Phosphorus cycling in the settlement lagoon of a treatment wetland

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The candidate confirms that the work submitted is his/her own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

The South Finger treatment wetland at Slimbridge, UK, was designed to treat water that has been impacted by the faeces of a dense population of waterfowl. The wetland system has been failing consistently in retaining phosphorus (P). It has been suggested that the settlement lagoon of the wetland is the cause for its failure regarding P, because the lagoon exports P in the summer months. The aim of this project was to understand the importance of the settlement lagoon in the overall budget of P, and to understand the mechanisms that result in such behaviour. This was achieved by measuring the fluxes of P in and out of the lagoon, as well as measuring the fluxes through the sediment water interface and the consumption/release of P by water column process. Also, an exhaustive study of the chemistry of the pore waters and of the different species of P in the sediments was carried out.

The data showed that the role of the settlement lagoon in the loading of P of the treatment wetland is minimal. The sediments of the settlement lagoon release dissolved P in the early summer, but this flux is much smaller than the mass of P that enters the lagoon at the same time. The failure of the treatment wetland is not related to the settlement lagoon, which has been performing satisfactorily in retaining suspended solids and particulate P, but to the inadequate retention time of the reed beds. This in turn is related to the original design of the wetland system.

The source of the P that is released in the early summer is the bird faeces that accumulate at the bottom of the lagoon through the winter. The accumulated faeces are consumed rapidly in the early summer when temperature increases and oxidisers are present in the pore waters the right conditions are present, releasing their P through the sediment water interface (SWI). This process commences in the early spring, with the appearance of an algal bloom, accompanied by high levels of dissolved oxygen and the deposition of fresh algae onto the lagoon sediments. Biodegradable algae is consumed by aerobic respiration above the SWI at this time. The faeces, buried within the anaerobic sediments, are not consumed significantly at this time however, because temperatures are still too

low. The bacterial activity within the sediments, during the early summer, is carried out mainly through iron and sulphate reduction.

At some time between March and June, temperatures increased and the degradation of freshly deposited algae accelerates. This releases large quantities of ammonium above the SWI, which triggers the combined process of nitrification-denitrification, with nitrate reaching deep into the sediments. The supply of nitrate into the sediments, accompanied by the increased temperatures, accelerates the consumption of the buried bird faeces and the release of their associated P through the SWI. By June, dissolved P is still released through the SWI, although the consumption of the labile fraction of the bird faeces slows down the rate of release. A small fraction of the released P is precipitated as apatite within the sediments, without reaching the water column.

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1 Introduction

1.1 Treatment wetlands

1.1.1 Historical development

In Europe, waste waters started to be treated in the mid 1800s, coinciding with the growth of big towns and cities with high population densities. Large towns produced large quantities of waste waters harmful to the public health and to the environment. The waste waters were not only domestic effluents, but they were also generated in the many industries that used to be located within the cities, such us slaughter houses, tanneries, printing presses, etc (Čížková 1998). Originally, the treatment consisted simply of the disposal of waste waters onto nearby lands. In the 1880s the treatment of waste waters became an industrial process when biological filters were introduced, and by 1910 activated sludge processes were developed. These last two processes rely on the consumption of organic matter in the waste water by microorganisms, in an aerobic environment (Čížková 1998). However, by 1950, European inland waters were being impacted by the runoff from over fertilized farm land and from pollution from sewage from decentralized small communities or industries, which was typically treated in septic tanks or ponds, of low purification efficacy (Vymazal 2011, Vymazal and Kröpfelová 2008). Dr Kathe Seidel started researching the use of different species of macrophytes for the treatment of decentralised pollution in Germany in the 1950s (Vymazal and Kröpfelová 2008). The research developed into treatment wetlands, during which Dr Seidel tried different layouts, soil types, plants species, etc (Vymazal and Kröpfelová 2008).

The advantages of the constructed wetlands were their low cost of construction and operation, but their rate of treatment was slower than conventional wastewater treatment technology. Constructed wetlands were shown to be well suited for treating effluents from small communities or as a final polishing step

of previously treated water from larger population centres. There was however scepticism from water treatment experts, who would not accept that macrophytes would grow well in polluted waters and that they would not be able to eliminate toxic substances (Sidel 1976). There were many prejudices among civil engineers about the viability of running constructed wetlands, for example regarding the production of odours and flies and their poor performances in cold weather (Veenstra 1998).

The first constructed wetlands were commissioned in the Netherlands in 1967, and in Hungary in 1968 to process pre treated waste water. In the US, the use of constructed wetlands also started in the 1960s for the treatment of municipal waste water (Vymazal 2011). Currently there are thousands of constructed wetlands around the world that treat municipal and industrial waste waters, agricultural runoff, mine drainage and storm waters (e.g. Dunbabin and Bowmer 1992, and Maynard et al 2009). In the UK, the Water Authority and the Water Research Centre investigated constructed wetland systems operating in Denmark in 1985, and by the end of that year the first constructed wetland was in operation in Britain. By the end of the century, there were probably 400 to 600 privately owned constructed wetlands in the UK, plus another 150 owned and operated by Severn Trent Water (Čížková 1998).

1.1.2 Free water surface constructed wetlands

There are different types of constructed wetlands that vary, for example, on whether water flows above or below the surface of the sediments, or whether plants are attached to the sediments or floating (See Figure 1.1). In this introduction and throughout the thesis, the free water surface (FWS) type of wetland will be discussed. FWS wetlands consist of a basin or number of interconnected basins filled with 20 to 30 cm of organic rich soil. They are typically planted densely with emerging macrophytes, in addition to other naturally transplanted species (Kadlec and Hey 1994). Water flows over the soil and around the emerging plants at depths between 20 and 40 cm (Vimazal 2011). The water should cover all parts of the wetland to maximise the use of all the

available surfaces for the chemical and biological reactions that will treat the water (Kadlec and Knight 1996). This is usually achieved by designing the basins as long and narrow channels (Reed et al 1998). Sedimentation of heavier particles occurs in the first few meters from the inlet. Vegetation reduces the water column mixing and the resuspension of particles from the sediments, allowing the settling of lighter particles that did not settle near the inlet (Čížková 1998).

Microorganisms are responsible for the removal of soluble organic compounds, which are mineralised both aerobically and anaerobically. Aerobic microorganisms are very effective in the breakdown of organic matter carried in the waste water, whereas anaerobic microorganisms also facilitate the breakdown of organic matter, but at slower rates (Shutes 2001). The decomposition of organic matter then will depend largely on the supply of oxygen to the waters and to the sediments. Oxygen is supplied to the shallow water column by diffusion through the water surface and also by photosynthesis mainly on the periphyton and by benthic algae (Kadlec et al 2000). Oxygen is supplied to the sediments through the emerging plants. Plants of large biomass, that grow in water saturated soils and that have an extensive root system are most commonly used in constructed wetlands. These usually are common reed (Phragmaites australis), and reedmace (Typha latifolia). The oxygen that the plants draw from the leaves down to the roots creates an area within the soil (the rhizosphere) that can sustain aerobic microorganisms (Shutes 2001).

The removal of nitrogen from FWS systems by the harvesting of plants is minimal, since the mass of N removed during an annual harvest is a small fraction of the total mass of N that has to be removed during one year from typical waste waters. Instead, N is mainly removed by nitrification/denitrification, and volatilisation. These processes are triggered when ammonium is oxidised to nitrate, in the presence of oxygen; and nitrate is used up by denitrifiers. FWS wetlands are typically oxygenated near the water surface and around the rhizosphere and ammonium is oxidised to nitrate in those aerobic zones by nitrification (Vymazal 2011). In turn, in anaerobic areas, the high organic content

of the waste water and the plant litter fuels denitrification. Finally elemental N and nitrous oxide are volatilised (Huang and Pant 2009).

FWS constructed wetlands can also remove disease-bearing microorganisms. This is achieved by a combination of processes such as filtration, exposure to UV radiation, sedimentation and oxidation. Many biological processes also occur that would destroy pathogenic organisms such as the excretion of biocides by some plants, predation by other microorganism and natural senescence (Gersberg et al 1987).

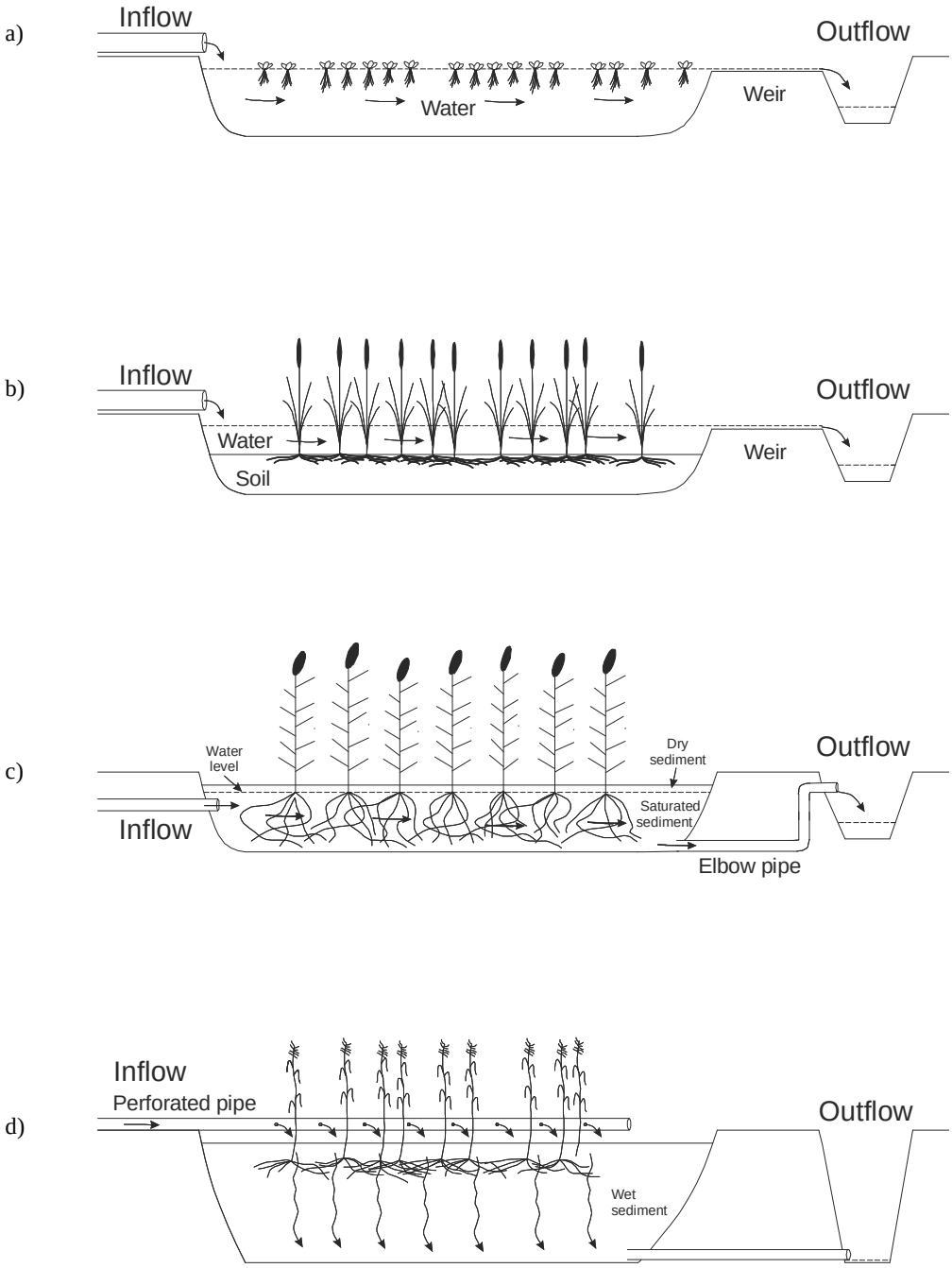


Figure 1-1: Four different types of constructed wetlands. a) constructed wetland with free floating plants; b) FWS constructed wetland; c) constructed wetland with horizontal subsurface flow; and d) constructed wetland with vertical subsurface flow (Vizamal 2007)

1.1.3 The retention of phosphorus by FWS constructed wetlands

The long term retention of phosphorus (P) by constructed wetlands is the result of physical, chemical and biological processes (Reddy et al 1999). These can be summarised as the accretion of plant litter containing P, sorption of P into pre-existing minerals and storage in biomass (Kadlec and Knight, 1996). Only the first process is sustainable, while the other two processes reach saturation and therefore cannot give a long term solution for the retention of P (Dunne and Reddy, 2005). Even the physical retention of P by accretion of detrital material in the wetland floor will depend on the P content of the litter, which is usually low (Reddy et al 1999) and on the capacity of the wetland to accumulate litter, which can be sustained by management of the wetland. Detritus laying on the floor of wetlands have lost up to 80% of the mass of P that the living plants originally held (Reddy et al 1999).

P adsorbs onto mineral surfaces, typically Al and Fe oxides, and with time it diffuses into the mineral lattice via absorption, but the processes are slow and Fe minerals have a limited capacity to absorb P (Reddy et al 1999). These processes are more efficient in soils with a higher inorganic fraction and in wetlands where water flows through the sediment instead than over the sediment surface. Subsurface flow wetlands (see Figure 1, c) and d)) therefore are efficient in the removal of P through adsorption-absorption mechanisms. Changing conditions of a constructed wetland may affect these processes. If the water column went anoxic, the sediment water interface (SWI) would also go anoxic and in reduced, anaerobic conditions, ferric iron would reduce to soluble ferrous iron, releasing previously bound P into the water column (Mortimer, 1941).

Co-precipitation is the combination of P with some metallic ions forming amorphous or poorly crystalline solids. The co-precipitation with Ca^{2+} ions is generally important in wetland soils at pH values higher than 7 (Faulkner and Richardson, 1989). Co-precipitation of P with Ca^{2+} taking place in FWS

wetlands results in authigenic apatite, which once precipitated is a permanent sink of P at pH values above 4 (Ruttenberg 1992).

In the water column, planktonic algae and microbial uptake can remove phosphorus rapidly, but the mass of P removed is low (Vimazal 2007), and P is rapidly remobilised from their detritus into the water column (Vymazal 2011). Planktonic algae and bacteria can also affect the retention of P indirectly by changing oxygen levels and pH through photosynthesis and respiration (Gachter and Meyer 1993). This affects mechanisms of P sorption into Fe minerals described above.

Soil bacteria can facilitate the burial of P by the production of refractory compounds rich in P, such as polyphosphates (Poly-P) (Gachter and Meyer 1993). However, they can also mobilise stored P directly by decomposing buried organic matter and releasing nutrients, and indirectly by changing redox conditions, which would affect sorption onto Fe minerals (Vimazal 2007). It has been suggested that microorganisms mediate in the precipitation of insoluble calcium-P minerals in the oceans, through the production of polyphosphates (Poly-P), that subsequently act as nucleus for the precipitation of authigenic apatite (Diaz et al 2008), but no study has been found of this process taking place in constructed wetlands. As with nitrogen, P removal by harvesting the emerging macrophytes is low (10 to 20 g P m^{-2} y^{-1}) when compared with the influx of P typical in treatment wetlands, which is typically one order of magnitude higher (Vimazal 2007).

1.2 The Slimbridge Wetlands Centre

1.2.1 Site history and description

The UK has a long history of nature conservation that dates back to the 1870s, when living conditions in the cities and evident damage caused in the countryside led to an increasing number of people to start discussing their behaviour towards

the natural world. In 1891 the Royal Society for the Protection of Birds was founded, and the idea of natural reserves was introduced by its members in the early 1900s. By 1930, The National Trust, the Royal Society for Nature Conservation, the British Ecological Society, and the Forestry Commission were already very active. Popular claim for public access to the countryside increased in the 1930s. In 1932 an organised mass trespassing on private land took place in the Peak District. These acts and pressure from the different conservation societies forced parliament to pass a series of laws that would culminate in the 1949 National Parks and Access to the Countryside Act (Evans, 1992).

As part of this nature conservation movement, a naturalist called Peter Scott inaugurated the Severn Wildfowl Trust, in 1946, which occupied seven hectares of natural wetland on the banks of the river Severn, in Slimbridge, Gloustershire. The Trust was the most successful of the post war conservation organisations created in Britain and led to similar trusts for the conservation of pheasants, hawks, etc (Fitter and Scott 1978). The Severn Wildfowl Trust was created as an observation and research centre, dedicated to the study of a captive collection of waterfowl and to the study of wintering wildfowl on the Severn estuary. The Wildfowl Trust became a success with the public immediately after creation, and its educational value has been as important as the value of its scientific research. The Trust has worked extensively in practical conservation, by creating new wetlands habitats and by breeding endangered species in captivity and reintroducing them to the wild in different parts of the world. The Severn Wildfowl Trust opened other centres in the UK and in America and in 1989 the trust changed its name to Wildfowl and Wetlands Trust (WWT) (Evans 1992).

The WWT site in Slimbridge now extends to 325 hectares, of which 50 hectares belong to the Visitor Centre and to the ponds where the captive collection is kept, and the rest is wild marshland. The site has been designated a Special Protection Area and a Special Area of Conservation according to Directives of the European Union, and as a Ramsar Site (McKenzie, 2010). The Visitor Centre (see Figure 1.2) is surrounded by marshland and agricultural land and it lies between the Gloucester and Sharpness canal and the river Severn. Water from the canal and from adjacent farmland enters the Visitor Centre and flows through several

interconnected ponds. The ponds are the habitat for the captive collection and for migrating wild birds. The permanent population of birds living on the ponds is 2000 wildfowl in summer, but it rises to 3000 when the migrating birds arrive in the winter months (Mckenzie and Vougioukalou 2010). The high density of birds living at the Visitor Centre affected the quality of the water flowing through the exhibit ponds, mainly as the result of uneaten feed and bird faeces. This caused relatively high suspended solids, biological oxygen demand, ammonia and phosphate (Mckenzie and McIlwraith 2012). This problem is common in water leaving bird reserves (Manny et al 1994). In 1994, the South Finger treatment wetland was installed downstream of the exhibit ponds to treat the out flowing waters before they reached sensitive areas of the River Severn.

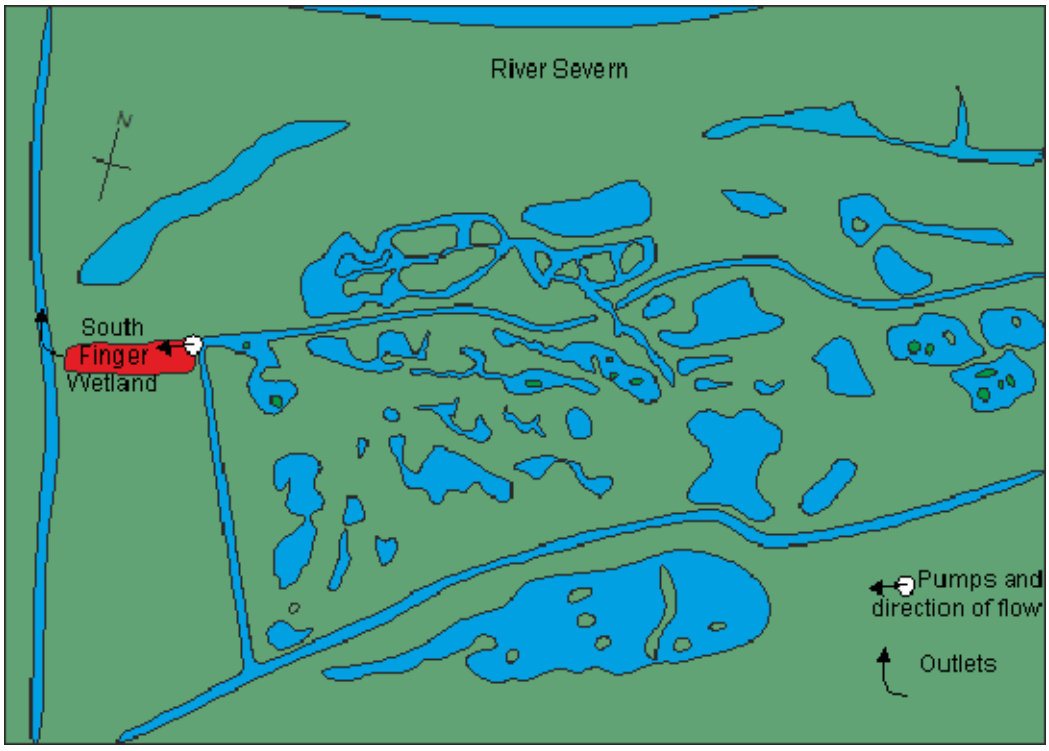


Figure 1-2: Layout of the WWT site, showing the SouthFinger Wetland. The ponds are interconnected (not all connections shown) and they discharge in the ditch immediately upstream of the South Finger Wetland.

1.2.2 The South Finger Treatment Wetland

1.2.2.1 Construction of the South Finger treatment wetland

In 1991, WWT commissioned the environmental consultancy Penny Anderson Associates to produce a draft outline for the construction of a treatment wetland that would clean effectively the water flowing out of the visitor centre and exhibit ponds (Millett, 1997). The objectives that WWT gave to the consultants for the design of the constructed wetland were (Mackenzie, unpublished draft).

- To meet the discharge consent levels
- To produce water that would meet nature conservation standards
- To combine the treatment of water with the creation of habitats for nature conservation
- To create an educational site

These objectives were developed into six broad approaches (Worral, 1997):

- Suspended solids would be encouraged to settle using ponds that would force the reduction of energy (velocity) of the inflowing particles
- The wetland would be of the FWS type, described in sections 1.1.2 and 1.1.3
- Cascades made of limestone would be used along the FWS wetland to encourage the aeration of the water and to promote the co-precipitation of P with Ca^{2+} (see section 1.1.3)
- Floating rafts would be deployed on the ponds to assist the treatment process
- Different types of plants would be used, to promote diversify and to avoid the failure of the whole system in case of the failing of one species of plants
- Wetland habitats would be created to mimic natural ones and to promote wildlife

In 1993 the wetland was excavated on a field used for cattle grazing next to the visitor centre. The excavated clays were used by the Environmental Agency (EA) to improve sea defences nearby. That meant that the costs of the excavation were covered by the EA and also that lining of the wetland was not needed because the wetland had a clay base. The treatment wetland was finished in 1994, when funds were finally raised to cover the costs for pumps and plants (Mackenzie, unpublished draft).

