elevated levels at this site.

Agriculture is the most probable source of the nitrates within the groundwater especially as the land to the west of the lakes is on top of limestone and therefore nitrates are easily lost into the groundwater. The karstic nature of the underlying geology makes it easy for the groundwater to reach to the lakes. The groundwater flow is likely to be lower during the summer than the winter.

5.2 Charophytes

The Bosherton Lakes are classified as an SAC partly due to the habitat created by the charophytes (JNCC 2008). There has been research into the phosphorus tolerance levels of the species present in Bosherton Lakes (Davidson n.d.). Figure 54 shows the mean Total Phosphorus levels in the lakes and the tolerance levels of the *Chara* levels suggested by (Davidson n.d.). The Eastern and Central Lake continue to have higher phosphorus levels than *C. globularis* and *C. hispida* can generally tolerate. However, the Central Arm has levels that would support *C. virgata* and possibly *C. vulgaris*. The Eastern Arm generally has levels above which most *Chara* can tolerate, though the levels of phosphorus in some areas, such as the upper section of the Lower Eastern Arm, do have lower levels that could possibly support *C. globularis* or *C. hispida*.

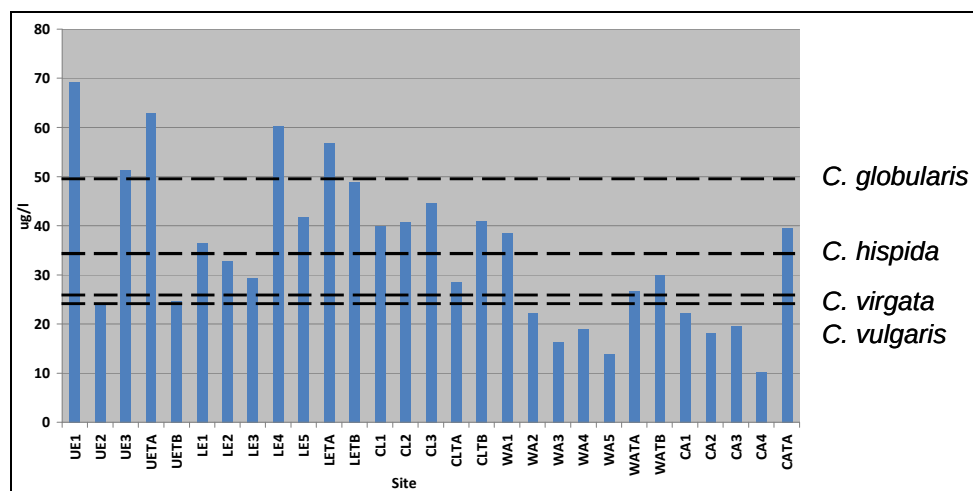


Figure 54: Mean of surface and bottom lake water TP levels (samples taken between 2nd and 4th June 2008) and charophyte TP tolerance levels taken from (Davidson n.d.)

Regular vegetation surveys are carried out on the lakes. They show that no *Chara* have been present within the Upper Eastern Arm and lower part of the Lower Eastern Arm since the records began in 1977, apart from in 1992 when *C. globularis* appeared in the Upper Eastern Arm. In the upper section of the Lower Eastern Arm there have been a few appearances of *C. globularis* (1986, 1995, 1998 and 2006), all of which again coincide with years of lower phosphorus levels shown by the EA nutrient data. *C. hispida* is the main species present in the Central Lake towards the overflow, though in 1995 and 1998 *C. globularis* was also present. This again coincides with the lower phosphorus levels within the mid-late 1990s. However, in the Central Lake near the Western Arm and Central Arm causeway both *C. hispida* and *C. globularis* have been present since the late 1980s, though *C. hispida* is most abundant; the greatest abundance again coincides with the decrease in phosphorus seen in this area in the mid-late 1990s. This possibly indicates that the most phosphorus-rich water is flowing towards the overflow rather than backing up towards the Central and Western Arms. *C. hispida* is the most abundant in the Western Arm with some appearances of *C. globularis*. The survey shows that *C. hispida* is most abundant in the top and middle of the Western Arm and the Central Arm. Therefore, it seems that there is little *C. virgata* or *C. vulgaris* present in the Bosherton Lakes, even in the Western and Central Arms. There is a more consistent presence of *Chara* within the Western and Central Arms that coincides with the consistently lower levels of phosphorus. This all shows that the *Chara* are most abundant in the areas that have lower phosphorus levels, the Western and Central Arms, whereas *Chara* are mostly absent from the stream-fed Eastern Arm, with its higher water and sediment phosphorus levels.

Nitrate levels may also be a risk to the *Chara*. Experiments in a shallow Danish lake have shown that high nitrate levels are a risk to submerged macrophytes only when the TP levels are above 0.1–0.2 mg/l, and that varying nitrate loads when there are low levels of phosphorus has no impact (González Sagrario et al, 2005). This seems to be supported by the continuing *Chara* growth in the Central Arm and upper Western Arm where there are low phosphorus levels but high levels of nitrates. There has been research that shows low TN:TP ratios can increase the risk of cyano-bacteria blooms (Smith 1983; Nøges et al 2008). An increase in algal blooms can have a negative impact on the *Chara* through a reduction in light. Downing and McCauley (1992) state that there needs to be over 30 µg/l Total Phosphorus in the water for the blooms to occur, even if the N:P ratio is low. Therefore, the areas that are most at risk at the moment according to this theory are the Lower Eastern Arm and Central Lake (Figure 33 Section 4.3). With this theory even if the nitrogen levels decreased within the Western and Central Arms, reducing the N:P ratio, the levels of phosphorus are still normally below 30 µg/l and therefore there is little risk of increased cyano-bacteria blooms. Reduced nitrates in the Upper Eastern Arm may increase the risk of blooms as the levels of phosphorus are higher in this area. The most regular appearances of cyano-bacteria occur in the Eastern Arm, though it can occur in other parts of the lake system on occasions, but the last significant bloom was in the early 1990s (Haycock 2008a pers comm). Therefore, even though the N:P ratios are low in some areas there does not seem to be an increased risk of significant cyano-bacteria blooms, nor do high levels of nitrate seem to have an impact on the *Chara* community. The evaluation of the affect of N:P ratios are based only on the records collected between 2nd and 4th June 2008.

The lack of *Chara* within the Eastern Arm may be because of the sediment thickness. The thicker and more fluid sediments in the Eastern Arm (Figure 7) can hinder *Chara* growth as they need a stable rooting medium and the thick sediments can mean the oospores may be lost as they sink into the sediment (Davidson n.d.). The sediment thickness is much lower in the Central Arm and varies in the Western Arm but is generally lower. Observations when taking the sediment samples also show a difference in the sediment structure with more cohesive sediments in the Central Arm.

5.3 *Climate Change*

The lake connectivity between the different ‘arms’ and the sea, as well as the nutrient dynamics within the catchment are all likely to be influenced in the future by climate change. Studies into the effects of climate change on shallow lakes are still in experimental stages and are not conclusive (Mooij et al 2007, Jeppesen et al 2007). However, the current conclusion is that future climate change may lead to a stabilisation of a turbid state as higher temperatures as well as a predicted increase in nutrient loading will lead to dominance of cyano-bacteria and other algal species during the summer; therefore nutrient level targets need to be lower than those presently set to compensate for predicted future increases in nutrient loading (Mooij et al 2007, Jeppesen et al 2007).

In the south-west of Wales there is predicted to be a decrease in summer precipitation as well as an increase in summer temperature and higher evapotranspiration (Hulme et al 2002). This will mean that the water levels within the lakes are likely to decrease during the summer/autumn, which could have an impact on the water quality by possibly providing less dilution of phosphorus released from the sediments (Miller 2007). The phosphorus release experiments in this current study, as well as those of previous studies, show that increased temperatures can stimulate the release of phosphorus from sediments (Kim et al 2003; Kim et al 2004; Spears et al 2007a). The lower water levels and increased summer air temperature will mean that there is likely to be an increase in the lake water temperature. This may lead to increased release of phosphorus through the stimulation of bacteria that can reduce iron-bound phosphorus, or through reduced dissolved oxygen contents that may lead to longer periods of anoxia and associated reduction of iron oxides (Boström et al 1988; Jensen and Andersen 1992; Spears et al 2007a). The increase in temperature may have more of an impact on the Eastern Arm as these sediments have the higher iron content. The separation of the ‘arms’ of the lakes may occur earlier in the summer due to the lower precipitation and higher evapotranspiration. This may have a positive effect in reducing the amount of connectivity of the nutrient-rich Eastern Arm with the Central Lake, Western and Central Arms and reduce the levels of nutrient rich waters transferring between them during the summer months.