1.2.2.2 Layout and operation of the South Finger treatment wetland

The layout of the South Finger treatment wetland can be seen in Figure 1.3. The individual sections of the wetland and their operation are described below:

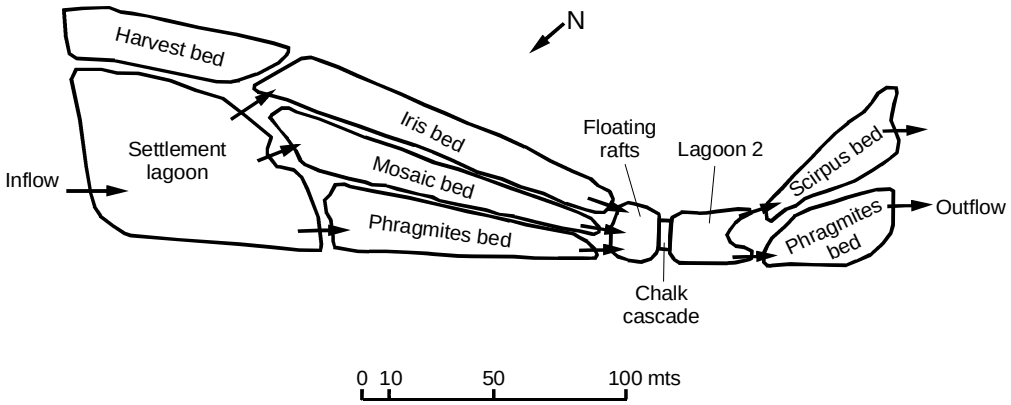


Figure 1-3: Layout of the South Finger treatment wetland, at the Wildfowl and Wetland Trust's site in Slimbridge.

Water leaving the exhibit ponds is collected in a ditch between the visitor centre and the wetland. The ditch has a lateral connection to a concrete pumping chamber. There is a weir in the ditch, just downstream of the pumping chamber to keep water levels high. This ensures that water reaches the right depth to trigger the pumps inside the chamber. During unusual high flow conditions, for example after a storm, excess water that cannot be taken up by the pumps runs

above the weir and flows untreated along a lateral ditch. A high level switch in the chamber is triggered when water levels rise in the ditch. The switch starts up the pumps within the chamber and these pump water from the chamber and the ditch into the settlement lagoon. The pumps stop automatically when a low level switch is triggered. There are two pumps inside the concrete chambers that are usually run alternately (Mckenzie and McIlwraith, 2012).

Settlement Lagoon

The settlement lagoon was originally 1.5 meters deep, and could hold a volume of approximately 2900m3. The water flow was 2000 m3 day^{-1}, resulting in a residence time, when constructed, of 35 hours. The settlement lagoon was designed to slow the velocity of the suspended solids contained in the inflowing water, and to make them settle on the bottom. The settlement lagoon was to be allowed to fill with sediments, which was expected to take 25 years. After that it would be converted into a reed bed or re-excavated (Millet 1997).

Harvest Bed

The harvest bed was designed to treat water from the settlement lagoon before flowing into the Iris bed. However the connection between the harvest bed and the Iris bed has never been established. Alternatively, the harvest bed has been used as a nursery for wetland plants (Mackenzie and McIlwraith, 2012) and to provide reed material needed for filters around the WWT site (Millet 1997).

The Treatment Beds

The treatment beds are of the FWS type, described in sections 1.1.2 and 1.1.3 above. This type of flow was chosen because it provides good habitat for wildlife and because of its ability to treat large volumes of water. The beds can be individually isolated for maintenance work (Millett 1997).

Floating Rafts Lagoon

The surface of this lagoon is almost all covered by rafts. The rafts had a mesh to hold several species of aquatic plants. The roots of the plants hang through the meshes into the water column. Microorganisms living on the root surfaces treat the water further (Millet 1997), as discussed in 1.1.2.

Chalk Cascade

The cascade is made of crushed limestone, covered with chalk. The turbulence of the water flowing over the cascade promotes oxygenation of the water. The materials for the construction of the cascade were chosen to promote the co-precipitation of P with Ca_2^+ ions (Millet 1997), and as described in 1.1.3. However, the surface of the stones soon became covered by algae, suppressing the co-precipitation of P (Worral et al 1997).

Scirpus and Phragmites beds

They operate similarly as the treatment beds, but they were excavated deeper in the clay to allow a longer contact between the water and the sediments, in order to promote the capture of P by the sediments (Millet 1997), as discussed in 1.1.3.

From the settlement lagoon, water flows by gravity down to the outlet of the wetland. Water flows out of the settlement lagoon when it reaches the level of three elbow-bend pipes. These three pipes are connected below ground to the three treatment beds (Iris, Mosaic and Phragmites). Water levels in the treatment beds are maintained by brick weirs built at the exit of the inflowing pipes and by elbow-bend pipes at the other end of the beds (See Figure 4). Water from the treatment beds run below ground through pipes into the Floating Rafts Lagoon. The inlets into the Floating Rafts Lagoon are below the water level. Downstream of the Floating Rafts Lagoon there is a chalk cascade, over which the water flows into the Lagoon 2. As with the settlement lagoon, elbow-bend pipes in the Lagoon 2 drive the water into the last two smaller treatment beds (Scirpus and Phragmites). Water exits the wetland through pipes under a track and into a ditch. This ditch, or rhine, discharges eventually into the river Severn, 500 meters .

	Settlemnt lagoon	Treatment beds			Rafted lagoon	Cascade lagoon	Polishing beds	
		Phragmites	Mixed	Iris			Phragmites	Scirpus
Area (m2)	2900	1725	2250	2000	550	950	1300	1000
Design Retention Time (hs)	35	6	8	7	6	11	2.4	3.1

Table 1-1: Surface areas and retention times of the different components of the South Finger wetland.

1.2.3 Retention of P by the South Finger wetland

Research undertaken on the South Finger wetland demonstrated that the wetland has been exporting orthophosphate every year since 2005, and possibly since 1996. The source of the excess orthophosphate is the settlement lagoon, while the rest of the constructed wetland has been unable to reduce the excessive fluxes (Stratford et al, 2010 and Palmer-Felgate, 2011a and 2011b. Observations similar to those made at the settlement lagoon have been reported in shallow lakes. For example Lake Blankensee in Germany has an average depth of 1.2 meters, and the majority of the TP in the water column in summer was reported to be generated within the lake (Ramm and Scheps 1997). Loch Leven in Scotland has a mean depth of 3.9 meters and an area of 13.3 km2. Water column SRP is depleted in spring due to the uptake of the spring algal blooms, while in late summer the peaks are produced by intense release from the sediments (Spears et al 2007). Further examples of shallow lakes that release phosphorus internally are given from lakes in Denmark (Søndergaard et al 2003), Sweden (Ryding 1985), Italy and the US, (Marsden 1989).

1.2.3.1 The settlement lagoon as the source of excess P

As discussed above, the settlement lagoon is the source of excess P within the South Finger wetland. P cycling in such shallow bodies of water has some

characteristics that differentiate them from deeper stratified lakes. Given the surface area to depth ratios of shallow lakes, the pool of P in the sediments is often more than 2 orders of magnitude larger than the pool of P in the water column. Therefore the levels of P in the latter depend largely on the fluxes through the SWI (Søndergaard et al 2003). Lake Ontario, in North America, has a mean depth of 89 meters, and the internal loading of P has been estimated to be 11% of the external load. On the other hand, in a number of shallow lakes in Sweden, the internal load of P is up to 4 times larger than all other external loads, averaged annually (Boström et al 1988a). The passage of P from the sediments into the layers in the water column where photosynthesis takes place is rapid and direct (Shaw and Prepas, 1990; Søndergaard et al 2003), therefore it has a critical impact on the primary productivity in the water column (Boström and Pettersson 1982).

The release of P from the sediments in shallow lakes happens mainly from aerobic sediments (Jensen et al 1992, Marsden 1989), and the rates of release from sediments in well oxygenated waters are often of the same magnitude as for anaerobic sediments (Boström et al 1988a). This disagrees with the classical model of Mortimer (1941) for deep lakes, but the inherent characteristics of shallow lakes help explain this:

- freshly produced organic matter in shallow lakes reaches the sediment surface quickly and almost intact
- the water column is subject to rapid changes in its physical and chemical conditions
- resuspension events are frequent

Large amounts of freshly produced organic matter falls onto the sediments of shallow lakes before decomposing. This is a rich source of organic matter for sediment microorganisms, which have a significant role in the uptake, storage and release of P, as long as the oxygen levels and other oxidisers like nitrate are present (Søndergaard et al 2003). It has been reported that in shallow lakes, up to 50% of the primary production is mineralised in the bottom waters or in the

sediments (Caraco et al 1990). Release of P originated from the decomposition of algae on the sediments surface of Lake Grevelingen and from the Loosdrecht Lakes in the Netherlands (Marsden, 1989). Mass balance calculations indicated that the release of SRP occurred on the top few centimetres of sediments, and it has been suggested that the P loading of the lakes was caused by the mineralisation of organic matter (Marsden, 1989). An additional effect of high concentrations of SRP near the sediment surface is that they lower the Fe:P ratios in those top layers, and it has been suggested that at Fe:P ratios below 15, orthophosphate would cross the oxic layer into the water column without being adsorbed by iron minerals (Jensen et al 1992, and Ramm and Scheps 1997).

Sediments in shallow lakes are exposed to more heterogeneous conditions than in deep lakes, because of the combined effects of weather, the circulation of water, shelter from nearby trees, buildings and fauna (Boström et al 1988a). That heterogeneity causes the formation and destruction of micro chemical gradients in the sediments and in the pore waters, related to temperature, pH or levels of oxygen (Boström et al 1988a). The chemical gradients change rapidly and unpredictably, and loosely-bound P or P in solution in the pore waters are continuously recycled into and out of the water column (Boström and Pettersson 1982) and wide variations in the release of P can occur in shallow lakes (Marsden 1989). Water column and sediment temperature in shallow lakes can span 20°C rapidly. This causes great variations in the rates of microbial activity and the releases of P associated with it (Sinke et al 1990). An increase in primary productivity, resulting from changing environmental conditions, causes an increase in pH (Sinke etal 1990) and higher pH trigger the release of orthophosphate from sediments, by ion exchange between OH^- and PO_4^{3-} on the surfaces of Fe oxy-hydroxides (Jensen and Andersen, 1992). Although the water column of shallow lakes is usually well mixed and oxygenated (Søndergaard et al 2003), it has been reported that under special weather conditions in summer, anoxia can set in the top millimetres of the sediments (Shaw and Prepas, 1990), or that even the water column can become anoxic overnight during warm and calm weather (Correll 1998). When this occurs, P stored in the oxic top millimetres of the sediments can be liberated as Fe minerals are chemically and microbially reduced (Søndergaard et al, 2003).

It has been reported that in shallow lakes, the top 10 cm of sediments can be subject to disturbance and mixing by water turbulence (Forsberg 1989), and that the release of dissolved P from pore waters after the resuspension of sediments or the mineralisation of resuspended sediments is significant (Boström et al 1988b). Also, the constant turbulence in the water column maintains steep concentration gradients between the SWI and the overlying water, accelerating the process of molecular diffusion between the two phases (Forsberg 1989). A shallow lake in Denmark showed increases of between 5 to 10 times the background levels of TP in the water column within days of high wind events (Søndergaard et al 2003). The same authors discussed that yearly variations in the internal P loading in other shallow lakes were controlled by wind mixing (Søndergaard et al 2003). Internal P loading of Lake Blankensee in Germany was also shown to be the result, in part, of disturbance of sediments by water turbulence (Ramm and Scheps 1997).

1.3 Aims of research, hypotheses and structure of the thesis

This project is part of WWT's plan to develop an understanding on the performance of the South Finger wetland, primarily regarding the retention of P. This project builds on the findings of Stratford et al (2010) and Palmer-Felgate (2011a and 2011b), who studied the retention or release of P by the South Finger wetland in the past. Their work indicated that the wetland exports orthophosphate, and that its source is the settlement lagoon, and they measured and suggested possible mechanisms for the release of P from the settlement lagoon. However, the proposed mechanisms were not quantified or studied in depth.

The general aim of this research project was to quantify and to understand in depth the mechanisms that resulted in the settlement lagoon exporting P. This was carried out by testing three main hypotheses, which are based on the likely behaviour of P in a body of water like the settlement lagoon (see Section 1.2.5):

1. *The sediments are the source of excess P that is discharged from the settlement lagoon in summer.* The discussion of this hypothesis was presented in Chapter 4.
2. *P released from the sediments in summer resulted mainly from the mineralisation of organic matter, and it was triggered by the increase in temperatures.* This hypothesis was discussed in Chapter 5.
3. *The organic matter that releases P is the combination of freshly deposited primary productivity and of bird faeces that accumulated in the sediments during the previous year.* This hypothesis was discussed in Chapter 5.

The historical performance of the settlement lagoon regarding P is presented in chapter 3. Chapter 6 includes a summary of the previous three chapters and Chapter 7 presents the conclusions and implications of the study presented in this thesis.

1.4 Relevance of the proposed study

The study of nutrient cycling and its effect on eutrophication of surface waters commenced in the 1900s and it is still intense, due to its relevance on water quality and management (Smith et al, 2003). In the last 40 years there has been a significant increase in the research of nutrient cycling, and many improvements have been made in order to prevent excessive N and P entering lakes, rivers and the sea. However, eutrophication continues to be one of the main problems in protecting our waters resources (Smith et al, 2003). Mainstone and Parr (2002) discussed in depth the mechanisms in which the introduction of reactive P in the water environment degrades the environment. The authors concluded that P in surface water systems should be brought back as close to background levels as possible. The negative effect of P in the water quality of surface waters is related with an increase in algal growth and production of organic matter. However, even this aspect of the research on eutrophication has been questioned recently. Hagerby et al (2006) concluded that in some instances high nutrients loadings

cause a decrease in productivity, indicating that the subject of euthrophication is far of having been fully understood. In the proposed work, nutrient levels and chlorophyll levels in the water column will be presented and their relationships, discussed.

A possible way of understanding the cycling of P in lakes is by estimating its loads and budgets, and by investigating internal nutrient dynamics and retention mechanisms. This approach was presented in Tang and Xie (2000), and it is also an important part of the proposed study. More complex models have been also applied to the study of nutrient cycling in lakes and these are being developed and improved constantly, for example the DYRESM–CAEDYM model described in Trolle et al (2008). Correlations between levels of nutrients, chlorophyll levels, transparency, solids in the water, weather and the time of the year were also discussed by James et al (2009), as well as in the proposed work.

The research presented in this thesis includes the study of the cycling of organic P, both in the sediments and in the water column. This species of P has not been studied in depth in the past and is currently a subject of intense research (McMahon and Read, 2013). The complexities of the relationships between living organisms, decomposing organisms and different species of organic P, such as polyphosphates, pyrophosphates, orthophosphates monoesters and others are discussed in detail in, for example, Reitzel et al (2007). The subject of organic species of P is among the latest areas of research in the water treatment industry, where microorganisms are manipulated to accumulate P from waste waters (McMahon and Read, 2013). The interactions of these organic species of P and of the phosphorus accumulating organisms, with other chemical species have also been investigated, in order to optimise the performance of water treatment plants (Saito et al, 2004, Saito et al, 2008, and Jie et al 2007). These studies have been complemented with techniques developed to enrich the culture of phosphate accumulated organisms in water treatment plants, in order to enhance the biological removal of phosphorus from waste waters (Hung et al, 2002). Novel methods for the quantification of organic species of P and of P accumulating organisms have also been developed recently (e.g. Aschar-Sobbi et al, 2008; Hupfer et al, 2008 and Diaz and Ingall, 2010).

The fate of P when it reaches the sediments has been studied for many decades (e.g. Mortimer, 1941), and the topic is still subject to intense research. This is in part because of its complexity, but also because the burial and release of P from lake sediments continue to impact the quality of surface waters (Mesnage et al, 2002), even well after loading of P has stopped (Reitzel et al, 2012). Different aspects of the cycling of P in lake sediments that have been being studied for the last 50-60 years are still being investigated. These include, among others, the effects of light and mechanical perturbation of sediments over the release and uptake of phosphorus from sediments (Gerhardt et al, 2010); or the relationships between water column processes, phosphorus release or uptake from sediments, and sediments types (Vicente et al, 2006), or the optimisation of classical methods (Kapanen, 2008) such as those presented in Hieltjes and Lijklema (1980) and Murphy & Riley (1962), for the study of sediment phosphorus. Many of these topics are discussed in the proposed work.

The interactions between sediments and water column P is still a relevant issue in modern research of lakes, and many of those characteristics are discussed in the proposed study. Resuspension events in shallow lakes and their effect on water column P have been studied in Holmroos et al (2009), and it was shown that those events can increase considerably the concentrations of TP and SRP in the water column. However, it was discussed that resuspension events can either release dissolved P into the water column or sequester dissolved P from the water column. The conditions for the different behaviors are related to the volume of water that reacts with the resuspended sediment, oxic conditions and pH (Koshi-Vähälä and Hartikainen, 2001). The effect of benthic fauna in the release of nutrients and turbidity of lakes is still a debatable subject, as was discussed in Torvainen et al (2005). That study obtained results that seemed to contradict previous ones, for example those which showed that chironomids (*vulg*. Blood worms) do affect turbidity of the overlying water but they do not impact the levels of P in the water column (Torvainen et al, 2005).

The impact of waterfowl on surface waters is a current matter of concern for lake and wetlands managers and many questions regarding this issue are currently

being studied. For example what is a sustainable population of birds? How to measure this? What are the direct and indirect impacts of bird populations of surface waters? (Chaichana et al, 2010, and Huang and Isobe, 2012). Some of these questions are studied thoroughly in the present work and contributed to the study of this important environmental issue.

The remediation of waters impacted by high levels of nutrients using constructed wetlands continues to be studied intensely. For example Venterink et al (2002) focused on the consequences that well established practices have on the release and bioavailability of P. The authors concluded that the common practice of flooding land to create artificial wetlands could in fact release large masses of P. The performance of treatment wetlands has often been unsatisfactory regarding the retention of P and the issue has been subject to recent research. For example, Stottmeister et al (2003) gave a comprehensive description of how plants and microorganisms affect the removal of nutrients from the polluted waters.

The proposed work is a contribution to the ongoing research, and contributes specially in the understanding of P cycling and measuring of fluxes of P in an organic rich aquatic system. In general, treatment wetlands contain inflowing reactive P for a short period of time before becoming saturated. For example Jin et al (2001) described very good results regarding retention of reactive P, in a series of pilot tests. However, Braskerud et al (2005) demonstrated that wetlands rapidly lose their capacity to contain reactive P, and that the settling of particulate P becomes their main form of P retention. Similar findings were reported in Braskerud (2002). Toet et al (2005) proved that a treatment wetland used to polish effluent from a sewage treatment plant succeeded in reducig the mass of P by only 5%. Concordantly, Scholz et al (2007) describes the design of treatment wetlands treating runoff form farmyards. The authors reported long term good performances of treatment wetlands, regarding P, when those were 1.3 to 1.4 times the surface area of the farmyard. However, these types of ratios between the wetland and the catchment area are impractical when the catchment is ten or hundreds of hectares, like the WWT site at Slimbridge.

The proposed research is focused on the settlement lagoon of a treatment wetland. In Peng et al (2007), it is discussed that wastewater stabilisation ponds have been understudied in the past and the interest in the cycling of nutrients in them has become more relevant as the use of stabilisation ponds for non-point pollution increased. That same study described how different forms of particulate P are more or less stable under different pH and redox conditions. Wastewater stabilisation ponds have also been recently studied as habitats that favour the luxury uptake of phosphorus by algae, as a mean or removing reactive P. The main factor favouring luxury uptake of P was concluded to be temperature, rather than light (Powell et al, 2008).

2 METHODS

This chapter describes the general field and analytical methods employed during this project. The rationale of why these methods were employed and other more specific methods are elaborated in detail in subsequent chapters.

2.1 Field methods

2.1.1 Description of the pond

The great majority of the field work was done in the settlement pond. The shape of the pond can be described as a quarter of a circle of radius 50m. That equates to a surface area of approximately 2000m2. The original depth of the pond was between 1.5 and 2 meters excavated in natural stiff clays, with a shallower shelf left to the south of the pond (Millett, 1997). Settling of solids has caused these depths to decrease through the years, and it has been reported that the current depths of the pond are 0.6 to 1 meter. The fresh sediments are very soft and dark grey to black in colour, with a reported mean LOI of 13.5 % (Palmer Felgate et al 2010). It has also been reported that there is a thick transition layer between the sediment and the water column (Palmer Felgate et al 2010). Typical H_2S smell and intense bubbling occurred when the sediments were disturbed.

In June 2011 a small stickleback was found floating dead in the water, suggesting the existence of a fish population in the pond, although live fish were not seen. The bottom of the pond is unvegetated but its edges are vegetated largely by Reedmace (Typha Latifolia), which has crept up to 3 meters into the pond. There are four rafts of about 1 square meter each, secured to the bottom of the pond (see Figure 2.2). Some vegetation grows on the rafts with their roots suspended inside the water column. In summer, a few floating macrophytes were observed but they were not identified.

The inlet pipe is to the north of the settlement pond and it is fed by centrifuge pumps that bring the waste water from the bird collections upstream. Three outlet pipes drain the pond by gravity when the water level reaches them (see Figure 2.1). The water is likely have a short residence time if it flows along the western half of the pond. On the other hand, water left in the eastern half of the pond will have an extended residence time until it reaches the outlets (Hossain et al 2005).

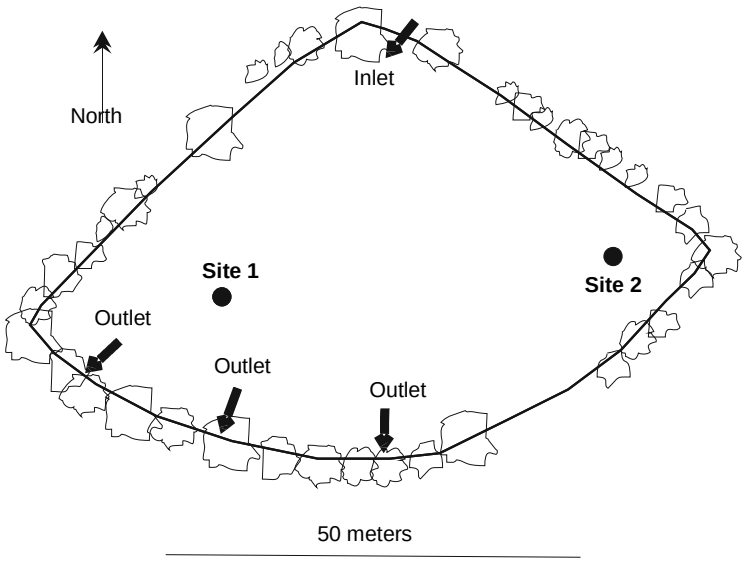


Figure 2-1: Plan view of the settlement pond at the South Finger constructed wetland, with detail of positions of inlets, outlets and sampling points 1 and 2.

The sampling of the pond in 2011 and 2012 was undertaken at sites 1 and 2. Site 1 was to the west of the pond, where water would have a relatively short residence time. Site 2 was to the east of the pond, where water would have a longer residence time (Hossain et al 2005).

The shape of the pond, the locations of inlet and outlets, the nature of the recently deposited sediment, the lack of vegetation on the bottom of the pond and the apparent lack of fish living in the pond were discussed during the testing of hypotheses 1,2 and 3 (see Section 1.5).

2.1.2 Weather observations and weather data

Weather observations were recorded every 4 to 6 hours during the sampling periods. These included air temperature, wind speed, wind direction and cloud cover. Air temperature was measured with an alcohol thermometer, left in the shade. Wind speed was estimated between forces 0 to 12 of the Beaufort scale. Wind direction was determined by knowing the orientation of the site. Cloud cover was determined as eighths of the sky covered. Detailed hourly weather information was supplied by The British Atmospheric Data Centre (BADC), from the Met Office Integrated Data Archive System. The data were from three weather stations in Gloucestershire: Cirencester, Westonbirt and Little Rissington. Weather data was also obtained from the online database of the Bablake Weather Station, in the West Midlands.

Observed weather conditions were incorporated in the testing of hypotheses 1, 2, and 3 (see Section 1.5).

2.1.3 Bathymetric survey

In order to confirm the reported depths of the pond, a bathymetric survey of the pond was carried out. The survey was undertaken in October 2010, using a rowing boat. A 2.5 meter, graduated staff was constructed to dip the pond. The staff was purposely light weight and with a flat and wide bottom. The staff was lowered and when a slight resistance was felt, this depth was recorded as that of the recently deposited silt. The staff was pushed through the newly settled material until it hit the stiff clay, and this depth was also recorded. The survey produced consisted of two superimposed surfaces: the top of the fresh and unconsolidated silt and the top of the original stiff clay liner. After the bathymetry survey was finished, a graduated staff was inserted in the bottom of the lagoon, extending above the water surface. The mark at which the staff crossed the water level was recorded, in order to adjust the depths of the lake, for future calculations, in case of the water level rising or dropping (see Figure 2.2).

Figure 2-2: Dipping the pond using a flat bottomed graduated wooden staff in October 2010. The boat is secured to one of the unvegetated rafts. On the left of the photograph, another raft can be seen with some vegetation on it

The depth of the water column and the volume of water in the pond were discussed in the testing of hypotheses 1,2 and 3 (see Section 1.5).

2.1.4 Water flow through the inlet

The water that has flowed through the different ponds of the WWT bird reserve is collected in a ditch upstream of the settlement pond of the South Finger wetland. The water in the ditch is then pumped into the settlement pond by two water-level activated pumps. These pumps operate intermittently depending on the water levels in the ditch. The two pumps also alternate in their operation, in order to extend their operational life. The running time of each pump is logged by two clocks in the control box.

During the March and June 2011 field work, it was necessary to know the volume of water that flowed through the inlet during the 24 hours sampling period. Given the configuration of the pumping system, it was necessary to know both the number of hours that each pump operated during the 24 hours sampling periods and the pumping rate of each pump. The operation times of each pump during the different 24 hours sampling periods could be read out from the clocks in the control box. The pumping rate of each pump was calculated as:

Equation 2.1:

Flow rate (m3 sec^{-1}) = cross section of inflowing water (m^2) x water velocity (m s^{-1})

The cross section of the inflowing water was calculated using trigonometry, knowing the diameter of the inlet pipe and the width of the top of the flowing water (chord), see Figure 2.3.

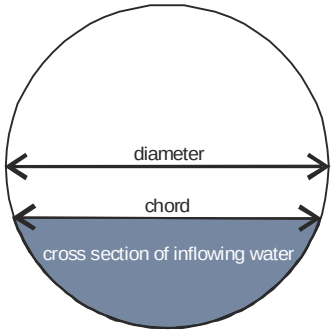


Figure 2-3: Cross section of the inlet pipe and flowing water.

The velocity of the inflowing water was measured using a propeller water velocity meter. Multiple measurements were made of each parameter to ensure good precision. The volume of water that flowed in each 24 hours sampling period then would be calculated as:

Equation 2.1:

$$V = (t_1 \times q_1) + (t_2 \times q_2)$$

Where:

V : Volume of inflowing water in 24 hours, in m^3

t_1 : Running time during 24hs of pump No1, in hours

q_1 : Pumping rate of pump No1, in $m^3 h^{-1}$

t_2 : Running time during 24hs of pump No2, in hours

q_2 : Pumping rate of pump No2, in $m^3 h^{-1}$

The flow rate of water through the inlet was discussed in the testing of hypothesis 1 (see Section 1.5).

2.1.5 Water sampling, frequency and replication

Water samples were taken whilst wearing disposable gloves. The water was taken using pre-rinsed syringes and kept in disposable polypropylene tubes. Each tube was given a unique serial number which was also written down in the field book, alongside the locality, time of sampling and any pre treatment given to the water sample (see Table 2.1). Disposable 0.45μm syringe filters were used for samples that needed filtering. Consistency in the sampling procedures was maintained by agreeing with the different persons involved in the field work on how the samples would be collected. Water sampling was done in rounds every 4 to 6 hours, over 24 hours in 2011 (see Table 2.2) and as spot samples in 2012. Each round in 2011 took approximately one hour to complete. The water samples were frozen on site and the frozen samples were transported to the laboratory in cool boxes, containing ice packs. After arrival, the water samples were stored frozen, until the analyses were carried out.

At noon of the 6th March 2011, every water sample (i.e. filtered, unfiltered, with oxidising agent or not), as well as every measurement of DO, temperature, etc, was taken 6 times from each of the sampling locations (i.e. inlet, sites 1 and 2 of the water column, water column incubation and benthic chambers). These were used to calculate the errors that resulted through the processes of sampling and analysis.

The methodologies for water sampling, frequency and replication are relevant during the testing of all three main hypotheses 1, 2 and 3 (see Section 1.5).

Analysis	Filtered	0.075g potassium peroxodisulphate added into 15ml tube
Soluble reactive P (SRP)	Yes	No
Total dissolved P (TDP)	Yes	Yes
Total P (TP)	No	Yes
NH4	Yes	No
NO3	Yes	No
SO4	Yes	No
Ca	Yes	No
Chlorophyll	Yes (filters kept)	No
Polyphosphates	No	No

Table 2-1: Description of the different pre treatment performed upon water samples in the field.

	March field trip							
	02/03/2011			03/03/2011				
inlet	16:00	18:40		02:05	07:32	09:48	12:46	17:00
water column	15:45	17:55	22:25	02:40	06:35	10:20	12:05	17:15
benthic chamber 1	17:05		22:34		06:45		12:10	
benthic chamber 2	17:45		22:46		07:00		12:35	
water column incubation	17:00		22:35		07:08		12:46	
	June field trip							
	06/06/2011			07/06/2011				
inlet	13:55	17:30	21:40	02:15	06:14	09:55	13:20	
water column		17:30	21:46	02:25	07:10	10:07	13:30	
benthic chamber 1	14:15	17:36	21:55	02:30	07:00	10:15	13:30	
benthic chamber 2	14:25	17:55	21:58	02:45	06:44	10:27	13:50	
water column incubation	14:35	17:45	22:09	02:35	06:50	10:24	13:45	

Table 2-2: Detail of the water sampling frequency during the March and June 2011 field works. The round at 12:00 on the 3rd March (shaded column) involved the sampling of 6 replicates from each locality, and for each analysis. This was used later to quantify the errors of the methods used during the project.

2.1.5.1 Sampling the inlet

Water from the inlet was sampled from land. Because of the great force of the water coming through the pipe, it was found easier to take a bulk sample in a 1 litre bottle and then take subsamples from there into the labelled disposable polypropylene tubes. The 1 litre bottle was rinsed with the flowing water before the bulk sample was collected.

The methodology for sampling the inlet is necessary for the testing of hypothesis 1.

2.1.5.2 Sampling the pond

The pond was sampled at localities 1 and 2, from a rowing boat. The samples were taken from 10cm below the water surface. The syringes were rinsed using pond water before the samples were collected. Care was taken to not disturb the sediment and water sampling was undertaken prior to any sediment or pore water sampling.

The methodology for sampling the pond was necessary for testing hypotheses 1 and 2.

2.1.5.3 In situ water column incubations

The in situ incubations were based on work done at Lake Toussaint, Canada by Rigler (1956). In that research project, lake water was placed inside large polyethylene bags suspended from floating frames and then sampled periodically. Using those samples, the author was able to determine fluxes of P taking place in the water column exclusively, in isolation from fluxes through the inlet or sediments. Also, the water in the bags experienced the same temperature and light conditions as the rest of the lake and then the results could be extrapolated to the whole body of water (Rigler, 1956).

For this project, water from the settlement pond was incubated in 90 litre heavy duty bags normally issued for disposal of clinical waste in laboratories. Double bags were secured to perforated PVC pipes of 32.5cm diameter and 0.9 meters long. The pipes were bought from Irrigation UK and the bags supplied by the laboratories at Leeds.

The pipes were sunk in the sediment until approximately 10 cm surfaced over the water. The bags were secured onto the top end of the pipe using cable ties and then filled with pond water. The pond water was collected with a clean bucket that had been rinsed in the pond. See Figure 2.4.

The methodologies for constructing, setting and sampling the water column incubations were relevant for testing hypothesis 1.

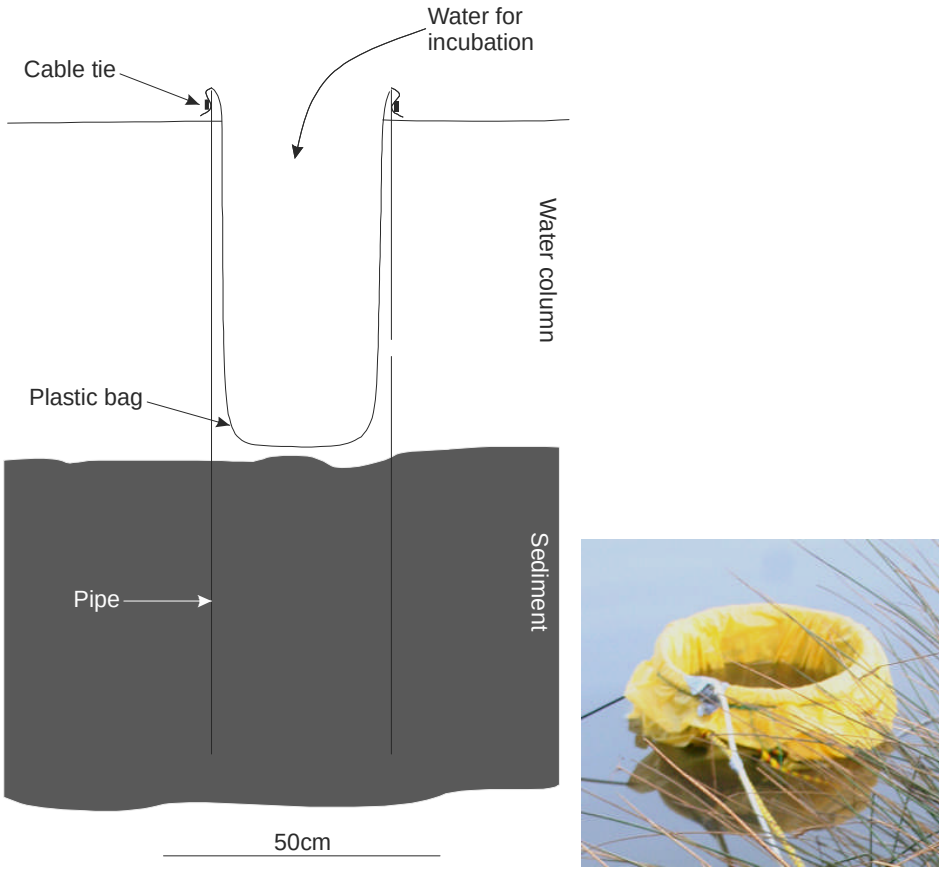


Figure 2-4: Cross section of a in situ water incubation and an incubation deployed in the pond

2.1.5.4 In situ benthic incubations

In situ incubations using benthic chambers were used to derive benthic fluxes of phosphorus. These results would complement fluxes calculated from pore water gradients (see section 2.1.8.1).

The benthic chambers were constructed with PVC pipe of 32.5cm diameter, purchased from Irrigation UK. The pipes were cut 1.2 meters long. Lids were constructed to seal the pipes from the top. The lids had two perforations, one to pass a hose for sampling and another to pass another hose, within which ran a wire, used to rotate a stirrer inside the benthic chamber (see Figure 2.5). The benthic chambers were lowered into the soft mud until they settled on the clay lining (see Figure 2.6). That ensured that the chambers would not sink further during the incubation period. Once in position, the benthic chambers were left uncovered for several hours to allow the dissipation of chemical species and the settling of particulate matter released during the deployment (Noffke et al 2012). Before they were sealed with the lids, the final heights of the benthic chambers were measured carefully, to know accurately the final volume of water that the chambers would hold.

Water from the benthic chamber was sampled through the hose and as described in 2.1.5. Before sampling, the water in the benthic chamber was stirred manually from the boat, by rotating the wire connected to the plastic stirrer inside the benthic chamber.

The methodologies for constructing, setting and testing the benthic incubations were relevant during the testing of hypothesis 1 (see Section 1.5).

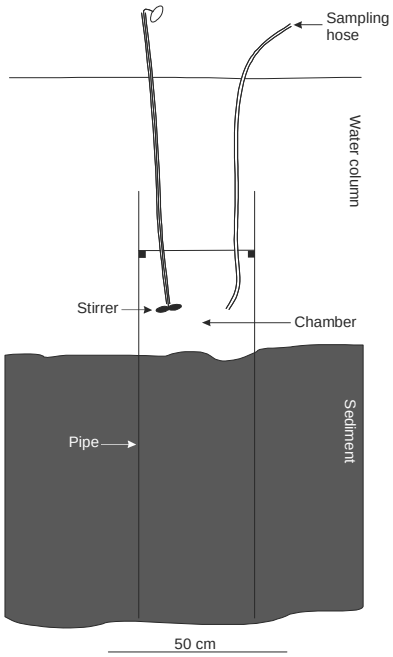


Figure 2-5: Cross section of a deployed benthic chamber

Figure 2-6: Deployment of a benthic chamber. Sections of the pipe that would not be part of the benthic chamber were removed, to make the chamber lighter and to minimise the suction effect when the chambers needed to be pulled out of the sediment.

2.1.6 Dissolved oxygen, pH and water temperature

Dissolved oxygen (DO), pH and water temperature levels were recorded during each sampling round. DO was measured with a Hanna HI 9142 dissolved oxygen meter. The DO meter was calibrated with water saturated with sodium sulphite, for the zero value and in water bubbled with air for the 100% value. pH and

water temperature were measured using a calibrated Jenway model 350 pH meter with temperature probe attached. In 2012, water temperature was measured using an alcohol thermometer.

DO from the inlet was measured from the water collected in the one litre bottle. DO in the pond and in the open column water incubation was measured by lowering the probe 20cm below the water surface. DO was not measured from water retrieved from the benthic chambers. pH and water temperature was measured similarly to DO, but they were also measured from the water from the benthic chambers.

The measurement of DO, pH and temperature were relevant for the testing of hypotheses 1, 2 and 3.

2.1.7 Sampling for chlorophyll

Water for the determination of chlorophyll was collected from the pond in 1 litre bottles. Before filtering, 100 to 200ml of the sampled water were poured into a glass measuring cylinder and the actual volume recorded in the field book. The known volume in the cylinder was then poured carefully onto 0.45 μm nitrate cellulose filter papers attached to a vacuum filtration system. The cylinder was swirled repeatedly to keep all particles in suspension before being poured onto the filter. The filters were removed carefully from the vacuum apparatus and placed in a labelled Petri dish. These were frozen until the analyses were performed. It took approximately 30 minutes between sampling and freezing.

Sampling for chlorophyll was necessary for the testing of hypothesis 1.

2.1.8 Pore water chemistry

2.1.8.1 Diffusive Equilibrium in Thin (DET) gels

DET gels (Davison et al., 1994; Krom et al., 1994; Mortimer et al, 1998) allow high resolution sampling of the chemistry of the pore waters using a thin (0.8mm) polyacrylamide gel. The gels are deployed vertically within a Perspex holder, part in the water column and part in the sediment. The Perspex holder has a window of approximately 2 by 15 cm that allows the diffusion of dissolved ions between the pore waters and the thin gel layer. The surface of the gel is protected from sediment fouling by a permeable 0.45 um cellulose nitrate filter. The ions in solution move through the filter into the thin gel by molecular diffusion, until the gel and the pore waters are in equilibrium. The chemistry of the in situ pore waters is then inferred by analysing the chemistry of the gel (Harper et al 1997, Davison et al., 1994; Krom et al., 1994; Mortimer, 1998).

The advantage of DET gels is that they allow the measurement of the in situ pore water chemistry during an equilibration that takes a relatively short time (Harper et al 1997) and with minimal perturbation of the in situ profile of pore water chemistry and redox conditions. They have been widely employed in the study of pore water chemistry in the marine and fresh water environments (e.g. Mortimer et al, 1998 and Jarvie et al, 2008, among others).

The DET gels were purchased from DGT Research Ltd. The Perspex holders were acid washed and rinsed thoroughly in deionised water. The gels, Perspex holders and filter papers were then assembled, stored in Milli Q water and bubbled with N_2 gas (Krom et al 1994) the night before the field work commenced to displace the dissolved oxygen.

Gels were deployed at Sites 1 and 2 from a rowing boat. The gels were attached to bamboo canes, to allow reaching the bottom of the pond through the water column. The gels needed to be 3 cm in the water column and the rest inside the sediment, although this was difficult to achieve due to the turbidity of the waters and the impossibility of seeing the way the gel probes were being inserted in the sediments. Therefore, the water was dipped carefully at the location where the

gels would be deployed, then the depth was marked on the canes, and the canes were lowered precisely down to that marked distance. However, due to inaccuracies caused primarily by the movement of the boat the gels were sometimes pushed accidentally too deep into the sediment, in which case it was not possible to record the chemistry at the sediment water interface.

The gels were left overnight to equilibrate with the surrounding natural waters. When the gels were retrieved, it was possible to see on the gel holder where the line of the sediment water interface had been. This was recorded for further interpretation of the pore water profiles. The retrieved gel holders were then taken to the side of the pond, wiped clean and the gel removed using clean tweezers and placed on a clean chopping board. The gel was sliced at 5mm resolution and stored in pre-weighted 1.5 ml centrifuge tubes, and these were stored in cool boxes and a refrigerator. The whole process took less than 5 minutes per gel. Gels that would be analysed for iron were placed in a solution of 0.01M sodium hydroxide immediately after retrieval, to fix the iron in its insoluble and immobile form (Davison et al, 1994). Those gels were sliced and stored as above in the laboratory, some 6 hours later.

In the laboratory, the tubes containing the gel slices were weighed, and therefore the weight and volume of each gel section was determined assuming a density of the gel sections of 1g ml^{-1} (Davison et al 1994). Then the extractants were added: 1.5 ml of Aristar 0.25 M sulphuric acid was added to the tubes containing gel samples that would be analysed for SRP; 0.3 ml of Milli Q water was added to the tubes containing gel samples that would be analysed for ammonium; 1 ml of Milli-Q water was added to the tubes containing gel samples that would be analysed for nitrate, sulphate and calcium; and finally, 1ml of 0.6 M Aristar nitric acid was added to the tubes containing gel samples that would be analysed for total iron. These were left overnight and the solutions were analysed for the required chemical species. The original concentrations in the gel, and by inference the pore waters concentrations, were then back calculated using the formula:

Equation 2.2:

$$C = \frac{(V_g \times 0.95 + V_e) \times conc}{V \times 0.95}$$

where:

C :	Pore water concentration (μM)
V_g :	is the volume of the gel sample, in μl, calculated from the difference between the empty tube and the tube with the gel sample in it, and assuming a density of the gel section of 1g ml^{-1}
0.95 :	accounts for the fact that in reality only 95% of the gel volume consists of water and the rest is the gel matrix
V_g :	is the volume of extractant in μl
$conc$:	is the measured concentration of the chemical species analysed, in μM

Pore water profiles can also be used to calculate the theoretical diffusive fluxes across the SWI of different chemical species, using the first law of Flick (Berner, 1980):

Equation 2.3:

$$J = - \Phi \ Ds \ (\delta c \ / \ \delta x \ )_{x=0}$$

Where:

Φ	is porosity
Ds	is the bulk sediment diffusion coefficient, calculated from the tracer diffusion coefficient (Li and Gregory, 1974), and where Φ is Φ^2 if $\Phi \leq 0.7$ or where Φ is Φ^3 if $\Phi > 0.7$ (Ullman and Aller, 1982).
$(\delta c \ / \ \delta x \ )_{x=0}$	is the gradient concentration at the SWI

Sampling pore water chemistry using DET gels was necessary for testing hypotheses1, 2 and 3.

2.1.8.2 O_2 probes

O_2 in pore waters were measured from sediment cores within minutes of being collected. An OX50 Unisense oxygen microsensor mounted on an automated system (both from Unisense, Denmark) was lowered from 1 to 2 centimeters above the sediment water interface into the sediment and O_2 levels were recorded every 0.2mm. The instrument was calibrated at 0 and 100% O2 saturation using solutions of sodium sulfite and by bubbling air respectively.

Measuring oxygen levels in pore waters was necessary for testing hypotheses 2 and 3.

2.1.9 Sediment sampling

Obtaining undisturbed sediment cores from the settlement pond presented special difficulties because of the lack of cohesion of the sediments and of their ease of disturbance during coring. There were several coring systems available that would have dealt with those difficulties: e.g. the commercially available Beeker Sampler from Eijkelkamp Agrisearch Equipment BV, or different designs that have been described in the scientific literature through the years: Elgmork 1962, Burke 1968, Axelsson and Hakanson 1978, etc. However, these options were economically unfeasible.