It is also predicted that there will be an increase in winter precipitation which may lead to increased erosion and sediment loads to the lakes (Hulme et al 2002). The increased sediment load may bring an associated increase in sediment phosphorus load in the Eastern Arm and possibly the Central Lake which may then lead to increased release in the summer. The increased sediment depth, especially loose sediment, within the lake may also be detrimental for the *Chara* as they prefer shallow more stable sediment. The

increased precipitation in the winter will also increase the leaching of nutrients to the groundwater and increase surface runoff. Therefore, not only might there be increased sediment loading to the lakes but also increased nutrient loading from agricultural runoff and leaching to the groundwater. The increase in nutrient loading and increased summer temperatures may also lead to a higher risk of cyano-bacteria blooms.

The UKCIP02 report predicts that there will be a small increase in summer windspeed though there is more uncertainty when predicting this compared to rainfall and temperature (Hulme et al 2002). This may increase the risk of phosphorus release from sediment. The lower lake levels will mean more of the water column is near to the sediment surface and any wind disturbance is likely to lead to increased sediment re-suspension that can help to release phosphorus built up in the sediment pore water and it can help maintain a diffusion gradient for release (Boström et al 1988; Pettersson 1998; Koski-Vähälä and Hartikainen 2001). The increased windspeed and associated increase in re-suspension of sediment may also increase the turbidity of the lakes which will again have a negative impact on the *Chara*.

Overall, the future climate changes will generally increase the risk of internal phosphorus loading from sediments during the summer, mainly within the Eastern Arm and possibly increasing the risk in the Central Lake. The Eastern Arm and Central Lake will also be more susceptible to the predicted increased sediment load in the future, and therefore the possible increase in sediment phosphorus load. There will also be an increased risk of external loading of nutrients in the winter due to increased precipitation, leaching and surface runoff. However, the decrease in summer precipitation may lead to lower external nutrient loading from runoff and erosion during the summer.

Land use changes that could occur in the future are important as they could reduce or exacerbate some of the predicted changes due to climate change, for example there may be less soil erosion if there is a decrease in arable farming. If nutrient application and stocking of animals decreases in the area or different farming practices are employed, there may be less need to worry about the future climate changes. The lake sediment phosphorus concentration may be decreasing, possibly due to weed cutting and sediment traps reducing the amount of phosphorus available for adsorption or deposition. Land use change may play more of a role in the risk of future nutrient enrichment than climate change. If external phosphorous loading linked to sediment can be decreased then the amount of phosphorus in future sediment layers within the lakes will be low. Nitrate loading in the streams and groundwater need to be addressed to reduce a risk of increased loads in the future due to climate change, especially as levels are already nearing the safe limits for drinking water.

There is also a separate risk to the Bosherton Lakes in rising sea levels and saline intrusion into the lakes via the overflow. The Central Lake and lower Western Arm are possibly most at risk as they are most connected to the overflow. The predicted decrease in summer water levels will also increase the salinity of the lakes as there will be less freshwater to dilute any saline water entering the lakes. Therefore, not only is the *Chara* in the Central Lake and Western Arm at risk due to nutrient levels but also they are at risk because of increased salinity.

5.4 Future Management

The main problems for the individual ‘arms’ of Bosherton Lakes in winter and summer, taking into account climate change and the findings of this study, are summarised in Figure 55.

<p><u>Central Arm</u></p> <p><u>Summer:</u></p> <ul style="list-style-type: none"> • Possible internal sediment phosphorus release • Nitrates from groundwater <p><u>Winter:</u></p> <ul style="list-style-type: none"> • Possible dissolved P from Eastern Arm/Central Lake phosphorus • Nitrates from groundwater 		<p><u>Upper Eastern Arm</u></p> <p><u>Summer:</u></p> <ul style="list-style-type: none"> • Internal sediment phosphorus release • Dissolved P and N in stream water. <p><u>Winter:</u></p> <ul style="list-style-type: none"> • External inputs from streams in dissolved P and N and sediment attached P
<p><u>Western Arm</u></p> <p><u>Summer:</u></p> <ul style="list-style-type: none"> • Possible internal sediment phosphorus release • Nitrates from groundwater in upper section <p><u>Winter:</u></p> <ul style="list-style-type: none"> • Possible Dissolved P from Eastern Arm/Central Lake phosphorus in lower section • Nitrates from groundwater may affect all of Western Arm 		<p><u>Lower Eastern Arm</u></p> <p><u>Summer:</u></p> <ul style="list-style-type: none"> • Internal sediment phosphorus release • Possible dissolved P and N in the lake water from Upper Eastern Arm affecting upstream part of the Lower Eastern Arm <p><u>Winter:</u></p> <ul style="list-style-type: none"> • External inputs of dissolved P and N in stream water and lake water from Upper Eastern Arm • Possible sediment attached P from streams due to increased connectivity with Upper Eastern Arm and increased flow
<p><u>Central Lake</u></p> <p><u>Summer:</u></p> <ul style="list-style-type: none"> • Inflow of nutrient-rich waters from the Eastern Arm prior to water levels dropping • Possible internal sediment phosphorus release <p><u>Winter:</u></p> <ul style="list-style-type: none"> • External inputs of dissolved P and N in lake water from Eastern Arm as more connectivity between lakes • Possible sediment attached P from suspended sediment in lake water from Eastern Arm 		

Figure 55: Summary of current and future problems requiring management in Bosherton Lakes

The main issues, in terms of phosphorus, that should be a priority in the future management of the lakes are reducing the vulnerability of the surrounding catchment to sediment erosion or increasing the effectiveness of preventing this sediment reaching the lakes. This is important to improve the quality of the Eastern Arm and possibly the Central Lake, especially with the predicted increase in precipitation during the winter. An influx of potentially phosphorus rich sediment from the surrounding agricultural land during the winter to the lakes may increase the potential for release from this sediment during the summer months. Managing the sediment influx to the lakes will also have an added benefit of helping reduce the rate of sedimentation of the lakes and therefore reduce the risk of the lakes infilling and becoming marshland. This is a separate issue in the lakes and only recently in 2007 was the upper part of the Western Arm, above the causeway, dredged as it had become almost completely silted up (Bob Haycock, personal communication, email 08/08/08).

Currently there are five sediment traps on the Cheriton Brook and Castle Dock stream as well as the One Arch Pond before the One Arch Bridge on the Merrion Stream. These are dredged every 2–3 years to remove sediment, though there are now less areas

available to put the sediment on after it has been removed (Bob Haycock, personal communication, conversation 04/06/08). Volunteers have built wooden dams in the streams in places to try and trap some of the sediment. The red sediment from the sandstone is easily identifiable and some of this is being given back to the farmers to apply to the land and also to demonstrate how much soil they are losing. Dredging in the Eastern Arm may remove the phosphorus rich surface layer and reduce the risk of re-suspension in the future, therefore reducing the risk of increased turbidity. If dredging is implemented it should be carried out mid-winter when the sediment phosphorus levels are highest (Spears et al 2007b). There are practical difficulties in doing this as the water levels will be higher. It may instead be possible to utilize the pipe that runs under the Central Lake from the Eastern Arm to flush water loaded with sediment from the Eastern Arm during the winter. It is important that annual weed harvesting in the lakes is continued to remove a large source of phosphorus to the lakes, though it is recognised that this may have an impact on the ecology of the lakes.

The sediment traps are possibly insufficient to deal with the high sediment load, which is only likely to increase in the winter with the predicted increase in precipitation. There are also problems in where to put dredged material from both the traps and the lakes. It may be more useful to address the loss of the sediment at the source rather than during transport or after deposition. With the proposed introduction of the NVZ the farming community will have to change their practices; therefore it is a good opportunity to also introduce changes that will help prevent soil erosion. Farmers should be encouraged to introduce practices that could reduce soil erosion such as change in ploughing techniques or possibly the introduction of buffer strips. Techniques that benefit the farmers by keeping the nutrient rich topsoils on the land should be encouraged. Farmers in an NVZ are required to comply with closed periods where it is prohibited to apply fertilisers or manures, to comply to limits on the amount of nitrogen that can be applied and have sufficient slurry storage (DEFRA 2008b). This would hopefully reduce the amount of nitrates applied to the land and reduce the likelihood that they would leach or runoff into the streams and groundwater. The introduction of the NVZ will help reduce the vulnerability of the lakes to the possible increased nitrate loading in the future due to climate change. The NVZ will be more beneficial in the future if there is the predicted increase in phosphorus loading as nitrates seem to have more of a negative impact on the *Chara* when there are higher phosphorus concentrations (Section 5.2). The NVZ may be required also as the levels of nitrates in the streams are nearing levels that are unacceptable for drinking water.

It should also be noted that there may be unknown sources of TRP that are entering the streams during the summer when diffuse sources are less of an issue, especially with the predicted decrease in precipitation. The high TRP levels in the headwaters of the Merriam and Cheriton Brook streams that are near built up areas may indicate that there are septic tanks or private sewers nearby. If this is found to be the case further management will be needed to prevent phosphorus entering the streams from these sources.

6 CONCLUSION

Bosherston Lakes are a Special Area of Conservation (SAC) under the Habitats Directive mostly because of the habitat, which, under Annex 1, is classified as 'Hard oligo-mesotrophic waters with benthic vegetation of *Chara* species' (JNCC 2008). This should be characterised by low nutrients and very clear water. There has been a problem with high nutrient concentrations and algal blooms within the Bosherston Lakes, particularly in the stream-fed Eastern Arm. It is important to understand the nutrient dynamics in Bosherston Lakes and the surrounding catchment as well as recognising the potential impacts of climate change in order to be able to efficiently manage the site in the future to preserve the important *Chara* habitat.

External sources of phosphorus have been managed in the past, with the diversion of the Stackpole STW (1984) and installation of silt traps (1994). There has also been some internal management, with the introduction of weed cutting in the 1990s. This has reduced the amount of Total Phosphorus entering the lake system during the summer, especially evident after the STW diversion. Some possible sources of phosphorus to the streams during the summer have been identified in this study as potentially due to unknown and poorly maintained septic tanks/private sewers or from agricultural land at the headwaters of the Merrion and Cheriton Bottom Streams. The phosphorus levels entering the lake cannot solely explain the concentrations within the lake; the lakes therefore appear to be suffering from internal loading. This study showed that the Total Phosphorus concentrations within the lake water correlate well to the sediment Total Phosphorus concentrations. Sediments in the Eastern Arm and Central Lake have the highest concentrations of Total Phosphorus in the sediment. From comparison with Rees (1989), the levels of phosphorus within the sediment may have decreased, with only the Upper Eastern Arm having levels typical of eutrophic lakes, though this is comparing the phosphorus rich top 1 cm of sediment with an average of the top 20 cm.

The Eastern Arm has the potential for most phosphorus release from the sediments and therefore is the most at risk from internal loading. This is shown by the Environment Agency data from 1994-2005 that indicate late summer peaks of orthophosphates in the Eastern Arm, suggested in previous studies to represent internal loading (Spears et al 2007). The Eastern Arm also has a higher proportion of iron-bound phosphorus, indicating a higher potential for release of phosphorus through redox reactions, and the highest pH in the water, which has been linked to increased phosphorus release rates, and the longer water retention times.

The nitrate levels within the streams, the Central Arm and the upper reaches of Western and Eastern Arms are high. The Central Arm and the upper Western Arm had the highest levels of nitrates, most likely due to the elevated levels within the groundwater. Nitrates are probably leaching into the groundwater from agricultural land to the west of the lakes. The Upper Eastern Arm also had high levels of nitrates due to the elevated levels in the stream water. The sources of nitrates to the streams during the summer seem to be at the headwaters of all three streams possibly entering the streams through groundwater inputs or through surface runoff from agricultural land during summer rainfall events.

It is concluded from the literature review and the records of algal blooms in the lakes that low N:P ratios have the most negative effect on the lakes through increased algal blooms when the phosphorus levels are high. Therefore, the Eastern Arm is most at risk in the future if the N:P ratio decreases as nitrate levels decrease with the introduction of the Nitrate Vulnerable Zone, and if the Total Phosphorus levels remain above 30 µg/l.

The affects of future climate change on shallow lake functioning are far from understood. However, it is likely that climate change will exacerbate the problems faced by the *Chara* due to possible increased nutrient and sediment loading to the lakes and increased salinity. Possibly the main risk to the lakes is the influx of phosphorus rich sediment, which is likely to be higher in the winter due to increased precipitation. The possible increase in phosphorus within the sediment may also lead to an increase in the amount of phosphorus released from the sediment in the summer. The predicted higher summer temperatures are also likely to increase the phosphorus release rates, as shown by the increase in phosphorus concentration released at higher temperatures in the experiment undertaken in this study, which reinforces the findings of the literature review. Increased nutrient and sediment loading can both, either indirectly or directly, lead to increased turbidity, which is detrimental to the *Chara*. The high nitrate levels may be more of a risk to the *Chara* in the future with higher summer temperatures increasing the risk of cyano-bacteria blooms. It is unlikely that the *Chara* will be able to survive in the Central Lake in the future due to possible salinity increases and it is likely that there will be continuing water quality problems in the Eastern Arm. Therefore, the Western Arm and Central Arm are the best option as refuges for the *Chara* in the future.

Future management needs to consider the potential impacts of climate change and the nutrient level targets should be set lower than is currently required to compensate for them. There may be unknown point sources within the catchment, such as septic tanks, and they need to be identified and managed accordingly. Land use is important and management of land within the catchment could reduce the impacts of climate change. Sediment and associated phosphorus is likely to be a continuing problem in Bosherton Lakes. The sediment traps should be maintained or enhanced and weed cutting should be continued, if it is not harmful to the ecology of the lakes. It is recommended that sediment erosion is addressed at the source rather than during transport or after deposition. The Nitrate Vulnerable Zone is important to reduce the elevated nitrate levels that may have more of an impact in the future when temperature increases make the lakes more favourable to cyano-bacteria blooms. It is also important as there are nitrate levels within the streams that are nearing the safe drinking water limit of 50 mg/l. With the proposed introduction of the Nitrate Vulnerable Zone the farming community will have to change their practices so it may also provide a good opportunity to introduce changes that will help prevent soil erosion.

7 RECOMMENDATIONS

To help understand the management requirements for the future it is recommended that the following is undertaken.

- Undertake a monthly sediment survey over one year to further understand the sediment and water phosphorus cycling within the different ‘arms’ of the lakes. It should be determined if there are higher phosphorus concentrations in the surface sediment in the winter and lower concentrations in the summer to confirm that there is release of phosphorus in the summer.
- Assess the concentrations of phosphorus in sediment within the rivers during the winter when sediment phosphorus inputs are likely to be highest. This may help to understand whether there is a high amount of phosphorus loaded sediment entering the streams.
- Liaise with local farmers to encourage the reduction of nutrient and sediment losses.
- Assess the quality of sediment within the lakes to see if it is suitable for application to farmland or assess areas available for sediment disposal.
- Survey the catchment for unknown point sources such as septic tanks and private sewers to assess whether there is a problem.
- Assess how the hydrology in the Western Arm may be affected if it was separated from the Central Lake.
- Monitor salinity levels within the Central Lake.

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APPENDIX A

Determination of Phosphate-P (TRP) in Water

1. Preparation of standard graph

1. Pipette 5ml of each phosphorus working standard into a labelled series of 50ml beakers.
2. Add, by dispenser, 5ml of 0.15% ammonium molybdate reagent and 1ml of ascorbic acid solution.
3. Swirl to mix and allow to stand for 30 minutes.
4. Measure the absorbance at 880nm.
5. Construct a graph of absorbance versus concentration (in mg/l).

2. Analysis of water samples

1. Pipette 5ml of water sample (unfiltered) into a labelled 50ml beaker.
2. Add, by dispenser, 5ml of 0.15% ammonium molybdate reagent and 1ml of ascorbic acid solution.
3. Swirl to mix and allow to stand for 30 minutes.
4. Measure the absorbance at 880nm.
5. If the absorbance of the sample is higher than the absorbance of the top standard, repeat the determination using a diluted sample, calling the dilution factor D.
6. Calculate phosphate-P concentration from calibration graph.

APPENDIX B

Determination of Total Phosphorus (TP) in Water by Persulphate Digestion

1. RANGE

- 0 - 500µg P/L

2. PRINCIPLE

- Total phosphorus in water is determined by potassium persulphate digestion followed by spectrometric measurement in solution.

•

3. LABORATORY SAMPLE

- Use water samples, which have been equilibrated to the laboratory temperature for one hour.
- Filtered samples should be pre-filtered through a 0.45µm membrane filter.
- Unfiltered samples should be stirred well using a magnetic stirrer, and sampled whilst stirring slowly.
- If the expected amount of phosphorus is greater than 500 µg P/l, dilute the sample using volumetric glassware and call the dilution factor D.