The coring system ultimately used was designed and tested by me. The basic mechanism of the corer is a diaphragm at its leading end that can be shut closed once the corer has been inserted in the sediment. The diaphragm catches the sediment inside the sampling tube, without disturbing the original sediment structure. The shut diaphragm is watertight, therefore the very unconsolidated

sediment together with the pore waters are kept in situ, as well as any overlaying water if present within the corer (See Figures 2.7, 2.8, 2.9 and 2.10).

The collected cores were frozen upright in cool boxes containing dry ice or in freezers. The frozen cores where transported to the laboratories within cool boxes containing ice packs. The cores where then extruded from the coring tubes and sliced every 1.5 cm, while frozen, using a tungsten carbide tipped hacksaw blade (from Draper, cat.No 19328). The frozen slices were placed in a freeze drier until dry. This was checked by weighing the slices every 24 hours, until the weight of the slices stopped decreasing. The weight of the frozen slices before and after drying was recorded. This information was used for the determination of the porosity of the sediment. See section 2.2.3.1.

Taking undisturbed sediment samples was necessary for testing hypotheses 2 and 3.

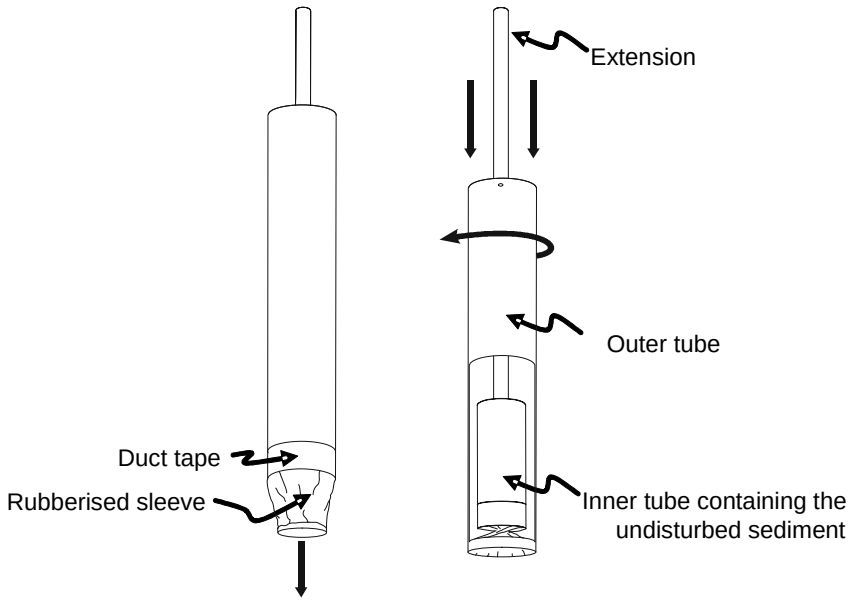


Figure 2-7: Basic mechanism of the coring system. Two tubes were connected by a rubberized sleeve (e.g. a washing up glove with fingers cut off). By rotating one tube against the other, the rubber sleeve closed in an iris-type seal.

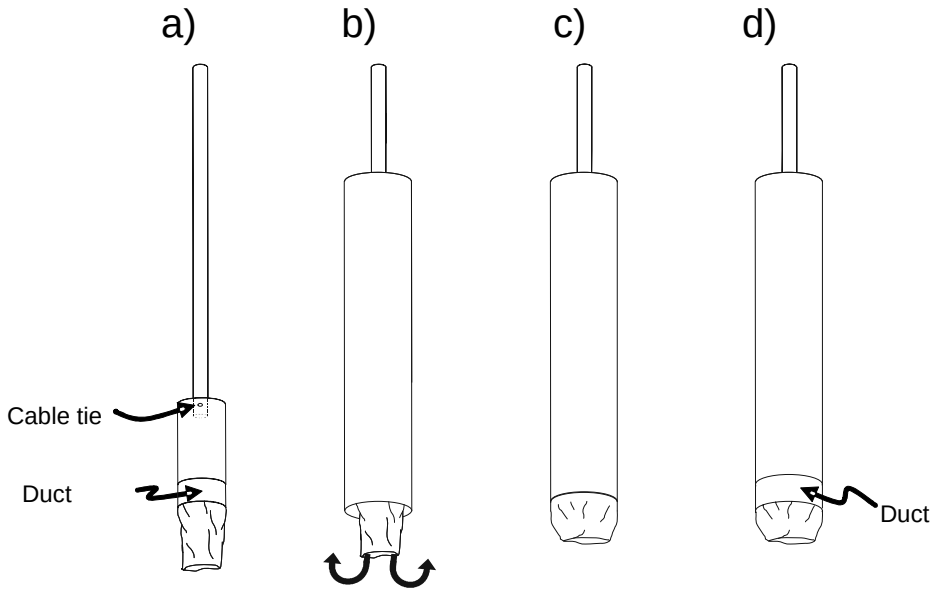


Figure 2-8: Construction of the corer. a) The rubber sleeve was attached to the inner tube using duct tape, and an extension pipe was secured by threading a cable tie through aligned holes on the tubes. b and c) The inner tube and extension were inserted into the outer tube and the rubber sleeve was then turned over the outer tube. d) The rubber sleeve was secured to the outer tube using duct tape.

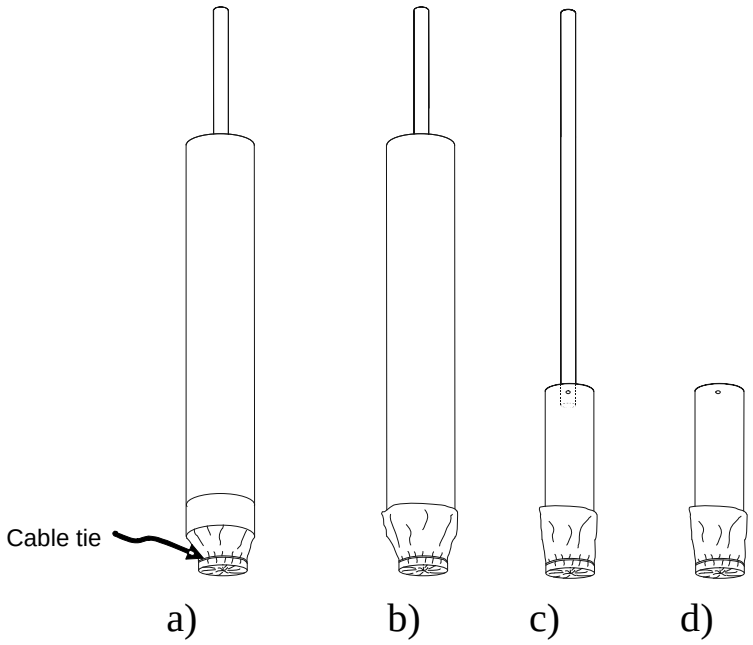


Figure 2-9: Recovery of the undisturbed cores. a) The rubberised sleeve wes secured onto the inner tube using a cable tie. b) The duct tape was peeled off the outer tube and then c) the outer tube was slid off keeping the inner tube always vertical. d) The extension handle wes disconnected from the inner tube. The inner tube containing the sampled core could then be stored, and a fresh inner tube inserted into the coring system to take the following core.

Figure 2-10: a) bringing the corer to the shore, upright with sample inside the inner tube b). detail of the inner tube with undisturbed sample inside. Holes were drilled on the outer pipe to allow water to drain easily when retrieving the corer and to have a better grip when pulling the tubes against the suction of the sediments

2.2 Analytical methods

2.2.1 Analysis of water samples

2.2.1.1 Speciation and analysis of phosphorus

Samples for the determination of the different types of phosphorus had been pre-treated in the field, according to Table 2.1. SRP was determined within 24hs of arrival to the laboratory by the phosphomolybdenum method (Murphy and Riley,

1962), using a Cecil-Ce 3041 photospectrometer. 0.5ml of 1N sulphuric acid was added to the tubes containing the samples for the determination of TDP and TP, and then these samples were digested at 121ºC for 45 minutes in an autoclave. After 45 minutes, the samples were allowed to cool and the samples for the determination of TP were filtered through 0.45µm syringe filters. The digested samples were then analysed for SRP. Particulate P was calculated as TP – TDP.

Standard curves were constructed on the day of analysis. Standards were prepared from stock solution and ranged between 0 and 25 µM P. Precision of the method was determined by calculating the relative standard deviation (r.s.d.), which was calculated by dividing the average of multiple standards by their standard deviation. This resulted in r.s.d. of 5%. Accuracy of the method was determined by calculating the relative error (r.e.) of multiple analysis (n=6) of a known concentration of phosphate, from the certified reference material LGC6020:

Equation 2.2:

$$r.e. = \frac{m - k}{k}$$

Where:
r.e.: relative error
m: the measured value of the reference material
k: the certified value of the reference material

The resulting r.e. for this method were < 4%.

Analysing the different species of P was relevant for testing hypotheses1, 2 and 3.

2.2.1.2 Determination of ammonium and nitrate

Ammonium was determined by a flow injection method (Hall and Aller 1992). The sample was injected into an alkaline carrier stream, so that the stable form of ammonia would be in the gas phase. The gas passed through a hydrophobic gas-permeable membrane. On the other side of the membrane there was an acidic stream, where the gas would be recovered. The effect of the new solute on the conductivity of the receiving stream was used to measure concentration (Hall and Aller, 1992). Standard curves for NH_4^+ determination were made between 0 and 75 uM NH4+, using NH4Cl diluted in Milli Q water. Data quality was checked with repeated ($n \geqslant 6$) measurements of the reference material WW1b. r.s.d were always < 4% and accuracy were < 15%, and where drift could be observed this was corrected.

Nitrate was determined by a Dionex Ion Chromatrograph (ICS-90), fitted with a AS14 column using conductivity detection. The integrations of peaks was done automatically by the Chromeleon software. They were checked manually and corrected when necessary. Standards curves for NO_3^- were made from KNO3 diluted in Milli-Q water, between 5 and 500 uM NO_3^-. The reference material Hamilton 20 was used to check data quality. The r.s.d. were < 4% and the r.e. were < 10%.

Determining concentrations of ammonium and nitrate was necessary for testing hypotheses1, 2 and 3.

2.2.1.3 Determination of chlorophyll

The method used was from Standard Methods for the Examination of Water and Wastewater, 19th Edition). Lights in the laboratory were switched off and work took place only with light from the corridor coming in through the door. This was done to minimise light exposure on the chlorophyll samples. The filter papers where defrosted and cut into small pieces. The pieces were then placed in a centrifuge tube with a round bottom. 2.5 ml of 90% v/v acetone was added to the centrifuge tube and the mix was pulped using a glass stirring rod. When the mixture became a fine suspension, an additional 12.5 ml of 90% v/v acetone was

added and then the tube was shaken vigorously. The tubes where then centrifuged at 3500pp rpm for five minutes. Approximately 10 ml of the supernatant were decanted into a clean tube, from which a subsample was taken for analysis.

The subsample was decanted into a quartz cuvette of 10mm path length, which was then inserted into a Cecil-Ce 3041 photospectrometer. Absorvances were measured at 665nm wavelength. The equation to calculate the content of chlorophyll was:

Equation 2.5:

$$Chl.a = \frac{11.9 \times A \times v}{d \times V}$$

Where:

$Chl.a$:	concentration of chlorophyll in $\mu g\ l^{-1}$
A:	absorvance units
v:	volume of solvent in ml. In this analysis v = 15
V:	volume of initial filtered sample in litres. Variable, recorded in the field book
d:	cell path length in centimetre. In this analysis d = 1

Determining levels of chlorophyll was necessary for testing hypothesis 1.

2.2.2 Analysis of DET gel sections

2.2.2.1 Determination of SRP

Before analysis, the extracts were diluted 4 times to reduce their acidity. The diluted extracts were measured by Murphy and Riley (1962) as described in 2.2.1.1 The original SRP concentration in the gel, and therefore in the pore

waters, was then calculated as in 2.1.8.1. Although the slicing of DET gels generated large numbers of samples, standards and samples were analyses in batches of 18. This was done to avoid significant changes in the blue colour of the reacted samples during the long time that would have taken to analyse larger batches.

Determination of levels of SRP from DET gel sections was necessary for testing hypotheses1, 2 and 3.

2.2.2.2 Determination of total dissolved iron

The determination of Total Dissolved Iron from gels was done following the method of Viollier et al (2000). 1ml of extract from the gel sections was added to a 1ml plastic cuvette. The following reagents were added:

- 100 µl of ferrozine colour reagent (0.492g $C_{20}H_{13}N_4O_6S_2Na$, 0.76g CH_3COONH_4 in 100ml Milli-Q water),
- 200 µl hydroxylamine hydrochloride solution (9.7g $H_2NOH.HCl$ in 100ml 2M HCl)
- 100 µl buffer solution (76g CH_3COONH_4 in 100ml Milli-Q water adjusted to pH 9.5 with NH4OH)

Absorvance was measured after 10 minutes at 562nm (Viollier et al, 2000). Calibration was done with stock solution, between 0 to 10µM Fe2+. Multiple checks (n>5) on repeated standards resulted in a rsd < 5%. Accuracy was checked by measuring the certified reference material ERM®-CA011a, and resulted in r.e. < 8%.

Determination of levels of dissolved iron from DET gel sections was necessary for testing hypotheses 2 and 3.

2.2.2.3 Determination of ammonium, nitrate and sulphate

The determination of ammonium and nitrate from gel extracts, as well as the standards and data quality checks were done as in 2.2.1.2. The determination of sulphate was done simultaneously with the determination of nitrate, using the same equipment and software.

Calibration curves for sulphate were constructed by measuring standards between 2 and 16μM SO_4^{2-}. Precision was calculated by repeating the measurements of standards and resulted in r.s.d. < 3%. Accuracy was calculated by comparing with certified reference material Hamilton 20, and r.e. were < 5%.

Determination of levels of ammonium, nitrate and sulphate from DET gel sections was necessary for testing hypotheses1, 2 and 3.

2.2.2.4 Determination of calcium

Ca^{2+} was measured with a DX-500 Ion Chromatography system measuring conductivity. Chromeleon was used to integrate the peaks and to check and correct manually when necessary. Standards were prepared from stock calcium standard solution (1000 mg l^{-1}) (VWR Scientific), between 0 and 60 μM Ca^{2+}. Precision was checked by measuring repeated standards and yielded r.s.d. < 3%. Accuracy was determined using the certified reference material ERM®-CA011a and r.e. were < 3%.

Determination of levels of calcium was necessary for testing hypotheses 2 and 3.

2.2.3 Analysis of sediment samples

2.2.3.1 Determination of porosity

Porosity (φ) is the ratio of volume of water in the void spaces to the total volume of the sediment:

Equation 2.6:

$$\varphi = \frac{v_w}{v_t}$$

Where:

φ: porosity

V_w: volume of water in the pore space

V_t: total volume of the sediment

Porosity was determined from each 1.5 centimetre section of sediment recovered. The volume of each section (V_t) was known because they all had the same thickness and the diameter of the coring tube was known. Volume of water in the void space (V_w) was inferred by recording the weight of each section before and after freeze drying them.

Determination of porosity was necessary for testing hypotheses 2 abd 3.

2.2.3.2 The SEDEX method

The SEDEX method (Ruttenberg et al, 1992) is a detailed speciation of solid phase P. The speciation is performed by sequentially extracting P from five operationally defined reservoirs in the solid sediments:

1) exchangeable or loosely sorbed P,
2) P bound to ferric oxides or oxyhydroxides,
3) authigenic carbonate fluorapatite + biogenic apatite + $CaCO_3$-bound P,
4) detrital apatite of igneous or metamorphic origins, and
5) organic P.

This is done in five progressive steps, using different leaches (see Figure 2.11) whose strength increase progressively, dissolving more insoluble phases in the process (Ruttenberg et al, 2009).

The advantages of the SEDEX method are:

1) it differentiates between authigenic/biogenic apatite and detrital apatite. This separation is relevant because while authigenic or biogenic apatite consumes pore water SRP, detrital apatite does not. Therefore, authigenic/biogenic apatite is a sink or reactive P, but detrital apatite is not.

2) The method also solves typical analytical artefacts of sequential extractions, such as the redistribution of P between steps. This is achieved by washing the sediments with $MgCl_2$ between steps (Ruttenberg et al 1992).

During this project, the solid phase extraction manifold (SPExMan) was employed (Ruttenberg et al, 2009). The use of the SPExMan avoids the loss of sample during the removal of the extract, and reduces the time and work load typical of sequential extraction protocols (Ruttenberg et al, 2009).Dried sediments from the sliced cores (see section 2.1.9) were weighted and poured in the reaction vessels of the SPExMan, which had 0.45μm filters attached. The SPExMan was re-assembled and the first extractant was added. The extracts were subsequently filtered out into 15ml centrifuge tubes and new extractants added as detailed in Ruttenberg et al (2009), see Figure 2.11. Errors were calculated performing the SEDEX method on multiple replicates of the same sample. The calculated precision for the different steps is detailed in Table 2.3:

step	rsd
I	3 %
II	24 %
II	7 %
IV	13 %
V	10 %

Table 2-3: calculated errors on the different steps of the SEDEX method

The extracts were analysed as described in 2.2.1.1 and the calibrations were done as described in 2.2.1.1, but the extracts and the standards had to be modified to correct for different interferences:

- Extracts in 1M $MgCl_2$ were analysed unchanged, and the standards were also prepared in 1M $MgCl_2$
- Extracts in CDB solution (see fig 2.11) were diluted 125 times, to a citrate concentration of 2.4mM (Eijsink et al 2000). Standards were prepared in a similar matrix
- Extracts in 1M Na-acetate were diluted 10 times and standards were prepared in a similar matrix
- Extracts in 1M HCl were diluted 10 times, and standards were prepared in 0.1M HCl

Speciation of P from sediment samples was necessary for testing hypotheses 2 and 3.

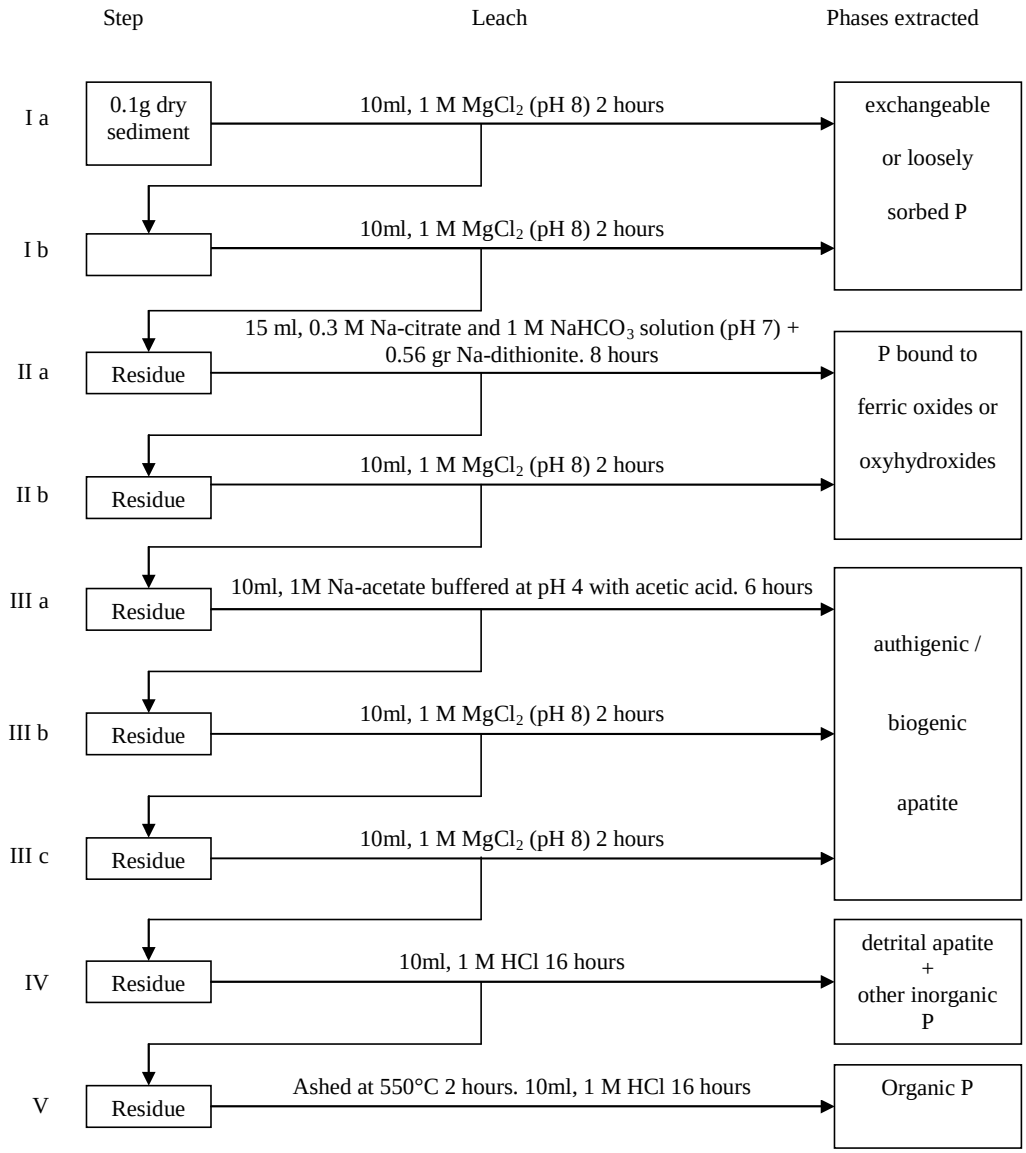


Figure 2-11: The five progressive steps, using different leaches of increasing strength, which dissolve increasingly insoluble phases of P in the process.

2.2.3.3 The Aspila method

The Aspila method is a rapid way to determine Inorganic P (IP), Organic P (OP) and Total P (TP) in lake and river sediments (Aspila et al, 1976), which has also been used in marine sediments (Eijsink et al, 2000). IP and TP are determined in two separate subsamples of the sediments, and their difference is defined as OP. Approximately 0.1 gram of dried sediment (see section 2.1.9) was poured into 15ml centrifuge tubes and the actual weight of sediment was recorded. 10ml of 1M HCl was added and the suspension was shaken for 16 hours. The suspension

was then filtered and the filtrate anlaysed as in 2.2.3.2. The P content in the filtrate determined IP. A separate 0.1 grams of dried sediment were poured in a crucible and ashed at 550°C for 2 hours. Once cooled, 10ml of 1M HCl was added to the crucible; this was sealed with Parafilm and shaken during 16 hours. The suspension was then filtered and the filtrate analysed for SRP as in 2.2.3.2. TP was determined by the P content in the filtrate of the ashed sample. OP was then calculated as the difference between TP and IP.