4. REAGENTS

- Potassium persulphate, AR
- L-Ascorbic acid, AR
- 0.505 mol/l sulphuric acid solution (RPU P1)
- Acid-antimony-molybdate reagent (RPU P2)
- Working reagent (RPU P3)
- Working standards 0 – 500 µg P/l (RPU P4)

5. DIGESTION PROCEDURE

1. Weigh into plastic weighing boats 0.15g ±0.01 g of potassium persulphate.
2. Wash the potassium persulphate into a labelled autoclave tube with 20ml of sample (2 x 10ml, measured by auto pipette).
3. Add 1.0ml of 0.505 mol/l sulphuric acid (RPU P1).
4. Place cap on tube and shake to mix. Loosen cap by half a turn.
5. Repeat steps 1 to 4 for each sample, using a clean pipette tip for each sample.
6. Repeat steps 1 to 4 for each working standard (RPU P4), using a clean pipette tip for each standard.
7. Repeat steps 1 to 4 using 20ml of deionised water as a blank digest.
8. Place the tubes into the autoclave containing about 7.5cm of water.
9. Replace the autoclave lid, engage and tighten the 2 fixed screws first, then tighten the others in opposite pairs. Continue tightening in opposite pairs, including the fixed pair.
10. Set the pressure at 121°C by turning the knurled knob on the lid inwards. Open the air vent (black knob).
11. Connect the autoclave to the mains and switch both LOW and MED switches on.

12. When steam escapes from the air vent (this will take between ten and fifteen minutes), tighten the black knob.
13. When the temperature reaches 121°C, turn the MED switch to off.
14. Digest for 1 hour $\pm$ 15 minutes.
15. Allow the autoclave to cool for at least 3 hours (or overnight) before carefully releasing the pressure by opening the air vent. Remove the lid by undoing the screws in opposite pairs, with the fixed screws being undone last.

6. PREPARATION OF STANDARD GRAPH

1. Carefully remove the top from each of the tubes containing the standards.
2. Add 1.0 ± 0.01 ml of working reagent (RPU 3) to each tube, replace the caps, and shake to mix.
3. Allow the colour to develop for 12 minutes.
4. Measure the absorbance at 880nm using spectrophotometer.
5. Construct a graph relating the absorbance to $\mu\text{g P/l}$.

7. DETERMINATION OF TOTAL PHOSPHORUS

1. Carefully remove the top from each of the tubes containing the samples and blank.
2. Add 1.0 ± 0.01 ml of working reagent (RPU P3) to each tube, replace the caps, and shake to mix.
3. Allow the colour to develop for 12 minutes.
4. Measure the absorbance at 880nm using spectrophotometer.

8. CALCULATION

- The results are expressed as $\mu\text{g/l}$ phosphorus.
- From the standard graph calculate mathematically the amount of P corresponding to the absorbance.
- Call the sample value V_s and the blank value V_b .
- $\mu\text{g/l of phosphorus} = (V_s - V_b)$
- If the sample has been diluted $\mu\text{g/l of phosphorus} = (V_s - V_b) \times D$

9. REFERENCE:

- Eiseneich, S.J., Bannermen, R.T., Armstrong, D.E. (1975) *A simplified phosphorus technique*. Environ. Lett. 9, 45 – 53.

APPENDIX C

Determination of TRP in Sediment using Sodium Hydrogen Carbonate Solution (SOP15)

1. Source

- This SOP is based on British Standard BS 7755: Section 3.6:1995 *Determination of phosphorus – Spectrometric determination of phosphorus soluble in sodium hydrogen carbonate solution* which is identical to ISO 11263:1994.

2. Scope

- This SOP specifies an extraction method to determine the content of soil phosphorus soluble in sodium hydrogen carbonate solution.
- This SOP is applicable to all types of air-dried soil samples.

3. Principle

- A soil sample is treated with a 0.5 mol/l sodium hydrogen carbonate solution at pH 8.5. The extract is then analysed by a spectrometric method.

4. Laboratory sample

- Use air-dried soil samples, for example sample pre-treated according to NR-SAS / SOP 1.

5. Reagents

- 0.15% m/v ammonium molybdate reagent (RPU 19)
- 1.5% m/v ascorbic acid solution (RPU 20)
- 0.05% m/v polyacrylamide solution (RPU 30)
- Sodium hydrogen carbonate reagent (RPU 31)
- 1.5 mol/l sulphuric acid solution (RPU 32)
- Phosphorus working standards (RPU 33)

6. Preparation of extracts

1. Weigh 5g ± 0.01 g of sample into a 250ml polypropylene bottle and add, by pipette, 100ml of sodium hydrogen carbonate reagent.
2. Shake on the side-to-side shaker (set at 300 min⁻¹) for 30 minutes ± 1 minute on the side-to-side shaker.
3. Filter the suspension immediately through a Whatman No. 2 filter (or equivalent) and retain the filtrate.
4. Carry out a blank extraction.

7. Preparation of a standard graph

1. Pipette 5ml of each phosphorus working standard into a labelled 100ml conical flask.
2. Add, by pipette, 1ml of 1.5 mol/l sulphuric acid and swirl.

3. Add, by pipette, 20ml of 0.15% m/v ammonium molybdate reagent, and 5ml of ascorbic acid solution. Swirl and allow colour to develop for 30 minutes but not more than 35 minutes.
4. Measure the absorbance at 880nm in the spectrophotometer according to the instructions provided.
5. Construct a graph relating the absorbance to μg of phosphorus present. [NOTE: not plotted against $\mu\text{g/ml}$]
6. The absorbance value of the top standard (35 μg of P) should read approximately 0.8. An absorbance of less than 0.7 or greater than 0.9 indicates an error and must be reported to senior laboratory staff and analysis of samples not continued.

8. Determination of extractable phosphorus

1. Pipette 5ml of each soil extract into labelled 100ml conical flasks.
2. Add, by pipette, 1ml of 1.5 mol/l sulphuric acid and swirl.
3. Add, by pipette, 20ml of 0.15% m/v ammonium molybdate reagent, and 5ml of ascorbic acid solution. Swirl and allow colour to develop for 30 minutes but not more than 35 minutes.
4. Measure the absorbance at 880nm in the spectrophotometer.
5. If the absorbance is higher than the top standard, repeat the determination using a diluted sample, calling the dilution factor d .

9. Basis of the Calculation

The results are expressed as phosphorus. From the standard graph calculate mathematically the amount of P corresponding to the absorbance. Call the sample value V_s , and the value of the blank, V_b .

- 5g of soil extracted with 100 ml of reagent;
- 5ml aliquot from 100ml;
- Measurement gives μg P.

then:

- 5ml to 100ml gives dilution of 20.

so:

- μg P in sample = $20(V_s - V_b)$

To convert μg to mg - multiply by 10^{-3} ; to get from 5g to 1kg, multiply by $1000/5$, thus:

- $\text{mg/kg} = 20(V_s - V_b) \times 10^{-3} \times 1000/5$

10. Expression of results

- Soluble phosphorus is calculated and recorded to one decimal place.
- Soluble phosphorus is reported to one decimal place.

11. Calculation

From the standard graph calculate mathematically (absorbance divided by the gradient of the line) the number of μg of phosphorus equivalent to the absorbances of the sample and blank determinations.

$$\text{mg/kg of Phosphorus}_{\text{extractable}} = 4 \times (V_s - V_b) \times d$$

where

- V_s is the μg equivalents of sample;
 - V_b is the μg equivalents of blank;
- d is the dilution

APPENDIX D

Determination of TP in Sediment using aqua regia (SOP17)

1. Source

- This SOP is based on US EPA Method 3051 and British Standard BS 7755: Section 3.13:1998 which is identical to ISO 11047:1998.

2. Scope

- This SOP describes a method for the determination of trace elements soluble in aqua regia.
- This SOP is applicable to all types of air-dried soil samples.

3. Principle

- The sample is extracted with a hydrochloric/nitric acid mixture using a microwave digestion system. The extract is then clarified and made up to volume with water. The trace metal content of the extract is then determined by atomic absorption or emission. The phosphorus content is then determined by a spectrometric measurement in solution.

4. Laboratory sample

- Use air-dried soil samples, for example sample pre-treated according to NR-SAS / SOP 1.

5. Apparatus

- Microwave digestion unit with associated digestion liner.
- 100ml volumetric flasks - kept specifically for trace element determinations.