Speciation of P using the Aspila method was necessary for testing hypotheses 2 and 3.

2.3 Sediment incubations

Incubations were prepared, sampled and analysed to study the effect of temperature on the release of SRP from sediments. The method employed is an adaptation of Nürnberg (1987). Sediment was sampled in June 2012 using the corer described in 2.1.9. The top of the core tubes containing the undisturbed sediment and overlying water were sealed immediately with Parafilm. They were stored upright in cool boxes with ice packs and transported to the laboratories in Leeds. Upon arrival, they were placed upright inside a sealed glove bag, which was then filled with nitrogen gas. Approximately 5 hours passed between coring and placing the cores in nitrogen gas.

Once the sediments were inside the glove bag in an anoxic atmosphere, the Parafilm was removed from the core tubes and the water overlying the sediments was discarded into a beaker using a syringe. The sediment cores were then emptied into a large bowl and homogenised thoroughly with a Teflon spoon. 15 ml pre-labelled centrifuge tubes were filled with the homogenised mud and placed in three different anaerobic jars, all in a nitrogen atmosphere. The three anaerobic jars containing the 15ml tubes with sediments were sealed, removed from the glove bag, and placed in three different incubators: one at 4°C, one at 15°C, and another at 20°C, to interpret later how temperature affected the release of P from sediments as discussed by Jensen and Andersen (1992).

Three 15 ml tubes were centrifuged and the supernatant analysed for SRP as in 2.2.1.1. Those values determined t = 0 of the incubation. After 24 hours, the anaerobic jars were removed from the incubators, placed inside a glove bag which was then filled with nitrogen gas. The three jars were opened and three 15ml tubes with sediment were removed from each jar. The anaerobic jars were sealed again inside the glove bag and returned to their respective incubators. The time that the jars stayed outside the incubators was approximately 30 minutes. The removed tubes were then centrifuged and the supernatants were filtered, frozen and analysed later for SRP. This operation was repeated at t = 2, 3, 4 and 5 days.

Preparation and sampling of sediment incubations were necessary for testing hypothesis 2.

2.4 Calculations

2.4.1 Water balance

Budgets of P in and out of the lagoon were calculated to understand the processes that controlled the cycling of P in March and June 2011. This approach required the quantification of the flows of water in and out of the lagoon. When flows were known, they were integrated with the concentrations of the different species of P, and the fluxes of P were thereafter calculated (Badr and Hussain, 2010).

Water mass balance was expressed by an equation that relates changes in water column volume in a given time with the rate of all the possible sources and loses of water (Chapra, 2008):

Equation 2.7:

$$S = \frac{dV}{dt} = Q_{in} - Q_{out} + G + P - E$$

Where:

S: Storage (m^3 d^{-1})
V: Volume (m^3)
t: time (days)
Q_{in}: total water inflow (m^3 d^{-1})
Q_{out}: total water outflow (m^3 d^{-1})
G: ground water flow(m^3 d^{-1})
P: precipitation (m^3 d^{-1})
E: evaporation (m^3 d^{-1})

Q_{in} was measured as described in 2.1.4. G was assumed to be insignificant since the settlement pond was dug in clay (Mackenzie, umpublished draft). Precipitation was measured during the field work by deploying a rainfall gauge on site. Values for E were calculated using an empirical formula (Hess 1996). The solution of the formula required the input of parameters such as time of year and latitude, cloud cover, air temperature, wind velocity and relative humidity. *d*V was measured during each 24 hours period from a staff graduated every 1 centimetre firmly inserted in the bottom of the settlement pond and extending above surface of the water. Finally Q_{out} was calculated by solving the equation above (see Figure 2.12).

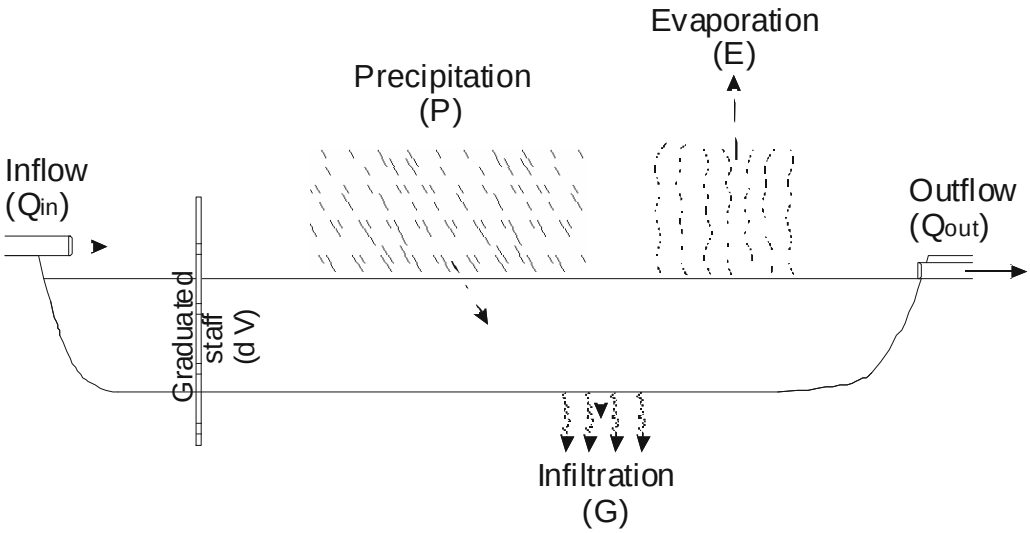


Figure 2-12: : Schematic representation of the different sources and loses of water considered for the calculation of the water balance. These include inflow (Q_{in}), outflow (Q_{out}), infiltration (G), precipitation (P), evaporation (E), and the daily changes in the volume of water (*d*V).

Calculation of the water balance was necessary for testing hypothesis 1.

2.4.2 Integration of the budgets of P

2.4.2.1 Mass balance of P in and out of the lagoon

The budgets of P (SRP, DOP or Part P) were calculated as the difference between fluxes in and out of the settlement lagoon. Fluxes into the settlement lagoon were calculated by integrating the volume of water that flowed into the settlement pond during a 24 hours period with the concentrations of SRP, DOP or Part P during that time. Each measured concentration of P was plotted against the time at which the corresponding sample was taken. The water that flowed through the inlet between each sampling instance was interpolated from the calculated volume of water that flowed through the inlet during the 24 hours of sampling (calculated as in Section 2.1.4). The mass of P that flowed through the inlet during the 24 hours sampling was integrated by using the trapezoidal rule for numerical integration, multiplying the average concentration of two consecutive sampling instances by the calculated volume of water that flowed

through the inlet during the time that passed between sampling, and then adding each trapezium. The fluxes of P through the outlets was calculated as the fluxes through the inlet but using the out flowing rate Q_{out} calculated as in Section 2.4.1 above, and the concentrations of P in the water column.

As discussed in Section 1.2.3.1, shallow lakes are very susceptible to external conditions such as air temperature, solar radiation, wind, etc. For example, it was known that DO had strong diurnal patterns in the settlement lagoon, being highest in the afternoon and lowest in the morning (Palmer-Felgate et al, 2011b) and, as discussed in Section 1.1.3, SRP levels are related in part to levels of DO. In order to account for diurnal variations in the cycling of P in the water column, the sampling was carried out several times in a 24 hours period, and 24 hour fluxes were integrated thereafter. Another reason for doing 24 hours sampling was that the inflow rates varied because the pumps work intermittently, and a reliable value for flow rate was necessary to calculate the flux of P into the pond, in order to construct the overall P budget. Therefore it was considered a better choice to calculate the total volume of water that flowed into the pond in a 24 hours period based on the numbers of hours that each pump worked. A final reason to sample during 24 hours periods was that some fluxes were quantified using in situ incubations (see Sections 2.1.5.3 and 2.1.5.4) that take a certain length of time to develop reliable results.

The decision for spring and summer sampling was based on historical data from the settlement lagoon and data from other shallow lakes in the literature that suggested that spring and summer were the two seasons when the cycling of P is active and most relevant in shallow lakes in temperate climates. Monitoring data from the settlement pond between 2005 and 2009 showed that the lowest values of SRP occurred in early spring and that they peaked in the early summer (Stratford et al 2010). This agreed with other regular measurements of SRP in the settlement pond (Palmer-Felgate et al, 2011b, and unpublished WWT monitoring data). The pattern also agreed with data from Lake Søbygaard in Denmark, with a mean depth of 1.0 meter (Søndergaard 1988) and was discussed by Marsden (1989) for shallow well mixed lakes in general. The reasons for the pattern of spring minimum and summer maximum release of SRP are frequently related to

the occurrence of algal blooms in early spring that take up SRP and favour the retention of P in the sediments, followed by the collapse of the algal blooms that create favourable conditions for the release of SRP from the sediments into the water column (e.g Spears et al 2007).

Calculating the mass balance of P in and out of the lagoon was necessary for testing hypothesis 1.

2.4.2.2 Integration of the internal budgets of P

The settlement lagoon system was divided into two, the water column and the sediments. This approach for the study of the sources and sinks of P in a shallow lake is similar to previous studies. In an assessment of the impact of soil erosion on the P budget of shallow Dutch lakes, these were divided into two main reservoirs: water column and sediments. The fluxes of P included in the study were the input of P, fluxes of P through the SWI and algal recycling of P in the water column (Golterman, 1973). A different study about the cycling of P in the eutrophic Withe Lake, in the US, also divided the system into water column and sediment. The fluxes quantified within the water column were the net change between dissolved P and particulate P, settling of particulate P and diffusion of SRP through the SWI (Lung et al 1976). In a study of the partitioning of P in lake sediments, the authors included a holistic model of P cycling in fresh water lakes. The system was principally divided in two: water column and sediments. The proposed cycling of P in the water column was a complex web that included SRP, phyto and bacterioplankton, zooplankton, benthic algae and bacteria and macrophytes (Spears et al 2007). This contrasted with another study of the partitioning of P in sediments of fresh water shallow lakes, where the authors neglected the cycling of P in the water column and they were only concerned with the fluxes through the SWI (Søndergaard et al 2003). In a study of the retention of P by wetlands and rivers, these systems were divided, again, between water column and sediments, and the water column was divided in areas planted with macrophytes or not. The cycling of P in the water column in those areas not

planted with macrophytes included Particulate P (organic and inorganic), DOP and SRP (Reddy et al 1999).

Internal fluxes of P (through SWI and within water column) were measured independently, to asses their contributions to the overall mass balance. The forms of P that were measured in the water column were Particulate P (Part P), Dissolved Organic P (DOP) and SRP. The budgets in and out of the lagoon and the internal fluxes of SRP, DOP and Part P were combined to obtain a complete cycle of P in the settlement lagoon (see Figure 3.3). Other parameters were measured to help interpret the results from the constructer cycles of P. These included weather conditions, Chl.a, DO, pH, NH_4^+ and NH_3^-.

The integrationof the internal budgets of P was necessary for testing hypothesis 1.

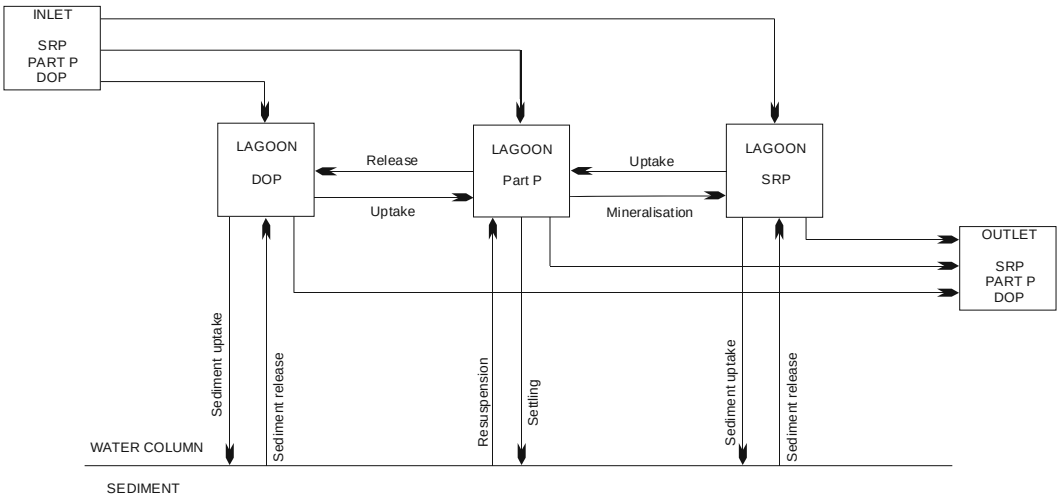


Figure 2-13: The proposed cycle of P that was used to quantify the fluxes of P in, out and within the settlement lagoon

2.4.2.3 Fluxes of P through the SWI

Fluxes of SRP through the SWI were calculated using Fick's first law (Berner, 1980). The calculation required knowing the differences in P concentration in the water column just above the SWI, and in the pore waters just below the SWI (see Section 2.1.8.1), by the use of DET gel probes.

Sometimes, fluxes of SRP through the SWI, when measured with gel probes, can be underestimated. For example, in a study of fluxes in a marine system, the calculated fluxes resulted 3.3 and 8.6 times lower than when measured with benthic chambers (Noffke et al, 2012). The difference was attributed to 1) poor resolution in the SRP profiles derived from gel samples that masked steeper gradients very close to the SWI, 2) the presence of a thick transition layer that confused the interpretation of the gel profiles, as also suggested also by Palmer-Felgate et al (2011b), 3) bioirrigation events not recorded by the minimal area of the sediments that is covered by the gel profiles, but that contributed to the increase in concentration of SRP within the benthic chambers (Noffke et al, 2012). The presence of a thick transition layer was also caused calculated fluxes of SRP to appear smaller than fluxes measured from sediment cores with overlying water (Slomp et at, 1998).

Since a thick transition layer was expected to be present between the water column and the sediment of the settlement lagoon (Palmer-Felgate et al, 2011b), and because bioirrigation was likely to occur, SWI fluxes for this work were also calculated from in situ benthic incubations (see Section 2.1.5.4). Benthic chambers were deployed at site 1 and site 2, and sampled every 4 to 6 hours during 24 hours as described in Sections 2.1.5 and 2.1.5.4. The fluxes were calculated as follow:

Equation 2.8:

$$\Delta\ mass = \Delta\ conc\ \ x\ \ volume$$

Where:

Δ mass:	difference in mass of SRP (or DOP) within the chamber after 24 hours period, expressed in µ moles
Δ conc:	difference in concentration of SRP (or DOP) within the benthic chamber after 24 hours period, expressed in µ M
Volume:	Volume of water in the benthic chamber

Δ conc was initially assumed to be the resultant of fluxes through the SWI. The *Δ mass* then obtained was attributed to the surface area of the bottom sediments covered by the benthic chambers and of the bottom waters (approximately 10 cm). The flux of SRP (or DOP) through the SWI of the whole settlement lagoon during the 24 hours sampled was calculated twofold. The Δ mass obtained form the benthic chamber deployed at site 1 represented the flux for the west half of the pond, and the Δ mass obtained form the benthic chamber deployed at site 2 represented the flux from the east half of the pond. Δ mass was then extrapolated from the area covered by each benthic chamber to half the surface area of the pond. The fluxes from both halves of the pond were then added and that resulted in the total flux of SRP through the SWI during the 24 hours sampling period.

Calculating the fluxes of P through the SWI was necessary for testing hypothesis 1.

3.2.4.2 Fluxes of P within the water column

The in situ water column incubations (see section 2.1.5.3) were based on work done at Lake Toussaint, Canada, by Rigler (1956). In that research project, large plastic bags were attached to frames floating on the lake's surface, and the bags were filled with lake water. By sampling the water within the bags regularly, the author was able to determine fluxes of P taking place in the water column exclusively, in isolation from fluxes through the inlet or sediments. Also, the water in the bags experienced the same temperature and light conditions as the rest of the lake and then the results could be extrapolated to the whole body of water (Rigler, 1956).

The incubations were also used to estimate the rate of settling of Particulate P, following the method described in Browman et al (1979). Samples were taken 10 centimetres below the water surface every 4 or 6 hours and analysed for Particulate P. The rate of settling of Particulate P was calculated from the drop in concentrations of Particulate P through time. However, it was acknowledged that the rate of settling estimated this way would have resulted in higher values than

those encountered in the rest of the settlement lagoon because the water within the plastic bags was more sheltered than the open waters outside them.

Calculating the fluxes of P within the the water column was necessary for testing hypothesis 1.

2.5 Release and retention of P from sediments

The main tool to study which processes caused the release or retention of P from sediments were the profiles of species of P, measured using the SEDEX method (see Section 2.2.3.2). These were obtained from cores collected in March and June 2011 and 2012. The subsequent profiles were compared and their similarities or differences allowed the inferences of which processes may have taken place during those periods of time.

Those inferences were sustained by the study of the profiles of pore water chemistry (see Section 2.1.8.1). These included pore water DO, ammonium, nitrate, dissolved iron and sulphate, for March and June, 2011 and 2012. The inference of processes related to P chemistry, by combining the interpretations of SEDEX profiles and of pore water profiles, has been done before, for example as reported by Ruttenberg and Berner (1993), or by Goldhammer etal (2010).

From the values of P measured using the SEDEX method, the mass of the different species of P were quantified, between the SWI and the bottom of the profiles. These depended on the normalised concentrations and on the porosity of the sediments. Knowing the masses of the different species of P stored down the profiles in March and June allowed to quantify how much P (in moles) was lost or gained through that period of time, and how much P was taken or lost from the pore waters. This approach is similar to that employed in a study of Loch Leven, Scotland, in which the differences in masses of P measured from sediments collected monthly were used to calculate the release of P from sediments (Spears et al 2007).

The quantification of the release of P from sediments by comparing the stored pools of particulate P of two samples taken at different times from the same sites has been reported before. In a study of Loch Leven, Scotland, the authors calculated the release of P from sediments using the differences in the masses of P measured from sediment samples collected monthly (Spears et al 2007). Through verbal communications with WWT management, it was known that the sediments of the settlement lagoon had never been dredged; therefore the in situ sediments would have represented the totality of the sediment profile as it was originally laid, between 1996 and 2012.

It was known, through verbal communications with WWT management, that the sediments of the settlement lagoon had not been dredged, and that therefore the cored sediments would have represented the material as original deposited. Parameters such as weather conditions and water temperature were also considered in the study of the sediments of the settlement lagoon.

Calculating the release or retention of P from the sediments was necessary for testing hypothesis 3.

2.6 Methods summary

The methods described in the previous sections were employed throughout the project, in order to address the different hypotheses, as described in Table 2-4.

Method (Section)	Hypotheses that were tested using each method
Description of the pond (2.1.1)	1-2-3
Weather observations and weather data (2.1.2)	1-2-3
Bathymetric survey (2.1.3)	1
Water flow through the inlet (2.1.4)	1
Water sampling, frequency and replication (2.1.5)	1-2-3
Sampling the inlet (2.1.5.1)	1
Sampling the pond (2.1.5.2)	1-2
In situ water column incubation (2.1.5.3)	1
In situ benthic chambers (2.1.5.4)	1
Dissolved oxygen, pH and water temperature (2.1.6)	1-2-3
Sampling for chlorophyll	1
Diffusive equilibrium in thin (DET) gels	1-2-3
O_2 probes (2.1.8.2)	2-3
Sediment sampling (2.1.9)	2-3
Speciation and analysis of phosphorus (2.2.1.1)	1-2-3
Determination of ammonium and nitrate (2.2.1.2)	1-2-3
Determination of chlorophyll (2.2.1.3)	1
Determination of SRP from DET gel sections (2.2.2.1)	1-2-3
Determination of iron from DET gel sections (2.2.2.2)	2-3
Determination of ammonium, nitrate and sulphate from DET gel sections (2.2.2.3)	1-2-3
Determination of calcium from DET gel sections (2.2.2.4)	2-3

Table 2-4 : List of methods used and the hypotheses (see Section 1.5) that were tested using each method

Method (Section)	Hypotheses that were tested using each method
Determination of porosity (2.2.3.1)	2-3
SEDEX method (2.2.3.2)	2-3
Aspila method (2.2.3.3)	2-3
Sediment incubations (2.3)	2
Water balance calculation (2.4.1)	1
Calculation of the mass balance of P in and out of the lagoon (2.4.2.1)	1
Integration of the internal budgets of P (2.4.2.2)	1
Calculation of the fluxes of P through the SWI (2.4.2.3)	1
Calculation of the fluxes of P within the water column (3.2.4.2)	1
Calculation of the release and retention of P from the sediments (2.5)	3

Table 2-4 (cont): List of methods used and the hypotheses (see Section 1.5) that were tested using each method

3 LONG TERM WATER QUALITY DATA

3.1 Water quality prior to the construction of the South Finger wetland

Studies undertaken prior to the construction of the South Finger wetland showed that water leaving the bird collection had elevated BOD_5 and suspended solids, and that nitrate, ammonia and phosphate were above the acceptable levels for water to be discharged into surface waters of conservation value (Worral et al 1997). Since data before the commissioning of the wetland in 1994 was not available, this was inferred from the 1995-1996 data from Millett (1997) (See Figures 3-1, 3-2 and 3-3). The parameters measured in that report were total suspended solids (TSS), biological oxygen demand (BOD_5), ammonia, nitrate and phosphate.

Turbidity inhibits light penetration and therefore photosynthesis, and this causes low levels of oxygen. Suspended solids affect the metabolism of plants, invertebrates and fish and it has negative aesthetic consequences (Ryan 1991). However, the negative effects of turbid waters discharging into a river vary depending on the turbidity of the receiving waters. For example an increase in turbidity of 50% of an already turbid river will have small effect, whereas an increase in turbidity of 10% of a clear stream will be noticeable (Ryan 1991).

Biological oxygen demand (BOD_5) is the drop in oxygen concentration in a water sample after 5 days of incubation at 20°C. It is an indication of the amount of aerobic respiration taking place in the water, fuelled by the presence of organic matter, and it is used as an indicator of organic pollution of water (O'Connor 1980).

Ammonia is toxic to fish at levels as low as 0.5 mg N l^{-1} (McKenzie and McIlwraith, 2012). Ammonia causes changes in hatching patterns and growth

rates, as well as altering the development of different organs. Excess nitrates and phosphates in rivers can lead to the eutrophication and hypoxia (dissolved oxygen < 2mg O_2 l^{-1}) in coastal waters (McKenzie and McIlwraith, 2012).