6. Reagents

- Hydrochloric acid (1.18 specific gravity)
- Nitric acid (1.42 specific gravity)
- 10% m/v lanthanum chloride solution
- 0.15% m/v ammonium molybdate solution (RPU 19)
- 1.5% m/v ascorbic acid solution (RPU 20)
- Phosphorus working standards (RPU 106)
- Cadmium working standard solutions (RPU 39)
- Chromium working standard solutions (RPU 40)
- Copper working standard solutions (RPU 41)
- Lead working standard solutions (RPU 42)
- Nickel working standard solutions (RPU 43)
- Zinc working standard solutions (RPU 44)
- Cobalt working standard solutions (RPU 45)
- Molybdenum working standard solutions (RPU 46)

7. Preparation of soil digests

1. Weigh $0.5\text{g} \pm 0.001\text{g}$ of sample into a labelled microwave digestion liner.

2. Add 6ml ± 0.1 ml of hydrochloric acid (1.18 specific gravity), and 2ml ± 0.1 ml of nitric acid (1.42 specific gravity) using another dispenser. Swirl the liner to mix the contents and if necessary wait for pre-reactions such as gas formation to subside.
3. Insert the liner into the pressure vessel and close the screw cap hand-tight.
4. Carry out a blank digest.
5. One of the sample vessels must be sealed using the p/T Sensor Accessory (this **must** be an actual sample not a blank). Expand the seal using the seal forming device and then screw the cap hand-tight in a clockwise direction until you reach the stop position. For correct pressure measurement, this sensor vessel has to be re-opened from the stop position by approximately 60°.
6. Place the sensor vessel in rotor position 1. Place the remaining vessels in the appropriate rotor positions (this is not number order, vessels **must** be spaced evenly within the rotor).
7. Put the lid on the rotor and then place it into the microwave. Ensure that the fume hood is on.
8. On the microwave menu start the method titled “NR-SAS SOP 17”.
9. At the end of digestion, place the rotor in the fume hood.
10. Vent each reaction vessel very carefully with the vent tube pointing away from you. Filter (using a Whatman 542 or equivalent) the contents of each liner into a separate 100ml volumetric flask. Rinse the liner and seals with demineralised water, adding this to the appropriate flask. Make up to volume with demineralised water.

8. Determination of phosphorus

Preparation of standard graph

1. Pipette 5ml of each phosphorus working standard into a labelled 100ml beaker.
2. Add, by dispenser, 20ml of 0.15% m/v ammonium molybdate reagent, and, by dispenser, 5ml of ascorbic acid solution. Swirl and allow colour to develop for 30 minutes but not more than 35 minutes.
3. Measure the absorbance at 880nm in the spectrophotometer.
4. Construct a graph relating the absorbance to μg of phosphorus present. [NOTE: not plotted against $\mu\text{g/ml}$]
5. The absorbance value of the top standard (35 μg of P) should read approximately 0.8. An absorbance of less than 0.7 or greater than 0.9 indicates an error and must be reported to senior laboratory staff and analysis of samples not continued.

Determination of phosphorus

1. Pipette 5ml of each sample digest into labelled 100ml beaker.
2. Add, by dispenser, 20ml of 0.15% m/v ammonium molybdate reagent, and 5ml of ascorbic acid solution. Swirl and allow colour to develop for 30 minutes but not more than 35 minutes.
3. Measure the absorbance at 880nm in the spectrophotometer.
4. If the absorbance is higher than the top standard, repeat the determination using a diluted sample, calling the dilution factor d .

Basis of the calculation

The results are expressed as phosphorus. From the standard graph calculate mathematically the amount of P corresponding to the absorbance. Call the sample value V_s , and the value of the blank, V_b .

- m g of sample digested to 100ml;
- 5ml aliquot from 100ml;
- measurement gives $\mu\text{g P}$.

then:

- 5ml to 100ml gives dilution of 20.

so:

- $\mu\text{g P in sample} = 20(V_s - V_b)$

To convert μg to mg - multiply by 10^{-3} ; to get from m g to 1kg, multiply by $1000/m$
thus:

- $\text{mg/kg} = 20(V_s - V_b) \times 10^{-3} \times 1000/m$
 $= 20(V_s - V_b)/m$

Calculation

From the standard graph calculate mathematically (absorbance divided by the gradient of the line) the number of μg of phosphorus equivalent to the absorbances of the sample and blank determinations.

$$\text{mg/kg of Phosphorus}_{\text{total}} = \frac{20(V_s - V_b)}{m} \times d$$

where

- V_s is the μg equivalents of sample;
- V_b is the μg equivalents of blank;
- m is the mass, in grams, of sample taken for digestion;
- d is the dilution factor (if necessary).

APPENDIX E

Determination of Nitrate – N using the Burkard SFA-2000 auto-analyser (SOP 32)

1. Source

- Method supplied by Burkard Scientific.
- ‘Automated Hydrazine Reduction Method’, p 4-90, Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995.

2. Scope

- This SOP describes a method for the determination of suspended solids and total oxides of nitrogen (TON) in water.
- This SOP is applicable to water samples.

3. Principle

- Nitrate-N in the sample is reduced to nitrite by copper-hydrazine solution. The resultant nitrite and any nitrite in the original sample reacts with sulphanilamide and N-1-naphthylethylenediamine to form a red azo dye that is measured at 520nm.

4. Laboratory sample

- Use water samples, which have been equilibrated to the laboratory temperature for one hour.

5. Reagents and [Colour coding]

- Nitrogen stock standard (RPU 64)
- 0.4 mol/l sodium hydroxide solution (RPU 71) [*green*]
- 0.2 mol/l sodium hydroxide solution (RPU 72) [*purple*]
- Copper sulphate stock solution (RPU 73)
- Hydrazine copper reagent (RPU 74) [*yellow*]
- Sulphanilamide solution (RPU 75) [*white*]
- Brij-35 wash solution (RPU 79)
- TON working standards - LOW (RPU 101)
- TON working standards - HIGH (RPU 102)
- Deionised water [*orange*]

6. Expression of results

- Suspended solids is calculated and recorded to one decimal place.
- The result for suspended solids is reported to one decimal place.
- TON is calculated and recorded to one decimal place.
- The result for TON is reported to one decimal place.

7. Determination of suspended solids

1. Place a 0.45µm membrane filter paper in an oven set at 105°C ±2°C for approximately one hour. Allow the filter to cool in a desiccator and weigh. Call this mass **W₁**.

2. Shake the water sample vigorously and immediately draw up 25ml of sample using a syringe and filter through the weighed 0.45µm filter, retaining the filtrate. This filtrate is used to determine TON.
3. Wash the syringe through the filter with three 25ml aliquots of demineralised water, discarding the washings.
4. Place the filter paper in an oven set at 105°C ±2°C for approximately one hour. Allow the filter to cool in a desiccator and weigh. Call this mass **W₂**.

$$\text{mg/l of suspended material} = (\mathbf{W_2} - \mathbf{W_1}) \times 40000$$

where

- **W₁** is the mass, in grams, of the filter paper;
- **W₂** is the mass, in grams, of the filter paper plus suspended material.

8. Preparation of auto-analyser

1. Connect to auto-analyser to the mains, and switch on the pumps, colorimeter, autosampler and chemistry modules required for Group 1.
2. Check all drain tubes are running to waste.
3. Place the sample wash tube and all water tubes in demineralised water. Place reagent tubes in Brij-35 wash solution (RPU 79).
4. Tension tubing, latch platens, and apply pressure to the pump tubes by moving the levers on the platens to on.
5. Turn on the pumps in continuous mode and run for about 30 minutes, checking that there are no leaks in the system. After the 30 minutes have elapsed ensure that the temperature of the TON channel is 37°C ±0.5°C.
6. Turn on the computer, double click on the Microstream icon. When Microstream has loaded select Group 1 (lower left of screen)
 - Select
 - File
 - Load form
 - Select form required
 - Open
7. Then
 - Select:
 - File
 - New file
 - Data file
 - Save
8. Enter the number of samples in the box (the total number of cups will be calculated)
 - Select
 - OK (the cup table will be generated).
9. Then
 - Select:
 - View
 - ADC readings (the ADC window will be displayed)
 - For nitrate-N and nitrite-N set the baseline to between 200 and 500 using the baseline zero screw inside the colorimeter.

10. Check cup table
 - Select:
 - Edit
 - Sample cups
 - Highlight file number and channel
 - Select;
 - Check value for standards and drifts are correct (sample identifiers may be entered at this stage or later).
11. Close cup editor
 - Select:
 - End
 - Yes
 - Quit.
12. If readings are high and baseline noisy suspect a bubble in the flow cell. This can be cleared by pinching the outlet tube from flow cell for 2-3 seconds and then releasing. If necessary, this can be repeated several times.

9. Measurement of TON

1. All reagents must be at room temperature. Place the reagent tubes for the analysis in their respective reagent containers and run for 15 – 30 minutes until a stable baseline is obtained, adjusted to between 200 and 500 (as above).
2. Load 2ml cups containing the standards [*red cups*], drifts [*green cups*], washes [*blue cups*] and samples [*colourless cups*] (all at room temperature) into the sample tray in the order displayed in the cup table. Check that the carousel is in the “home” position, and reset if necessary. If the autosampler needs resetting, press *7## on the front panel.
3. To start the run:
 - Select:
 - Go
 - Yes
4. To enter sample identities: (this can be done at any time, before, during or after the run).
 - Select:
 - Edit
 - Sample cups
 - Highlight the file required
 - Select
 - Enter sample identities into the table
 - End
 - Yes
 - Quit
5. To print a calibration graph: (this can be done at any time after the results for the standards have been displayed in the table)
 - Select:
 - Graph
 - Calibration graph
 - Highlight the required file and channel

- Select: Print

10. Sample result over calibration

- The auto-analyser has been calibrated to measure TON in a sample up to a concentration of 25 mg N/litre. If the concentration in the sample exceeds this upper limit, then the sample must be diluted using volumetric glassware (dilution factor D). The calculated result will then be multiplied by the dilution factor to give mg N/litre in the sample.