The concentrations of TSS, BOD_5, ammonia and nitrate leaving the visitor centre and the exhibit ponds in the mid-1990s were similar to those encountered in a shallow lake used by migrating birds at the Bosque del Apache National Wildlife Refuge in the US (Brandvold et al, 1976), where BOD_5 levels were 337.5 µM O_2 (between 160 and 320 µM O_2 at WWT), ammonia levels were 39.3 µM NH_3^+ (between 70 and 140 µM NH_3^+ at WWT), nitrate levels were 88.0 µM NO_3^- (between 100 and 350 µM NO_3^- at WWT). Orthophosphate was higher in the water leaving the Visitor Centre (between 16 and 64 µM PO_4^{3-}) than in the water in the lake at Bosque del Apache (5.0 µM PO_4^{3-}).

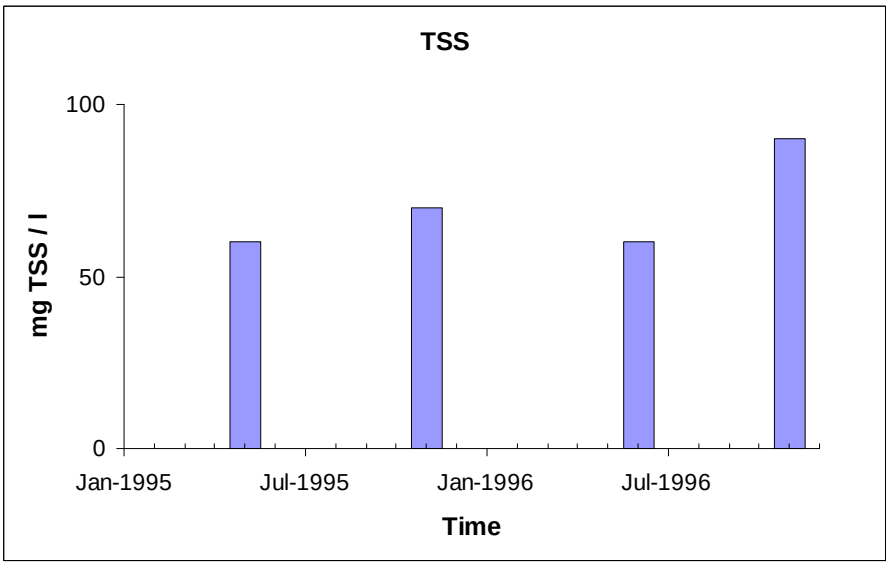


Figure 3-1: Levels of TSS in water leaving the Visitor Centre prior to the construction of the South Finger wetland in 1994, inferred from 1995 and 1996 data

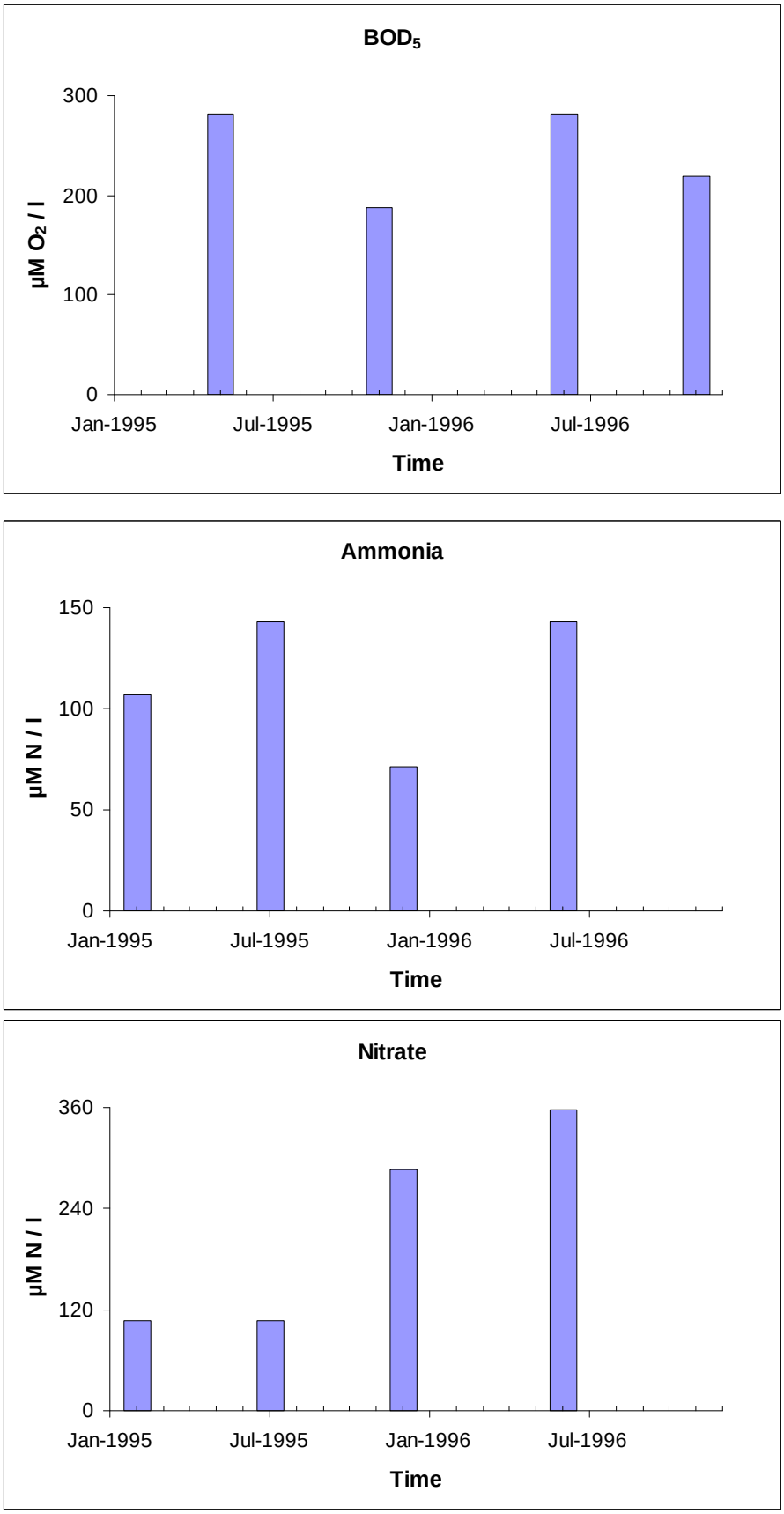


Figure 3-2: Levels of BOD5, ammonia and nitrate in water leaving the Visitor Centre prior to the construction of the South Finger wetland in 1994, inferred from 1995 and 1996 data

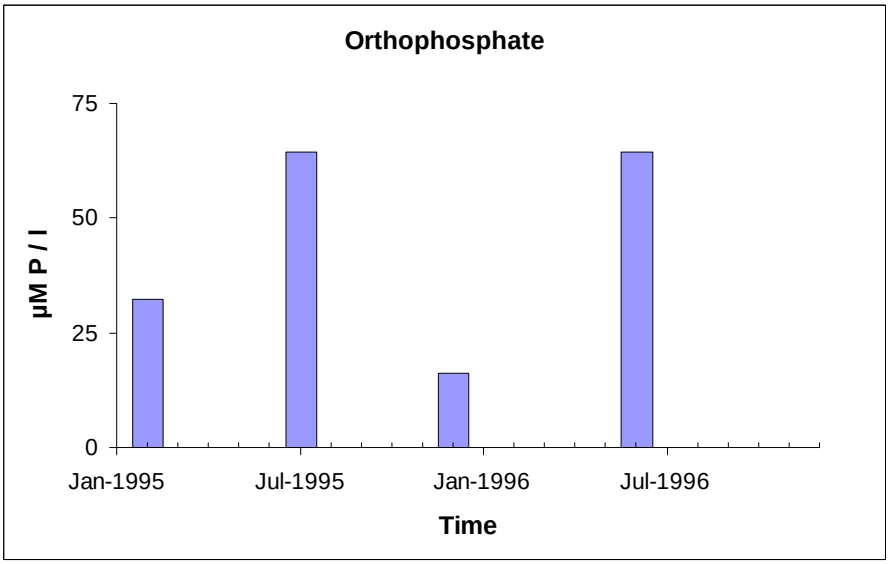


Figure 3-3: Levels of orthophosphate in water leaving the Visitor Centre prior to the construction of the South Finger wetland in 1994, inferred from 1995 and 1996 data

There are numerous examples of FWS constructed wetlands that have been able to treat water of the quality presented by the effluents of 1995-1996. The levels of suspended solids reported for the water exiting the Visitor Centre are high. They were similar to those reported from wastewater from a dairy farm, which were successfully removed using a constructed wetland (Tanner, 1996).

Levels of BOD_5 (between 5 and 10 mg O_2 l^{-1}) in the water leaving the Visitor Centre in 1995-1996 were relatively low. Steinmann et al (2003) reported concentrations of BOD_5 in communal waste water from rural (low density) communities in south Germany, of 34mg O_2 l^{-1} during the late 1990s, which were successfully treated locally using small constructed wetlands. Waste water from high density populated areas, on the other hand, can present BOD_5 levels of over 100mg O_2 l^{-1}, even after secondary treatment (Kaseva 2004).

Ammonia levels at Slimbridge in 1995-1996 (between 1 and 2 mg N l^{-1}) were relatively low for untreated waste water. The average concentration of ammonia from single-family domestic effluent was measured at 48 mg NH4-N l^{-1} in a study in the US in 2002 (Steer et al 2002) and domestic effluent in China has been reported to contain 19.4 mg NH4-N l^{-1} of ammonia (Song et al 2006). The

levels of ammonia in the effluents from the Visitor Centre compare to those reported by Brandvold et al (1976) for a natural shallow lake with high density of migrant birds, or by Schultz et al (2003) for effluents from trout farming in rivers in Germany. Success in the removal of ammonia in treatment wetlands however varies according to the availability of oxygen (Reed and Brown, 1992), temperature and biological activity. Song et al (2006) reported removal of ammonia from 19.4 to 11.3 mg N l^{-1}, and the authors attributed the relative low performance to low temperatures, which promoted high solubility of ammonia and the inhibition of plant growth. Crites et al (1997) reported zero removal of ammonia in a FWS treatment wetland, attributed to high biological activity, low oxygen conditions and low temperatures.

Nitrate levels in the water leaving the Visitor Centre in 1995-1996 were low (between 1.5 and 5 mg N l^{-1}), similar to those reported for the Santa Ana River for 1992-1993. Water from that river was diverted through a FWS that reduced nitrate concentrations to about 0.1 mg $l^{-}1$ NO_3^- (Reilly et al 2000). The authors concluded that the removal of nitrate was maintained by high amounts of organic matter that fuelled the metabolism of denitrifying bacteria, helped by warm temperatures. Oostrom and Russell (1994) agreed that removal of nitrates can be very effective, even from highly polluted waters, as long as a source of carbon is available to fuel denitrifying microorganisms, and that rates of denitrification improve at higher temperatures.

The values of orthophosphate coming out the Visitor Centre were comparable to other surfaces waters in the UK. Jarvie et al (2006) reported SRP (mainly orthophosphate) concentrations between 0.25 and 2.25 mg P $l^{-}1$ for the river Aire, which crosses dense urban/industrial areas. The performance of constructed wetlands for the retention of orthophosphate varies. Concentrations of orthophosphate in secondary sewage effluent decreased drastically when treated in nine pilot FWS wetlands in Australia (Greenway and Woolley, 1999). For example, 8.1 mg P l^{-1} was reduced to 2.8 mg P l^{-1}. Those are very significant falls in concentration, but they are not unusual for pilot schemes (Greenway and Woolley, 1999).These levels of retention of phosphorus are not sustainable in treatment wetlands, as described in Section 1.1.3. On the other hand, Myanard et

al 2009 reported on two mature constructed wetlands for the treatment of the farm runoff before it reached the San Joaquin River, in the US. The mature wetlands achieved poor reduction of orthophosphate, from 0.2 to 0.18 mg P l^{-1} and from 0.15 to 0.094 mg P l^{-1}. Greenway and Woolley (1999) discussed how the Mackay wetland, in Australia, started its operation with a reduction of orthophosphate of 55% during the first 6 months of operation, decreasing to only 8% for the following 10 months, and after that, concentrations of orthophosphate in the effluents exceeded those of the inflow.

Summarising, water leaving the Visitor Centre prior to the construction of the South Finger treatment was in many aspects of better quality than many UK rivers and similar to natural lakes with high densities of waterfowl. There had been many examples where water of similar quality could be treated successfully using FWS wetlands. Orthophosphate, however, presented a challenge from the outset of the South Finger project (Worral et al 1997), because the capacity of FWS wetlands in the retention of orthophosphate was not reliable and tended to decrease with time.

This chapter presents the results of previous research carried out in the South Finger wetland. Its aim is to present the possible causes for the performance of the wetland regarding, primarily, the retention or release of P. This is a preliminary study of the South Finger wetland, previous to the scientific research presented in chapters 4 and 5. The results presented and discussed in this chapter allowed the formulation of the hypotheses that were tested in chapters 4 and 5 and that allowed a deep understanding of the cycling of P in the South Finger wetland.

3.2 Retention of P by the South Finger wetland

Levels of orthophosphate leaving the South Finger wetland have been high, and this was acknowledged one year after commission (Worral et al 1997). The wetland followed the pattern of a decrease in the capacity to retain P described by Greenway and Woolley (1999) (see section 3.1), and since 1996 the

concentration of orthophosphate in the outflow has exceeded that of the inflow. 2008 and 2009 experienced particularly large differences between the inflow and outflows (see Figure 1.8). The chalk cascade, designed to promote the co-precipitation of P with Ca^{2+} ions became covered by an algal biofilm shortly after installation (Worral et al 1997). As explained in section 1.1.3, constructed wetlands cannot indefinitely remove P.

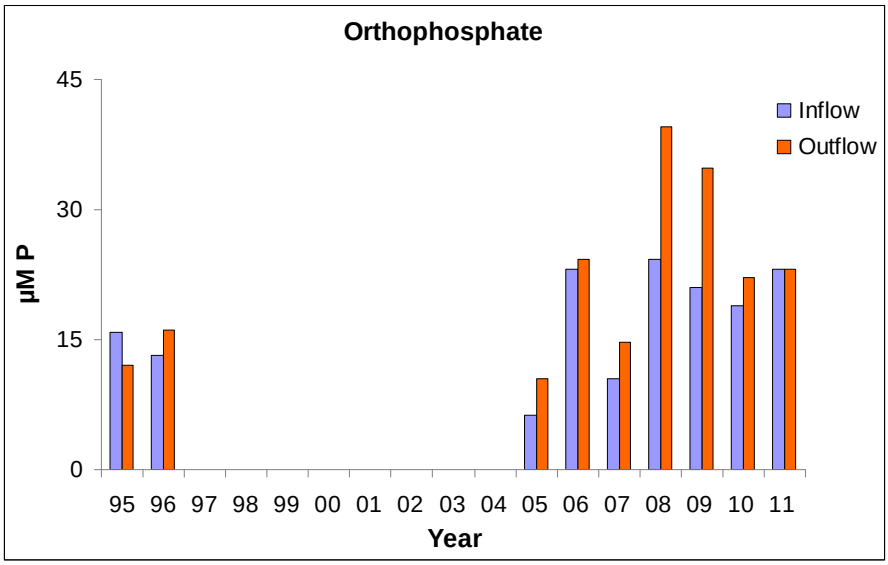


Figure 3-4: Levels of orthophosphate at the inlet and outlet of the South Finger wetland, as monitored after commission in 1995 and then since 2005.

WWT management saw potential conflicts with future Environmental Agency discharge consents, which were likely to include standards for orthophosphate set at 21 µM PO_4^{3-}. For this reason WWT undertook a series of research and monitoring programs to understand P cycling and other water quality problems (Mackenzie and Vougioukalou, 2010). This involved:

- Continuous monitoring of water quality of the South Finger wetland since 2005.
- Commissioning the Centre for Ecology and Hydrology (CEH) to monitor flow and nutrients reduction across the system between 2006 and 2010, and for the installation of an automated weather station and a flow meter. CEH's research focused first on the differences on nutrient uptake in the three different reed beds (Fisher et al 2009), and then the research

evolved to the dynamics of nutrients in the whole system (Stratford et al 2010 other studies not published).

- CEH extended the research of the South Finger wetland as part of the PhD project of Elizabeth Palmer-Felgate, who looked at cycling of phosphorus in the settlement lagoon in 2009 (Palmer-Felgate et al 2010 and Palmer-Felgate et al 2011b, and PhD Thesis).
- Further research on the uptake of nutrients by plants on floating rafts, comprehensive surveys of invertebrates to asses ecological status of the system (Mackenzie and Vougioukalou, 2010).

During a study undertaken in 2005-2006 on the South Finger wetland, it was realised that concentrations of total P (TP) and orthophosphate barely changed as water flowed over the reed beds. Concentrations of orthophosphate leaving the reed beds were in general 3 µM P higher than those in the water entering the beds. Orthophosphate tended to be retained in the reed beds during the growing season only (decreases in concentrations of about 7 µM P), while the releases of orthophosphate occurred in October and November (increases of concentrations between 13 and 16 µM P) (Fisher et al 2009). The same study demonstrated that the retention of orthophosphate occurred during periods of long residence times related to low flow conditions (Fisher et al 2009).

A second study on the performance of the wetland, undertaken by CEH highlighted the decrease in performance of the wetland. The number of occasions during which the wetland system became a source of orthophosphate increased between 1995 (36% of the sampling instances) and 2007 (89% of the sampling instances) (Stratford et al 2010). In order to study these results further, the budgets of P in the settlement lagoon were investigated for the first time. The authors demonstrated that the concentration of orthophosphate leaving the pond was higher than the concentration entering the pond on 63% of the samples taken. It was also noted that release of SRP from the settlement lagoon was seasonal and that occurred mainly between May and June, while during the rest of the year concentrations of SRP did not change between the inlet and outlet of the settlement lagoon (Stratford et al 2010).

Unpublished data from 2007 showed that the concentration of SRP increased from 11 in the inlet to 18 µM P in the settlement lagoon and that the rest of the wetland reduced that concentration to a mean of 16 µM P (Stratford et al 2009). During the same period, Particulate P (PP) decreased from 14 to 8 µM P in the settlement lagoon but the rest of the wetland only managed to decrease that level to a mean of 7 µM P (Stratford et al 2009) (See Table 1.3). These results agree with the study by Fisher et al (2009), in that the reed beds barely reduce the levels of orthophosphate and with other studies that showed that suspended solids, which include PP, are not efficiently removed by the South Finger wetland (MacKenzie and Vougioukalou, 2010 and MacKenzie and McIlwraith, 2012). Statford et al (2010), therefore, demonstrated that the export of orthophosphate from the South Finger wetland was the result of the combination of the settlement lagoon exporting orthophosphate and of the rest of the wetland failing to retain P.

	SRP (µM P) 2007 mean	**PP (µM P) 2007 mean**
Settlement lagoon inlet	11	14
Settlement lagoon outlet	18	8
Wetland outlet	16	7

Table 3-1: The combined effect of the settlement lagoon and the reed beds on the retention of P by the South Finger wetland

In order to understand why the settlement lagoon became a source of SRP during spring and summer, new studies were carried out by CEH. These showed that in June, the sediments of the settlement lagoon released SRP into the water column (Palmer Felgate et al 2011a). The studies also showed sulphate reduction taking place in the sediment close to the sediment water interface (SWI), which was an indication of reducing conditions in the sediments within centimetres of the SWI. The authors proposed two mechanisms for the release of SRP, from the sediment into the water column: the breakdown of organic matter by sediment microorganisms and the dissolution of Fe_3^+ minerals under reducing conditions (Palmer Felgate et al 2011a).

Further studies of the settlement lagoon were carried out in 2009 (Palmer-Felgate et al. 2011b). This second time, the fluxes of SRP from the SWI were compared with the production of SRP in the water column during the breakdown of planktonic algae. An algal bloom was observed in March, but by June it had collapsed. The collapse of the algal bloom lead to low levels of oxygen in the water column, caused by a reduction in the rate of photosynthesis and an increase in respiration of microorganisms feeding on the planktonic algae (Palmer Felgate et al 2011b). From May, the levels of dissolved P increased in the water column in conjunction with ammonium levels. This indicated that the breakdown of organic matter by microorganisms was resulting in the mineralisation of organic P into dissolved P. The increases in dissolved P were diurnal with maxima in the mornings and minima in the afternoons, attributed to photosynthetic uptake during the daylight hours, which stopped during the night (Palmer Felgate et al 2011b).

The profiles of pore water SRP (see Section 2.2.2) confirmed the flux of SRP from the water column into the sediments in March and the release of SRP from the sediments into the water column in June (Palmer Felgate et al 2011b). The authors suggested mechanisms for the release of P from the sediments into the pore waters and the water column: The aerobic and anaerobic breakdown of organic matter by microorganisms which caused the mineralisation of organic P; and the dissolution of Fe^{3+} oxides into Fe^{2+} and of other metal-phosphate minerals under reducing conditions. The fluxes of SRP being mineralised in the water column by planktonic respiration and the fluxes through the SWI were calculated. The results of these calculations indicated that the settlement lagoon exported SRP in 2009, and that the majority of the excess SRP was liberated during the breakdown of organic matter that took place in the water column, rather than having flowed through the SWI (Palmer Felgate et al 2011b).

3.3 General performance of the South Finger wetland

Millet (1997) presented the results on the performance of the South Finger wetland for 1995-1996. Performance of the South Finger treatment was also monitored since 2005 (Mackenzie and McIlwraith, 2012). The parameters measured varied, but typically they included TSS, BOD_5, ammonia, nitrate and phosphate, summarised in Figures 3.5 and 3.6. These include wetland inlet and outlet concentrations, taken from the inflow pipe into the settlement lagoon and the averages of the outflows of the Scirpus and Phragmites beds. The results are averaged by year (Mackenzie and McIlwraith, 2012).

The South Finger wetland performed satisfactorily in the removal of suspended solids during 1995-1996, but since 2005 the performance it decreased, particularly in 2008 and 2009. This resulted in numerous breaches of the discharge consents. The poor performance was due to storms, disturbance during maintenance work and due to algal blooms (Mackenzie and McIlwraith 2012). The occurrence of storm events and the subsequent impact on suspended solids were detailed by Mackenzie and Vougioukalou (2010) and Palmer-Felgate (2011b). Occurrence of algal blooms in the settlement pond was reported for 2009 (Palmer Felgate et al 2011b). Algal blooms were also noticed during 2011 and 2012, as it is discussed in Chapter 4.

Litter accumulation caused poor water distribution over the reed beds, where large areas of the beds were bypassed (Mackenzie, unpublished draft). This has been reported as a cause for the increase of suspended solids in constructed wetlands as the base of the reed beds is eroded in those areas where the preferential flow occurs (Braskerud, 2001). Also, high water velocities of the short-circuited flows would hinder settlement of particles. Finally, shallow unvegetated ponds, like the settlement lagoon of the South Finger wetland, are very likely sources of resuspended sediment (Braskerud, 2001).

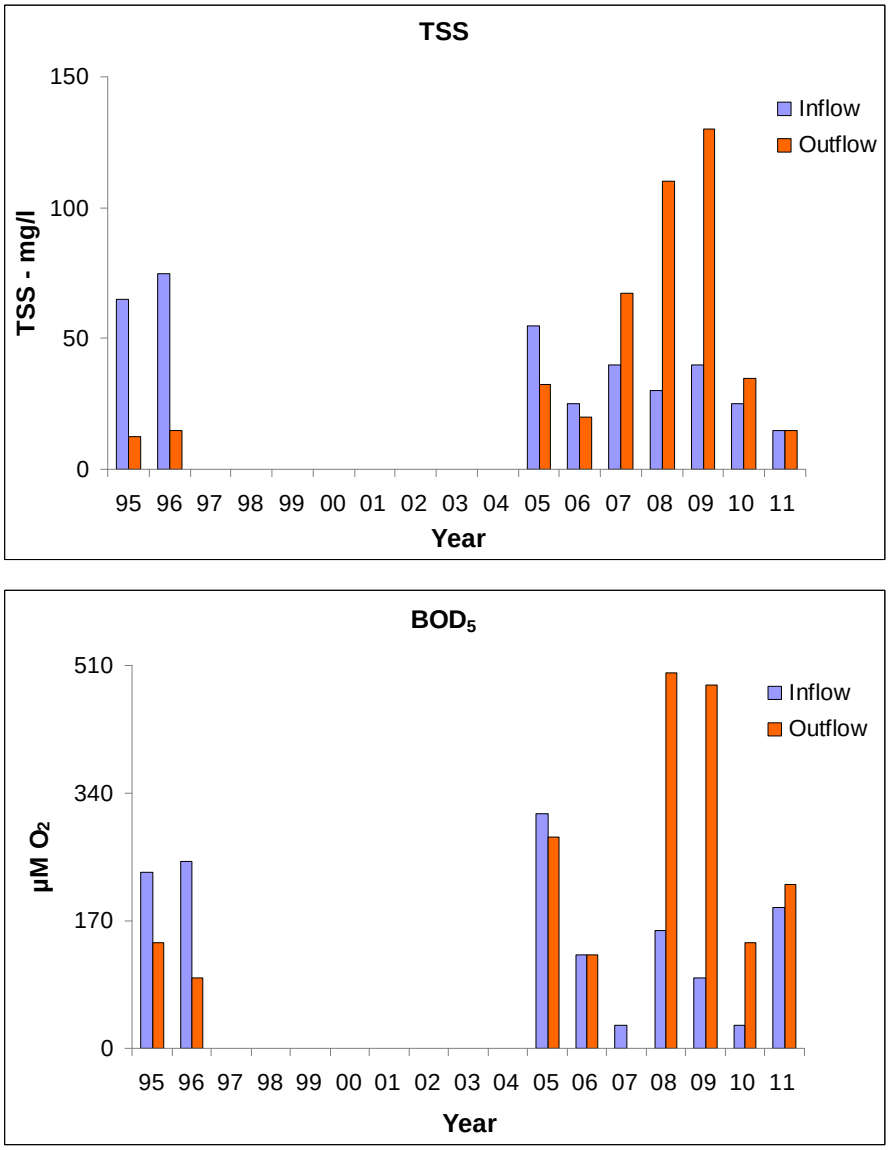


Figure 3-5: Levels of TSS and BOD_5 at the inlet and outlet of the South Finger wetland, as monitored after commission in 1995 and then since 2005.

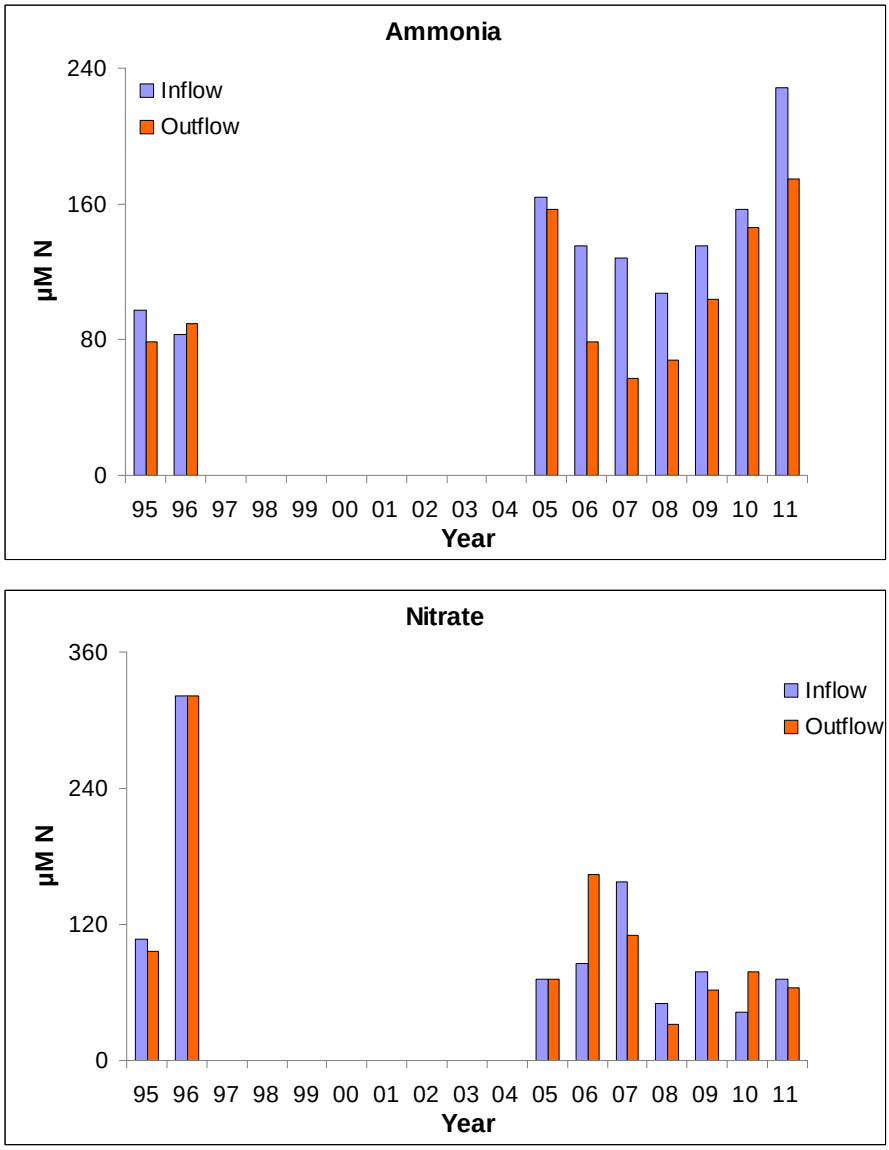


Figure 3-6: Levels of ammonia and nitrate at the inlet and outlet of the South Finger wetland, as monitored after commission in 1995 and then since 2005.

BOD_5 at the exit of the wetland met consistently the discharge consent, although the rate of removal was not always satisfactory. Mackenzie and McIlwraith (2012) indicated that the high levels of suspended solids flowing out of the wetland were high in organic matter, which produced high BOD_5 at the outflow. This coincides with other observations regarding the occurrence of algal blooms in the settlement pond (Palmer Felgate et al 2011b). Other causes for the low reduction of BOD_5 levels can be the poor oxygenation of the reed beds and low rate of microbial breakdown of organic matter (Reddy and D'Angelo, 1997).

Levels of ammonia and nitrate in the effluents were satisfactory during the monitored periods. Free surface flow wetlands are not ideal for the removal of N-species because the processes involved require a high density of microbial organisms in aerobic and anaerobic conditions simultaneously, and this is better achieved by sub surface flow wetlands (Kadlec and Knight, 1996). However, the performance of the South Finger wetland regarding the removal of ammonia and nitrate is comparable to other satisfactory free surface flow constructed wetlands across the world (Vimazal 2007).

Finally, water through the wetland had residence times (when constructed) of 60 hours, of which 35 were spent in the settlement lagoon. The settlement lagoon was never intended to treat the water chemically or biologically, therefore the residence time through the chemically/biological active part of the wetland was 25 hours (see Table 1.1). That is considered a short residence time for a free water surface wetland, where chemically or biologically active surfaces are limited. Hench et al (2003) successfully designed free water surface wetlands to treat domestic effluents, with residence times between 6 to 8 days. For more polluted waters, Cronk (1996) recommended residence times of at least 12 days for the treatment of wastewater from dairy and swine operations. Verhoeven and Meuleman (1999) recommended, in general, residence times of 10 days for free water surface wetlands. The erratic and not always satisfactory results of the South Finger wetland therefore, could be the result of the short residence times with which it was designed.

4 BUDGETS OF PHOSPHORUS IN THE SETTLEMENT LAGOON

4.1 Introduction

Recent research showed that in the settlement lagoon of the South Finger wetland, algal blooms occurred in early spring, and that they collapsed in summer (Palmer-Felgate et al, 2011b), and also that the lagoon releases SRP, peaking in summer (Stratford et al, 2010, and Palmer-Felgate et al, 2011b). However, that research did not show definitive evidence of the source of the released P within the settlement lagoon in summer.

Algal blooms develop in early spring, when light is no longer limited (Sommer 1994). This is related to an increase in solar radiation and in the length of the daylight hours (Huber et al, 2008). The algal blooms usually collapse in late spring/early summer (Sommer, 1986). The collapse of algal blooms is attributed to different environmental factors. Principally, the rates of grazing of zooplankton exceed the rates of algal production in early summer (Lampert et al, 1986). Also, exhaustion of a nutrient can cause the collapse of the phytoplankton before grazing becomes important. Palmer-Felgate (2011b) showed that silica became the limiting nutrient in the settlement lagoon prior to the collapse of a diatom bloom. Similar conclusions were reached for the collapse of spring algal blooms in Lake Müggelsee, a shallow lake near Berlin (Huber et al 2008).

It has been reported repeatedly that seasonal algal blooms are followed in summer by internal loading of phosphorus in shallow lakes (e.g. Vollenweider and Kerekes, 1982; Jeppesen et al, 2005). In the shallow Lake Balaton, in Hungary, algal blooms were also present in spring, followed by internal loading of P in the summer (Istanovics, 1988). Bioavailable P taken up by planktonic microorganisms kept the levels of orthophosphate in spring low (between 0.03 and 0.06 μM P). The settling of planktonic organisms transported the bioavailable P from the water column to the sediments (Istanovics, 1988), and

the organic matter reached the surface of the sediments intact. Higher temperatures in summer promoted bacterial decomposition of the fresh organic matter deposited near the surface of the sediments. This resulted in the production of inorganic P that was released back to the water column (Istanovics, 1988). This process triggered other mechanisms such as a reduction of oxygen levels and reduction of pH, which in turn resulted in dissolution of some Ca^{2+} and Fe^{3+} minerals and their associated P (Istanovics, 1988). Another example is Lake Glaningen, in Sweden, which has a mean depth of 1.5 meters and that also experienced algal blooms in March, which collapsed by July, coinciding with a peak in orthophosphate released from the sediments. It was concluded that the release in July was caused by mineralisation of fresh organic matter by sediment bacteria (Ryding 1985).

The aim of the work presented in this chapter was to understand the principal processes that control P cycling in the settlement lagoon of the South Finger wetland. This was carried out by testing the hypothesis that the sediments are the source of the excess P in the settlement lagoon in summer. Whether this is caused by the rapid mineralisation of the settled primary productivity or not will be discussed in chapter 5.

4.2 Results

4.2.1 Weather observations

The early spring sampling took place the 2nd and 3rd of March 2011, and the summer sampling, on the 6th and 7th of June 2011. Weather stayed dry during the sampling in March. Temperatures were above freezing, with the lowest at 2ºC near midnight and the highest at 6ºC around noon. The first day of sampling remained clear and calm, but the 3rd of March stayed overcast almost continuously, and winds were estimated to have risen to 20 mph from the SW. Daylight started at 6:20 hours and it became dark at 18:15 hours.

During the June sampling, temperatures ranged between 8 and 21ºC, with minima at midnight and maxima in the early afternoon. The sky was partially cloudy on the 6th, with light winds. Wind increased in the afternoon, accompanied by showers. 8mm of rain fell during the night, and it was collected and stored for analysis. During the 7th, the wind increased significantly, estimated at 20-30 mph from the W, and showers were frequent during the day. Daylight started at 4:00 hours and it became dark at 22:30 hours.

Water temperatures in the settlement lagoon in March ranged from 4 to 7 ºC. In June, these reached values between 16 and 18 ºC.

4.2.2 Bathymetry survey

The settlement lagoon was dipped at 17 points (see Figure 4.1). The clay lining was found to be at about 1.5 meters below the water surface and the top of the unconsolidated sediment, at about 0.7 meters below the water surface. The clay lining is shallower at the south of the lagoon. From this survey, the calculated volume of water in the pond is 1700 m^3.

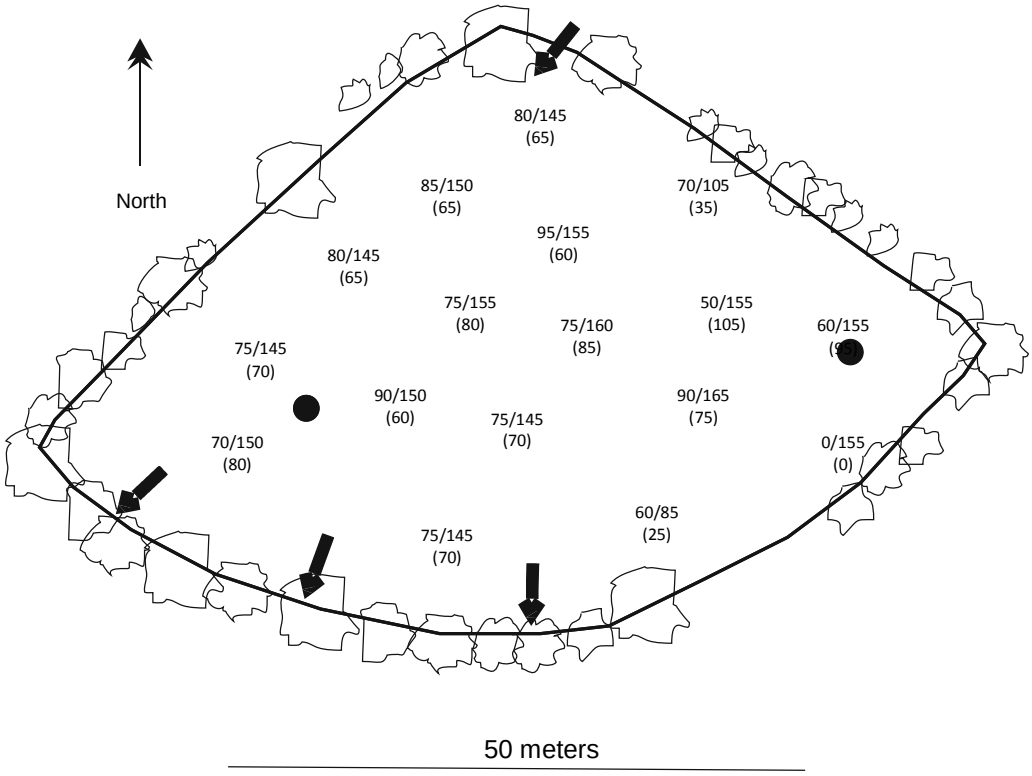


Figure 4-1: Bathymetric survey of the settlement lagoon. First figure is the depth to the black unconsolidated material. Second figure is the depth to the clay lining. Figure between brackets is the thickness of unconsolidated material

4.2.3 Water balance

The level of the water was read out from the installed gauge and recorded in the field book. Water levels at the settlement lagoon remained constant throughout the March and June field work. The level of the water during the March and June visits was the same as when the bathymetry survey was carried out, therefore the volume of water in the pond was estimated to be 1700 m^3 in those two occasions as well.

The working rates of the pumps were 150 $m^3\ h^{-1}$ (st.dev 4 $m^3\ h^{-1}$, n = 11) for Pump No.1 and 120$m^3\ h^{-1}$ for Pump No.2 (st.dev 4 $m^3\ h^{-1}$, n = 17). During the March sampling, Pump No.1 worked for 4.55 hours, in 24 hours, and Pump No.2 worked for 11.84 hours, in 24 hours. In June, Pump No.1 worked for 2.26 hours, in 24 hours, and Pump No.2 worked for 21.63 hours, in 24 hours. The volumes of

water that flowed through the inlet therefore were 2100 m^3 in March and 2900 m^3 in June (see Table 4.1).

		March	**June**
Pumps flow rate		**Running times of pumps**	**Running times of pumps**
PUMP 1	150 m3/h	4.55 h	2.26 h
PUMP 2	120 m3/h	11.84 h	21.63 h
TOTALS		**2100 m^3**	**2900 m^3**

Table 4-1: Calculation of the volume of water that flowed through the inlet during the two sampling instances described in this chapter, based on working hours of each pump and their pumping rates.

The calculated values for evaporation (Hess 1996) were 1.5 mm day^{-1} in March and 4.5 mm day^{-1} in June. Since the surface area of the lagoon is 2400 m^2, the volumes of water lost by evaporation represented 4 m^3 in March and 11 m^3 in June. The 8 mm of rain that fell in the night of the 6th June represented and input of 19 m^3 of water. The volume of water that flowed out of the settlement lagoon, calculated as described in Section 3.2.1 was therefore 2096 m3 in March and 2908 m3 in June (see Table 4.2).

Chapra (1997)	dV/dt	=	Qin	-	Qout	+	G	+	P	-	E
March	0	=	2100	-	**2096**	+	N/A	+	0	-	4
June	0	=	2900	-	**2908**	+	N/A	+	19	-	11

Table 4-2: Water balance calculations, corresponding to the two sampling instances described in this work.

4.2.4 Phosphorus

4.2.4.1 SRP

Concentrations of SRP through the inlet, during the sampling period in March varied between 0.9 and 2.9 µM P (see Figure 4.2), while concentrations of SRP in the settlement lagoon where slightly lower, between 0.9 and 1.3 µM P (see Figure 4.3). SRP in the water column incubation, isolated from inflowing water and the sediments, decreased steadily during the sampling period in March, from 1.0 to 0.4 µM P (see Figure 4.4); and SRP within the benthic chambers also decreased steadily, during the sampling period in March, from 1.2 to 0.8 µM P (see Figure 4.5). DET gel profiles showed a maximum levels of SRP 1cm above the SWI, between 50 and 70 µM P, that decreased both above and below the SWI (see Figure 4.6).

During the sampling in June, SRP through the inlet varied between 16 and 19 µM P, showing a diurnal pattern of maxima around noon and minima before sunset (see Figure 4.2). Concentrations of SRP increased in the water column, with values between 22 to 24 µM P (see Figure 4.3). SRP inside the water column incubations varied between 21 and 23 µM P, showing a diurnal pattern of maxima at night and minima in the afternoon (see Figure 4.4). SRP within the benthic chambers increased linearly from 24 to 31 µM P during the sampling period of June (see Figure 4.5). DET gel profiles showed maximum levels of SRP at 1.5 cm below the SWI, with 360 µM P at Site 1 and 390 µM P at Site 2. Concentrations of SRP decreased to background levels 5cm above the SWI. Within the sediments, levels of SRP varied between 200 and 300 µM P (see Figure 3.21).