11. Shutting down the auto-analyser on completion of determinations

1. Place all reagent tubes in Brij-35 wash solution (RPU 79) and wash through the system for 30 minutes.
2. When the wash is completed, switch off the pumps, release the pressure, unlatch the platens and release the tension on the pump tubes.
3. Turn off the autosamplers, pumps, chemistry units and colorimeters at the mains.
4. To format and print the results, first turn on the printer.
 - Select:
 - Edit
 - Format results
 - Highlight the required file
 - Select
 - Check the box beside the results required (e.g. standards, unknowns, user types)
 - O.K.
5. To print the full data, first turn on the printer.
 - Select:
 - Calculate
 - Print
 - Highlight required file
 - Select
6. Close all open files, exit from Microstream, close down the computer, and turn off at the mains.

APPENDIX F

Determination of Total Nitrogen using the Burkard SFA-2000 Auto-Analyser (SOP 28)

1. Source

- Based on a method supplied by Burkard Scientific.
- Automated Hydrazine Reduction Method', p 4-90, Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995.

2. Scope

- This SOP describes a method for the determination of suspended solids and dissolved total nitrogen.
- This SOP is applicable to water samples.

3. Principle

- Nitrogen compounds are oxidised on-line by persulphate in alkaline solution to nitrate. Nitrate is then reduced by copper-hydrazine solution to nitrite. The resultant nitrite reacts with sulphanilamide and N-1-naphthylethylenediamine to form a red azo dye that may be measured at 520 nm.

4. Laboratory sample

- Use water samples, which have been equilibrated to the laboratory temperature for one hour.

5. Reagents and [Colour coding]

- Carbon stock standard (RPU 58)
- Nitrogen stock standard (RPU 64)
- Phosphorus stock standard (RPU 65)
- Carbon and nitrogen working standard (RPU 67)
- Carbon, nitrogen and phosphorus working standard (RPU 69)
- Nitrogen and phosphorus working standards (RPU 70)
- 0.4 mol/l sodium hydroxide (RPU 71) [*yellow*]
- 0.2 mol/l sodium hydroxide (RPU 72) [*red*]
- Stock copper sulphate solution (RPU 73)
- Hydrazine-copper reagent (RPU 74) [*green*]
- Sulphanilamide (RPU 75) [*blue*]
- Potassium persulphate solution (RPU 76) [*orange*]
- Borate buffer (RPU 77) [*brown*]
- Nitrogen working standards (RPU 78)
- Brij-35 wash solution (RPU 79)

NOTE: the autoanalyser can be used to measure total nitrogen, dissolved organic carbon and total phosphate-P concurrently. There is therefore a choice of working standards depending on which combination of analyses are required.

6. Expression of results

- Suspended solids is calculated and recorded to one decimal place.
- The result for suspended solids is reported to one decimal place.
- Dissolved total nitrogen is calculated and recorded to one decimal place.
- The result for dissolved total nitrogen is reported to one decimal place.

7. Determination of suspended solids

5. Place a 0.45µm filter paper in an oven set at 105°C ±2°C for approximately one hour. Allow the filter to cool in a desiccator and weigh. Call this mass **W₁**.
6. Shake the water sample vigorously and immediately draw up 25ml of sample using a syringe and filter through the weighed 0.45µm filter, retaining the filtrate. This filtrate is used in the digestion to determine organic carbon.
7. Wash the syringe through the filter with three 25ml aliquots of demineralised water, discarding the washings.
8. Place the filter paper in an oven set at 105°C ±2°C for approximately one hour. Allow the filter to cool in a desiccator and weigh. Call this mass **W₂**.

$$\text{mg/l of suspended material} = (\mathbf{W_2} - \mathbf{W_1}) \times 40000$$

where

- **W₁** is the mass, in grams, of the filter paper;
- **W₂** is the mass, in grams, of the filter paper plus suspended material.

8. Preparation of auto-analyser

1. Connect to auto-analyser to the mains, and switch on the pumps, colorimeter, autosampler and chemistry modules required for Group 3 analyses (including the Dymax pump).
2. Check all drain tubes are running to waste.
3. Place the sample wash tubes and all water tubes in demineralised water.
4. Place all reagent tubes in Brij-35 wash solution (RPU 79).
5. Tension tubing, latch platens, and apply pressure to the pump tubes by moving the levers on the platens to on.
6. Turn on the pumps in continuous mode and run for about 30 minutes, checking that there are no leaks in the system.
7. Turn on the computer, double click on the Microstream icon. When Microstream has loaded select Group 3 (lower left of screen)
 - Select
 - File
 - Load form
 - Select form required
 - Open
8. Then
 - Select:
 - File
 - New file
 - Data file
 - Save
9. Enter the number of samples in the box (the total number of cups will be calculated)

- Select:
 - OK (the cup table will be generated).
12. Then
- Select:
 - View
 - ADC readings (the ADC window will be displayed)
 - For total nitrogen set the baseline to between 200 and 500 using the baseline zero screw inside the colorimeter.
13. Check cup table
- Select:
 - Edit
 - Sample cups
 - Highlight file number and channel
 - Select;
 - Check value for standards and drifts are correct (sample identifiers may be entered at this stage or later).
14. Close cup editor
- Select:
 - End
 - Yes
 - Quit.
13. If readings are high and baseline noisy suspect a bubble in the flow cell. This can be cleared by pinching the outlet tube from flow cell for 2-3 seconds and then releasing. If necessary, this can be repeated several times.

9. Measurement of total nitrogen

6. All reagents must be at room temperature. Place the reagent tubes for the analysis in their respective reagent containers and run for 15 – 30 minutes until a stable baseline is obtained, adjusted to between 200 and 500 (as above).
7. Load 4ml cups containing the standards, drifts, washes and samples (all at room temperature) into the sample tray in the order displayed in the cup table. Check that the carousel is in the “home” position, and reset if necessary. If the autosampler needs resetting, press *6# on the front panel.
8. To start the run:
 - Select:
 - Go
 - Yes
9. To enter sample identities: (this can be done at any time, before, during or after the run).
 - Select:
 - Edit
 - Sample cups
 - Highlight the file required
 - Select
 - Enter sample identities into the table
 - End

- Yes
- Quit
- 10. To print a calibration graph: (this can be done at any time after the results for the standards have been displayed in the table)
- Select:
- Graph
- Calibration graph
- Highlight the required file and channel
- Select: Print

10. Sample result over calibration

- The auto-analyser has been calibrated to measure total nitrogen in a sample up to a concentration of 10 mg N/litre. If the concentration in the sample exceeds this upper limit, then the sample must be diluted using volumetric glassware (dilution factor D). The calculated result will then be multiplied by the dilution factor to give mg N/litre in the sample.

11. Shutting down the auto-analyser on completion of determinations

7. Place all reagent tubes in Brij-35 wash solution (RPU 79) and wash through the system for 30 minutes.
8. When the wash is completed, switch off the pumps, release the pressure, unlatch the platens and release the tension on the pump tubes.
9. Turn off the autosamplers, pumps, chemistry units and colorimeters at the mains.
10. To format and print the results, first turn on the printer.
- Select:
- Edit
- Format results
- Highlight the required file
- Select
- Check the box beside the results required (e.g. standards, unknowns, user types)
- O.K.

11. To print the full data, first turn on the printer.
 - Select:
 - Calculate
 - Print
 - Highlight required file
 - Select
12. Close all open files, exit from Microstream, close down the computer, and turn off at the mains.

APPENDIX G

Site	TRP (mg/g)	TP (mg/g)	Site	TRP (mg/g)	TP (mg/g)	Site	TRP (mg/g)	TP (mg/g)	Site	TRP (mg/g)	TP (mg/g)
UE1	0.075	0.86	LE3	0.018	0.47	CL3	0.026	0.42	WA5	0.007	0.35
UE2	0.055	0.67	LE4	0.011	0.26	CLTA	0.016	0.28	WATA	0.029	0.47
UE3	0.049	0.55	LE5	0.021	0.48	CLTB	0.027	0.30	WATB	0.024	0.39
UETA	0.028	0.54	LETA	0.019	0.54	WA1	0.027	0.27	CA2	0.009	0.11
UETB	0.028	0.49	LETB	0.020	0.53	WA2	0.015	0.17	CA3	0.010	0.10
LE1	0.028	0.53	CL1	0.021	0.31	WA3	0.013	0.17	CATA	0.033	0.30
LE2	0.024	0.45	CL2	0.025	0.30	WA4	0.014	0.15			

Table G1: Sediment TRP and TP concentrations. The top 20cm of sediment was sampled at each site during the survey on 3rd – 5th June 2008. These results are the mean of two replicates from each sediment sample.

APPENDIX H

Site	TRP ug/l	Total P ug/l	Site	TRP ug/l	Total P ug/l	Site	TRP ug/l	Total P ug/l
Surface UE1	1	41	Surface LETA	0	71	Surface WA4	0	23
Surface UE2	0	25	Surface LETB	0	32	Surface WA5	0	12
Surface UE3	0	72	Surface CL1	0	34	Surface WATA	0	22
Surface UETA	0	73	Surface CL2	0	46	Surface WATB	0	29
Surface UETB	0	19	Surface CL3	0	37	Surface CA1	0	14
Surface LE1	1	38	Surface CLTA	5	33	Surface CA2	0	15
Surface LE2	0	27	Surface CLTB	0	49	Surface CA3	0	18
Surface LE3	0	34	Surface WA1	0	40	Surface CA4	0	7
Surface LE4	1	41	Surface WA2	0	22	Surface CATA	0	15
Surface LE5	0	40	Surface WA3	0	21			

Table H1: TRP and TP concentrations in the surface lake water samples from the survey undertaken on the 3rd-5th June 2008. The TRP concentrations are from one analysis from the surface water sample and the TP concentrations are a mean of two replicates from the surface water sample.

Site	TRP ug/l	Total P ug/l	Site	TRP ug/l	Total P ug/l	Site	TRP ug/l	Total P ug/l
Bottom UE1	1	97	Bottom LETA	0	43	Bottom WA4	0	15
Bottom UE2	0	23	Bottom LETB	0	66	Bottom WA5	0	16
Bottom UE3	0	31	Bottom CL1	0	46	Bottom WATA	0	31
Bottom UETA	1	53	Bottom CL2	0	36	Bottom WATB	0	31
Bottom UETB	0	30	Bottom CL3	0	52	Bottom CA1	0	31
Bottom LE1	0	35	Bottom CLTA	0	24	Bottom CA2	0	21
Bottom LE2	0	39	Bottom CLTB	0	34	Bottom CA3	0	21
Bottom LE3	0	24	Bottom WA1	0	37	Bottom CA4	0	14
Bottom LE4	1	79	Bottom WA2	0	22	Bottom CATA	0	64
Bottom LE5	0	44	Bottom WA3	0	11			

Table H2: TRP and TP concentrations in the bottom lake water samples from the survey undertaken on the 3rd-5th June 2008. The TRP concentrations are from one analysis from the bottom water sample and the TP concentrations are a mean of two replicates from the bottom water sample.

Site	TRP ug/l	Total P ug/l	Site	TRP ug/l	Total P ug/l	Site	TRP ug/l	Total P ug/l
UE1	1	69	LETA	0	57	WA4	0	19
UE2	0	24	LETB	0	49	WA5	0	14
UE3	0	51	CL1	0	40	WATA	0	27
UETA	0	63	CL2	0	41	WATB	0	30
UETB	0	25	CL3	0	45	CA1	0	22
LE1	1	36	CLTA	3	29	CA2	0	18
LE2	0	33	CLTB	0	41	CA3	0	20
LE3	0	29	WA1	0	39	CA4	0	10
LE4	1	60	WA2	0	22	CATA	0	40
LE5	0	42	WA3	0	16			

Table H3: TRP and TP concentrations shown as a mean of the surface and bottom lake water samples from the survey undertaken on the 3rd-5th June 2008.

APPENDIX I

Month	June	July	Mean	June	July	Mean
Site	TRP ug/l	TRP ug/l	TRP ug/l	Total P ug/l	Total P ug/l	Total P ug/l
Ch/St	87	144	115	110	147	128
ST2	58	89	74	76	92	84
SPRING	37	51	44	55	51	53
ST1	52	68	60	63	69	66
MOUTH EA	33	107	70	48	108	78
MW	200	774	487	226	736	481
LY	31	50	41	43	51	47
S	40	41	40	39	42	40
OB	41	55	48	49	56	52
WW	3	10	7	0	0	0
Q	0	21	11	0	0	0

Table I1: TRP and TP concentrations for stream water samples collected on 11th June and 8th July and a ‘summer 2008’ mean (mean of 11th June and 8th July 2008 samples). The June and July sample results are a mean of three triplicates.

APPENDIX J

Month	June	July	Mean	June	July	Mean
Site	TRP ug/s	TRP ug/s	TRP ug/s	TotalP ug/s	TotalP ug/s	TotalP ug/s
Ch/St	100	184	142	126	188	157
ST2	97	115	106	125	119	122
Spring	3	0	1	3	0	1
ST1	58	60	59	70	61	65
MouthEA	21	52	36	31	52	41
Sampson	345	202	274	337	207	272
Lyerry	10	12	11	14	13	13
Warren House	178	310	244	201	305	253
White Well	3	10	7	0	0	0
OB	693	611	652	828	622	725

Table J1: TRP and TP loads based on stream water samples and discharge data collected on 11th June and 8th July, and a ‘summer 2008’ mean (mean of 11th June and 8th July 2008 loads).

APPENDIX K

Site	Nitrate-N mg/l	Total N mg/l	Site	Nitrate-N mg/l	Total N mg/l	Site	Nitrate-N mg/l	Total N mg/l
Surface UE1	3.24	3.6	Surface LETA	0.04	0.3	Surface WA4	0.71	1.2
Surface UE2	2.09	2.3	Surface LETB	0.03	0.4	Surface WA5	1.96	2.2
Surface UE3	1.68	2.0	Surface CL1	0.00	0.3	Surface WATA	0.40	0.8
Surface UETA	1.47	1.9	Surface CL2	0.00	0.2	Surface WATB	0.28	0.6
Surface UETB	1.80	2.1	Surface CL3	0.00	0.3	Surface CA1	0.92	2.0
Surface LE1	0.10	0.6	Surface CLTA	0.00	0.2	Surface CA2	1.84	1.9
Surface LE2	0.01	0.4	Surface CLTB	0.00	0.2	Surface CA3	2.10	2.0
Surface LE3	0.00	0.2	Surface WA1	0.02	0.3	Surface CA4	1.48	1.9
Surface LE4	0.01	0.3	Surface WA2	0.10	0.5	Surface CATA	1.81	1.9
Surface LE5	0.01	0.3	Surface WA3	0.33	0.8			

Table K1: Nitrate-N and TN concentrations in the surface lake water samples from the survey undertaken on the 3rd-5th June 2008. The Nitrate-N concentrations and TN concentrations are a mean of three replicates from the surface water samples.

Site	Nitrate-N mg/l	Total N mg/l	Site	Nitrate-N mg/l	Total N mg/l	Site	Nitrate-N mg/l	Total N mg/l
Bottom UE1	3.52	3.9	Bottom LETA	0.04	0.3	Bottom WA4	1.42	1.7
Bottom UE2	1.97	2.3	Bottom LETB	0.06	0.4	Bottom WA5	2.29	2.6
Bottom UE3	1.84	2.0	Bottom CL1	0.00	0.2	Bottom WATA	0.53	1.0
Bottom UETA	1.47	1.7	Bottom CL2	0.00	0.2	Bottom WATB	0.39	0.7
Bottom UETB	1.72	1.9	Bottom CL3	0.00	0.3	Bottom CA1	1.01	1.8
Bottom LE1	0.14	0.6	Bottom CLTA	0.00	0.2	Bottom CA2	1.99	2.0
Bottom LE2	0.00	0.3	Bottom CLTB	0.00	0.3	Bottom CA3	2.20	2.2
Bottom LE3	0.02	0.3	Bottom WA1	0.00	0.3	Bottom CA4	1.16	1.5
Bottom LE4	0.00	0.3	Bottom WA2	0.09	0.4	Bottom CATA	0.39	0.9
Bottom LE5	0.01	0.2	Bottom WA3	0.29	0.7			

Table K2: Nitrate-N and TN concentrations in the bottom lake water samples from the survey undertaken on the 3rd-5th June 2008. The Nitrate-N concentrations and TN concentrations are a mean of three replicates from the bottom water samples.

Site	Mean Nitrate-N mg/l	Mean Total N mg/l	Site	Mean Nitrate-N mg/l	Mean Total N mg/l	Site	Mean Nitrate-N mg/l	Mean Total N mg/l
UE1	3.38	3.7	LETA	0.04	0.3	WA4	1.07	1.5
UE2	2.03	2.3	LETB	0.05	0.4	WA5	2.12	2.4
UE3	1.76	1.97	CL1	0.00	0.28	WATA	0.46	0.9
UETA	1.47	1.77	CL2	0.00	0.23	WATB	0.33	0.7
UETB	1.76	2.00	CL3	0.00	0.32	CA1	0.97	1.87
LE1	0.12	0.6	CLTA	0.00	0.20	CA2	1.91	1.93
LE2	0.01	0.4	CLTB	0.00	0.23	CA3	2.15	2.12
LE3	0.01	0.3	WA1	0.01	0.3	CA4	1.32	1.7
LE4	0.01	0.3	WA2	0.10	0.5	CATA	1.10	1.4
LE5	0.01	0.3	WA3	0.31	0.8			

Table K3: Nitrate-N and TN concentrations shown as a mean of the surface and bottom lake water samples from the survey undertaken on the 3rd-5th June 2008.

APPENDIX L

Month	June	July	Mean	June	July	Mean
Site	Nitrate-N mg/l	Nitrate-N mg/l	Nitrate-N mg/l	Total N mg/l	Total N mg/l	Total N (mg/l)
Ch/St	9.20	8.92	9.06	10.00	10.03	10.02
ST2	7.82	7.31	7.57	8.83	8.03	8.43
SPRING	7.49	6.77	7.13	8.63	6.97	7.80
ST1	8.12	7.89	8.01	8.57	8.10	8.33
MOUTH EA	6.24	5.70	5.97	7.03	7.50	7.27
MW	6.35	5.71	6.03	7.53	7.67	7.60
LY	2.76	2.55	2.66	3.47	2.67	3.07
S	4.82	4.41	4.62	5.77	5.67	5.72
OB	4.33	3.81	4.07	5.03	5.13	5.08
WW	4.41	4.27	4.34	5.37	4.63	5.00
Q	0.37	0.00	0.19	0.53	0.10	0.32

Table L1: Nitrate-N and TN concentrations for stream water samples collected on 11th June and 8th July and a ‘summer 2008’ mean (mean of 11th June and 8th July 2008 samples). The June and July sample results are a mean of three triplicates.

Month	June	July	Mean
Site	Nitrate (NO ₃) mg/l	Nitrate (NO ₃) mg/l	Nitrate (NO ₃) mg/l
Ch/St	40.76	39.53	40.14
ST2	34.66	32.40	33.53
SPRING	33.20	29.99	31.59
ST1	35.96	34.97	35.46
MOUTH EA	27.66	25.24	26.45
MW	28.13	25.28	26.71
LY	12.24	11.28	11.76
S	21.34	19.55	20.44
OB	19.18	16.89	18.04
WW	19.52	18.93	19.23
Q	1.65	0.01	0.83

Table L2: Nitrate (NO₃) concentrations for stream water samples collected on 11th June and 8th July and a ‘summer 2008’ mean (mean of 11th June and 8th July 2008 samples). Nitrate (NO₃) concentrations calculated by multiplying Nitrate-N by 4.43.

APPENDIX M

Month	June	July	Mean	June	July	Mean
Site	Nitrate-N mg/s	Nitrate-N mg/s	Nitrate-N mg/s	Total N mg/s	Total N mg/s	Total N mg/s
Ch/St	11	11	11	11	13	12
ST2	13	9	11	14	10	12
Spring	1	0.01	0.29	1	0.01	0.50
ST1	9	7	8	10	7	9
MouthEA	4	3	3	5	4	4
Sampson	42	22	32	50	28	39
Lyerry	1	1	1	1	1	1
Warren Hou	6	2	4	7	3	5
White Well	5	4	4	6	5	5
OB	73	43	58	85	57	71

Table M1: Nitrate-N and TN loads based on stream water samples and discharge data collected on 11th June and 8th July, and a ‘summer 2008’ mean (mean of 11th June and 8th July 2008 loads).

Month	June	July	Mean
Site	Nitrate (NO ₃) mg/s	Nitrate (NO ₃) mg/s	Nitrate (NO ₃) mg/s
Ch/St	47	50	48
ST2	57	42	50
Spring	3	0.04	1.29
ST1	40	31	35
MouthEA	18	12	15
Sampson	184	96	140
Lyerry	4	3	3
Warren Hou	25	10	18
White Well	22	19	20
OB	324	191	258

Table M2: Nitrate (NO₃) loads calculated using the Nitrate (NO₃) stream water concentrations and discharge data collected on 11th June and 8th July, and a ‘summer 2008’ mean (mean of 11th June and 8th July 2008 loads).

APPENDIX N

Site	Rank of TP mg/g in the lake sediment	Site	Rank of Mean TP (μg) in the lake water	Rank sed - Rank water	Rank ²
CA3	1	CA3	5	-4	16
CA2	2	CA2	3	-1	1
WA4	3	WA4	4	-1	1
WA2	4	WA2	6	-2	4
WA3	5	WA3	2	3	9
LE4	6	LE4	25	-19	361
WA1	7	WA1	15	-8	64
CLTA	8	CLTA	10	-2	4
CLTB	9	CLTB	19	-10	100
CATA	10	CATA	16	-6	36
CL2	11	CL2	18	-7	49
CL1	12	CL1	17	-5	25
WA5	13	WA5	1	12	144
WATB	14	WATB	12	2	4
CL3	15	CL3	21	-6	36
LE2	16	LE2	13	3	9
LE3	17	LE3	11	6	36
WATA	18	WATA	9	9	81
LE5	19	LE5	20	-1	1
UETB	20	UETB	8	12	144
LETB	21	LETB	22	-1	1
LE1	22	LE1	14	8	64
UETA	23	UETA	26	-3	9
LETA	24	LETA	24	0	0
UE3	25	UE3	23	2	4
UE2	26	UE2	7	19	361
UE1	27	UE1	27	0	0
Sum Rank ²					1564
Spearman's rank correlation					0.522589

Table N1: Spearman's Rank Correlation Coefficient calculation between TP in the lake sediment and lake water (mean of surface and bottom lake water samples).

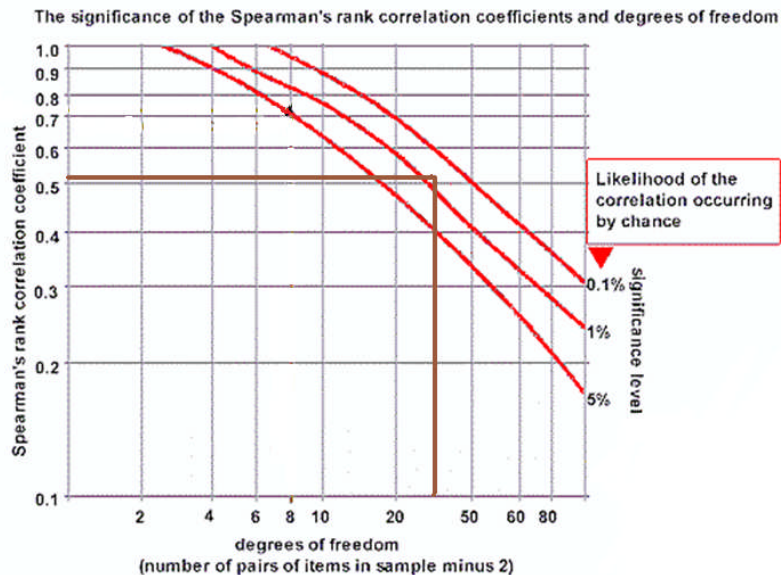


Figure N1: Degrees of freedom showing the significance of the Spearman's Rank Correlation Coefficient. The brown line shows that there is only around 1% chance that the correlation between the sediment TP and water TP concentration occurred by chance.

Grid Refernces: Bosherton Lakes and streams

Lake sample station	Easting	Northing	Stream sample station	Easting
UE1	197763	196025	MW	193754
UE2	197735	195871	Ly	195580
UE3	197723	195730	S	196977
UETA	197673	195736	OB	197552
UETB	197743	195742	MouthEA	197954
LE1	197704	195742	ST1	197943
LE2	197695	195300	ST2	198121
LE3	197709	195092	Spring	197531
LE4	197749	194900	Ch/St	198728
LE5	197645	194765	Q	195925
LETA	197659	195306	WW	196619
LETB	197721	195306		
CL1	197580	194579		
CL2	197668	194457		
CL3	197562	194689		
CLTA	197522	194557		
CLTB	197607	194609		
CA1	197388	194689		
CA2	197305	194829		
CA3	197266	194899		
CA4	197281	194832		
CATA	197403	194719		
WA1	197314	194591		
WA2	197134	194634		
WA3	196991	194728		
WA4	196854	194838		
WA5	196778	194936		
WATA	196997	194750		
WATB	196979	194710		

Northing

197366

196887

196584

196347

196362

196542

196478

197298

197266

195129

195038