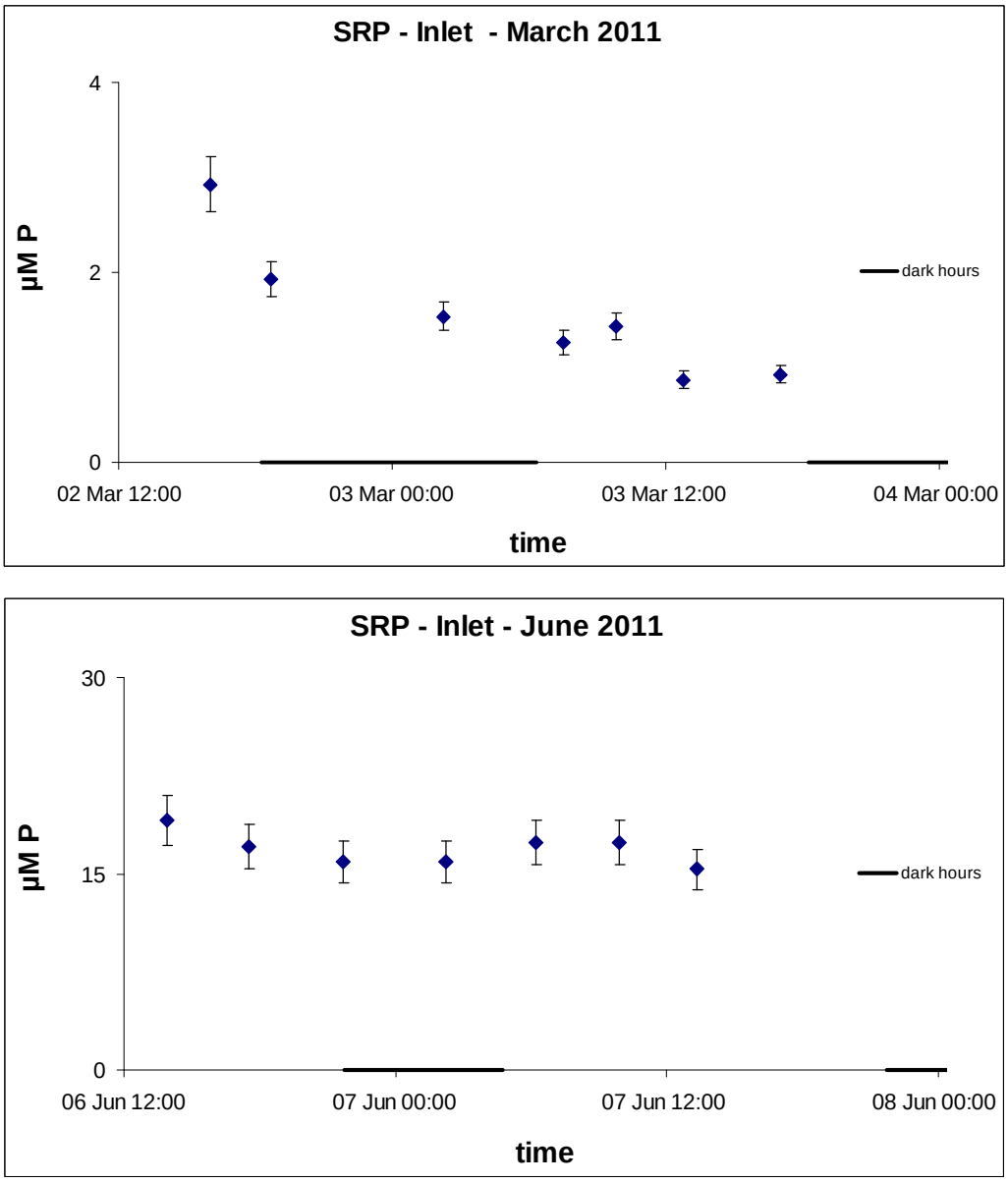
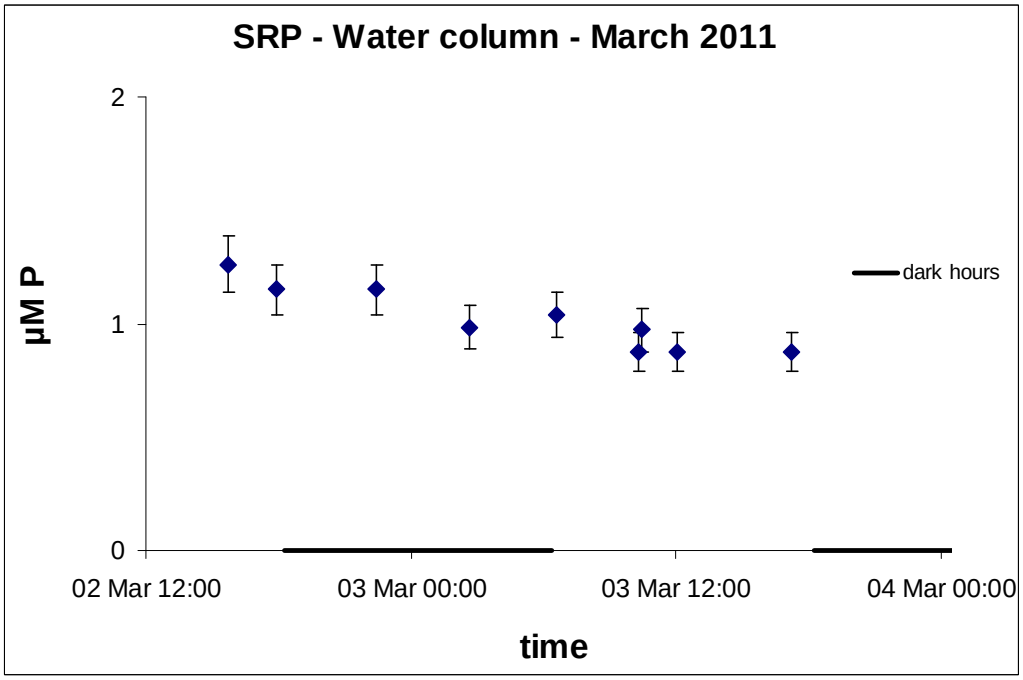


Figure 4-2: Concentrations of SRP through the inlet, for March and June, 2011. Error 10%, n=6.



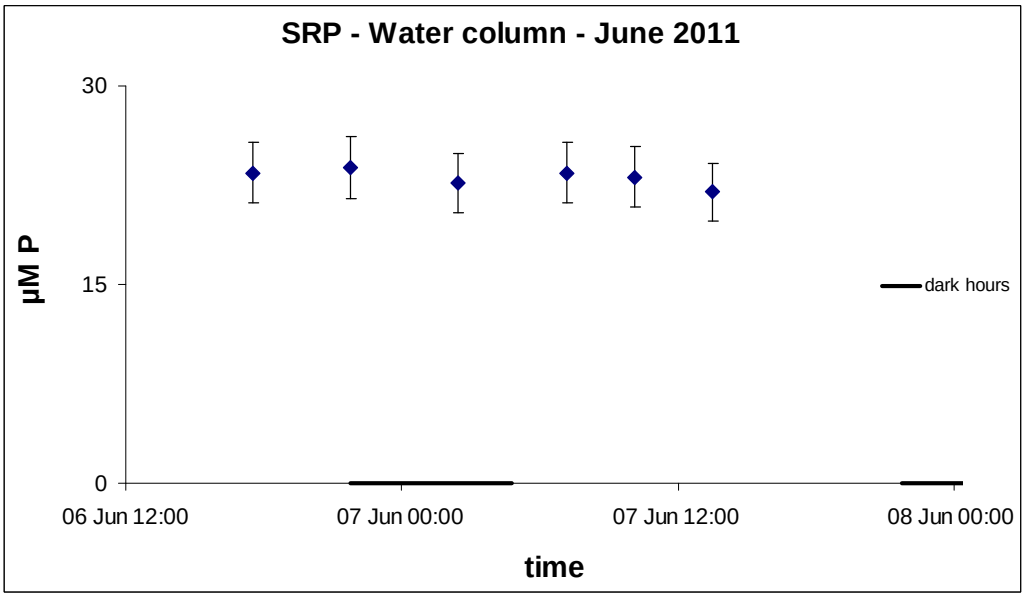


Figure 4-3: Concentrations of SRP in the water column, for March and June, 2011. Error 10%, n=6.

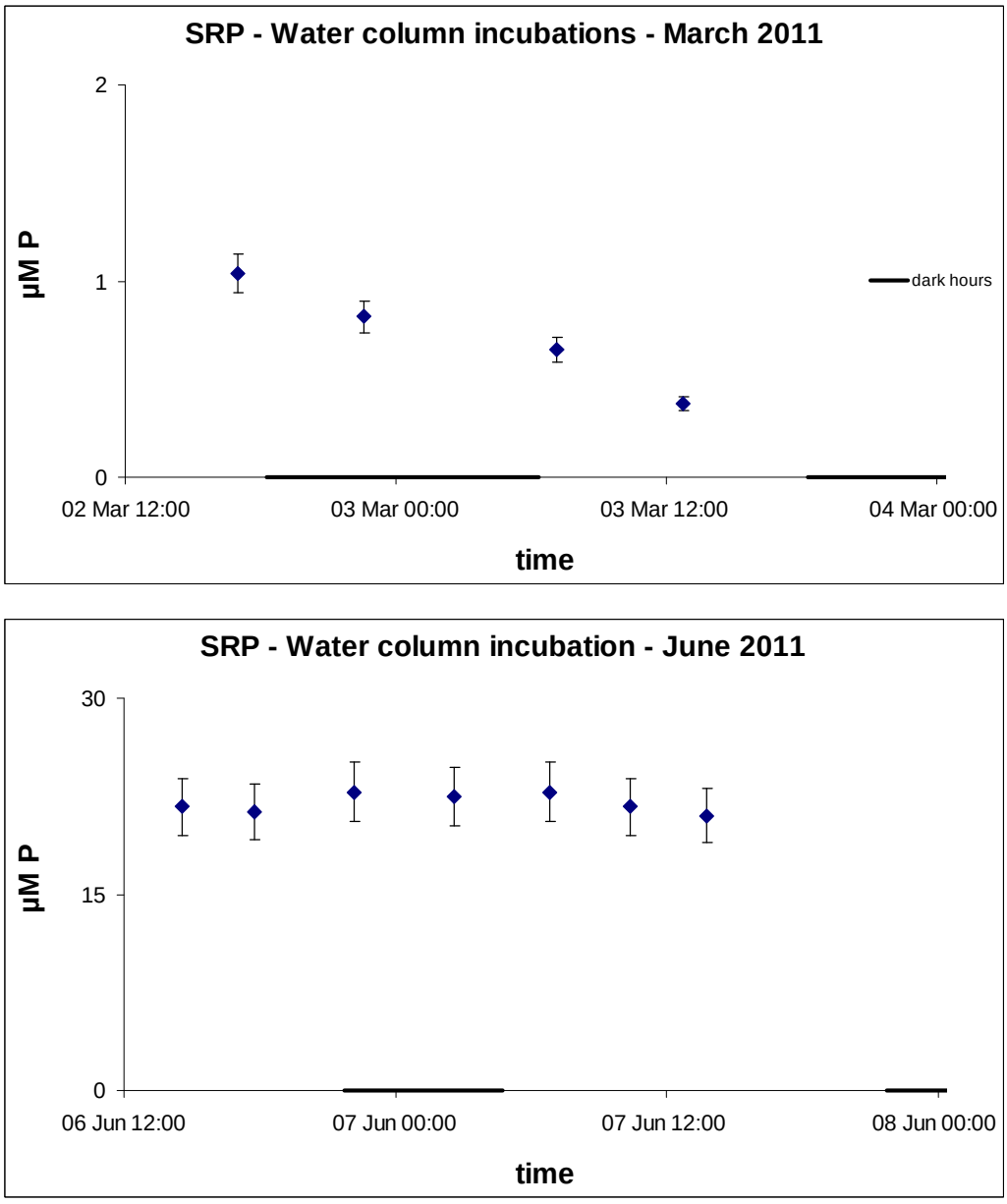
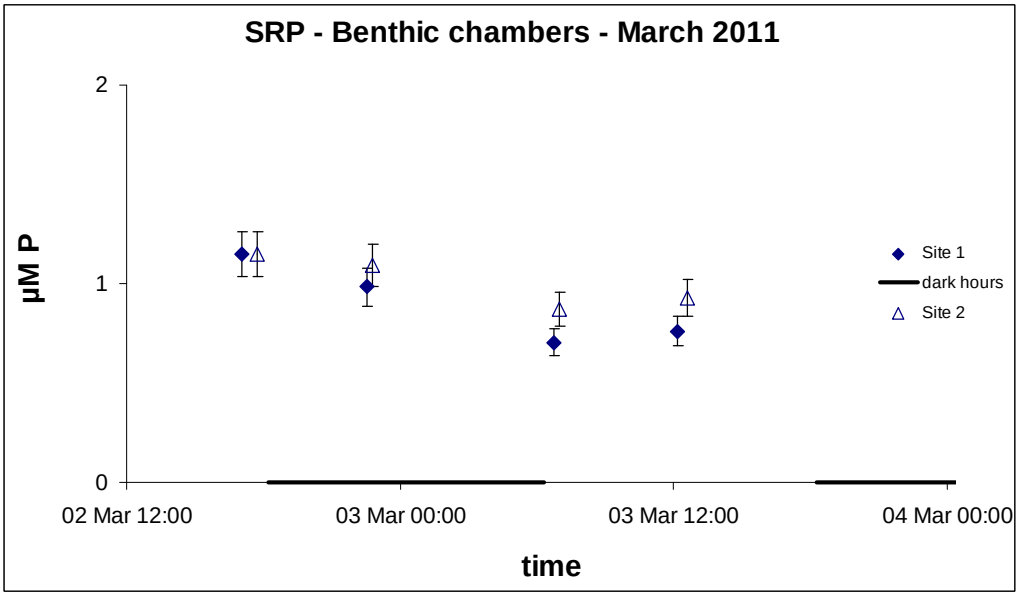


Figure 4.4: Concentrations of SRP inside the water column incubations, for March and June, 2011. Error 10%, n=6.



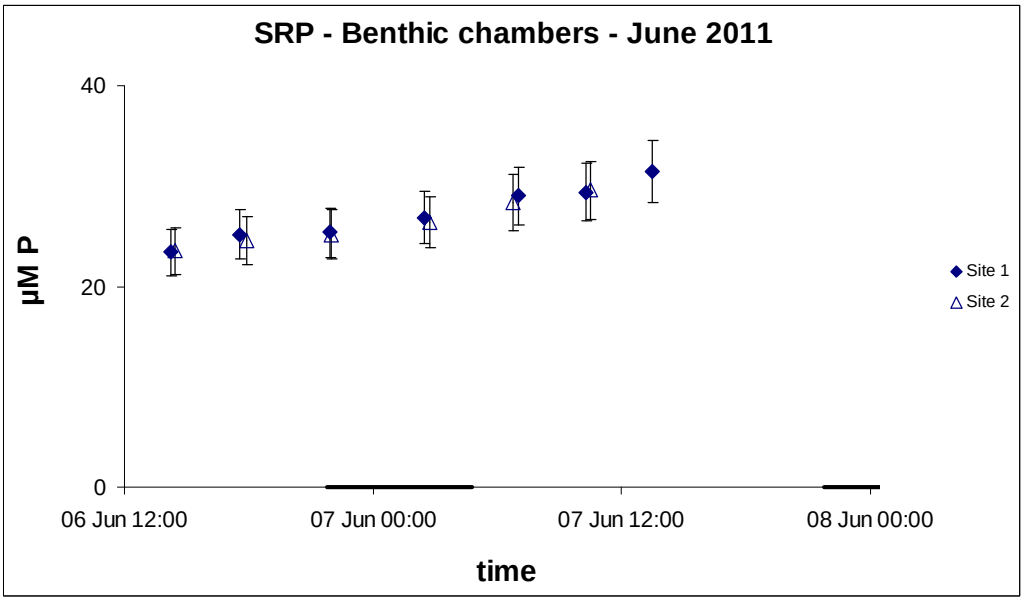


Figure 4-5: Concentrations of SRP inside the benthic chambers, for March and June, 2011. Error 10%, n=6.

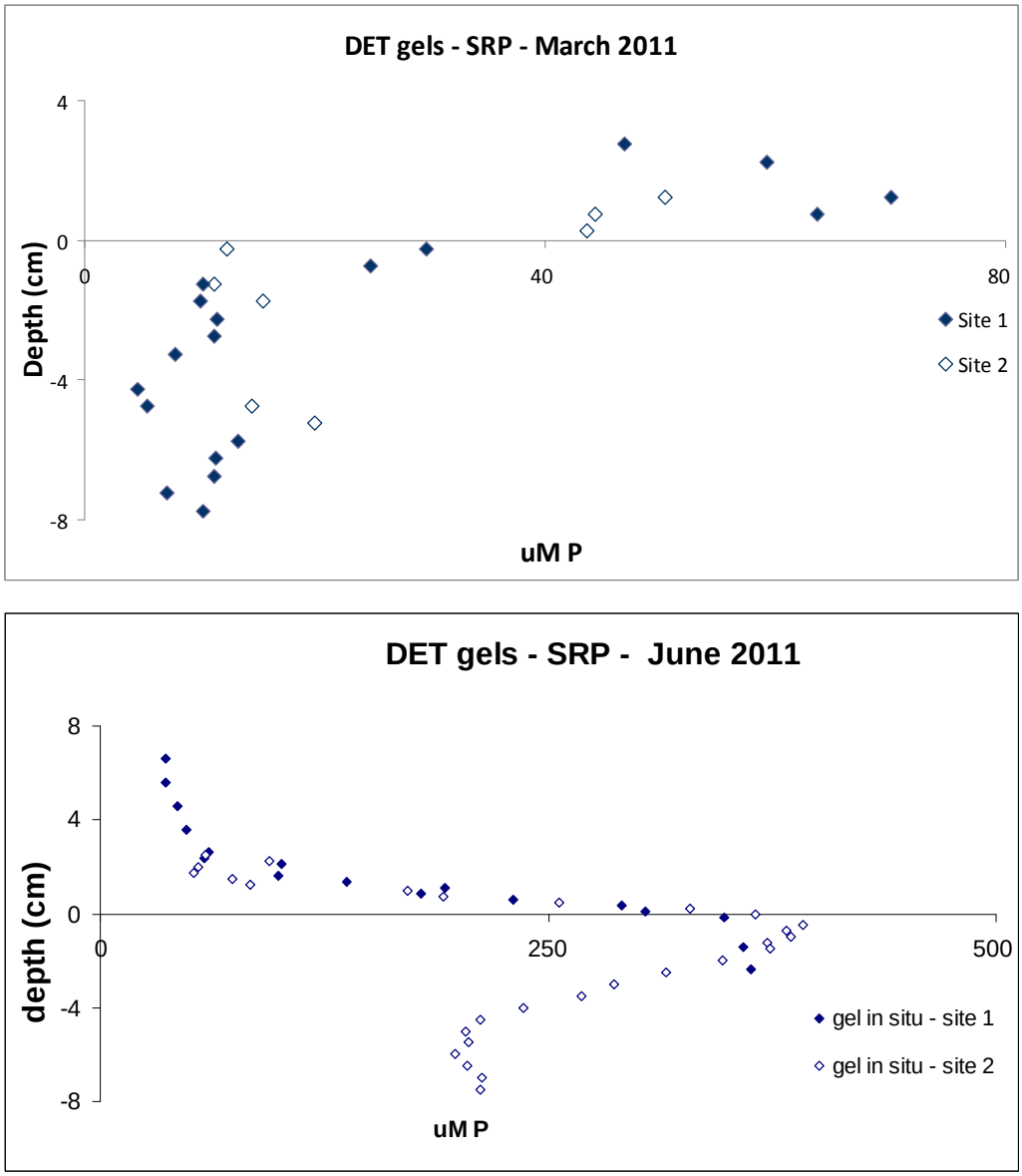
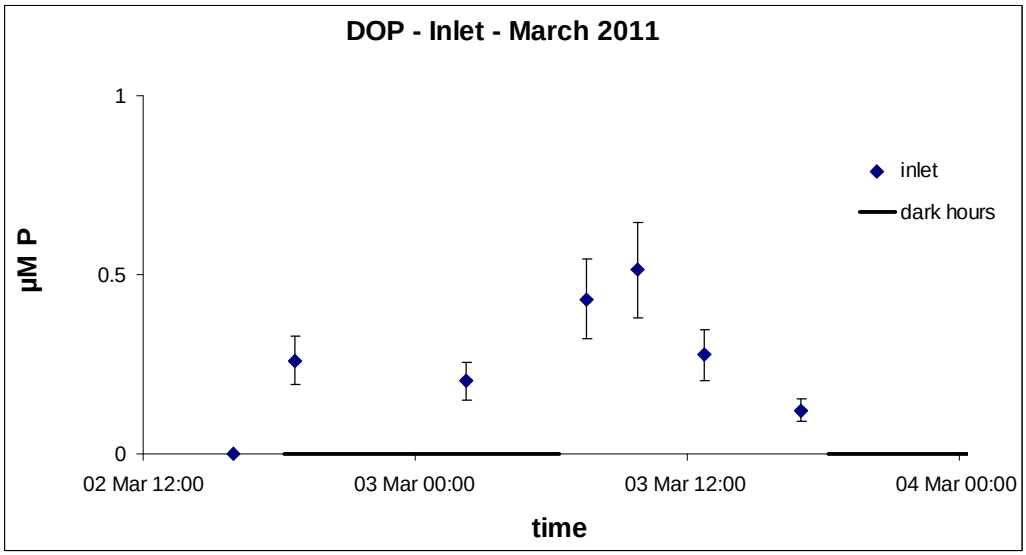


Figure 4-6: Concentrations of SRP at the bottom of the water column and through the SWI, sites 1 and 2 for March and June, 2011.

4.2.4.2 Dissolved organic P (DOP)

During the March sampling period, concentrations of DOP flowing into the settlement lagoon ranged from 0.1 to 0.6 µM P (see Figure 4.7). Similar values were measured in the water column, with highest values at 0.6 µM occurring during the night and lowest values at 0.1 µM P, at noon (see Figure 4.8). DOP in the water column incubation increased slightly from 0.18 to 0.23 µM P (see Figure 4.9), while Values of DOP within the benthic chambers in March differed between Site 1 and Site 2. Values at Site 1 varied between 0.2 and 0.8 µM P, while values at Site 2 remained between 0.0 and 0.1 µM P (see Figure 4.10).

Levels of DOP through the inlet in June varied between 19 and 25 µM P, peaking during the night and with lowest levels at noon (see Figure 4.7). DOP in the water column increased to values between 22 and 25 µM P, also with maxima during the night and minima at around noon (see Figure 4.8). DOP in the water column incubations varied between 23 and 26 µM P. DOP in the benthic chambers in June increased steadily from 24 to 32 µM P during the sampling period (see Figure 4.10).



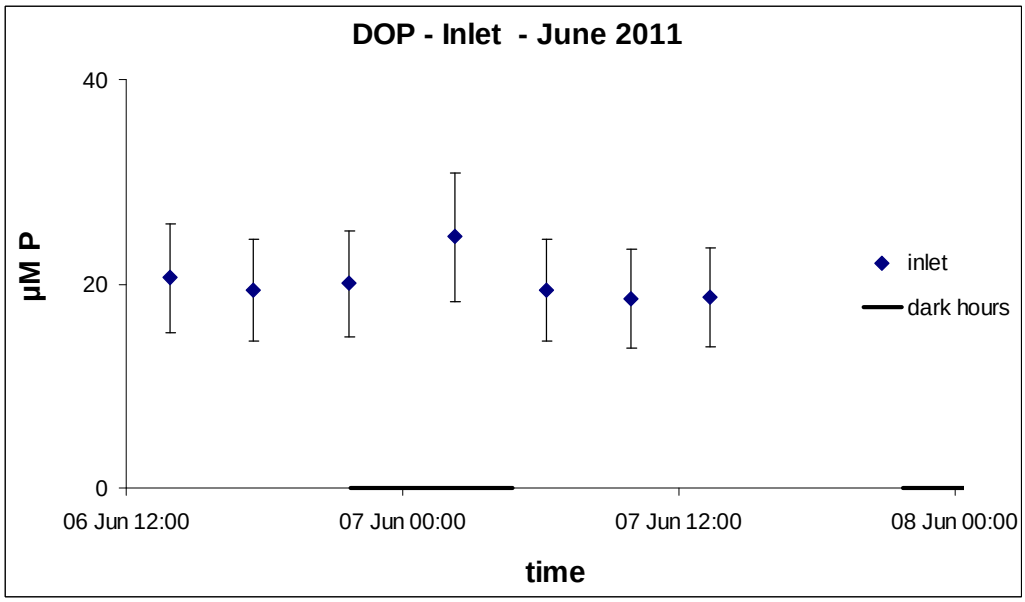
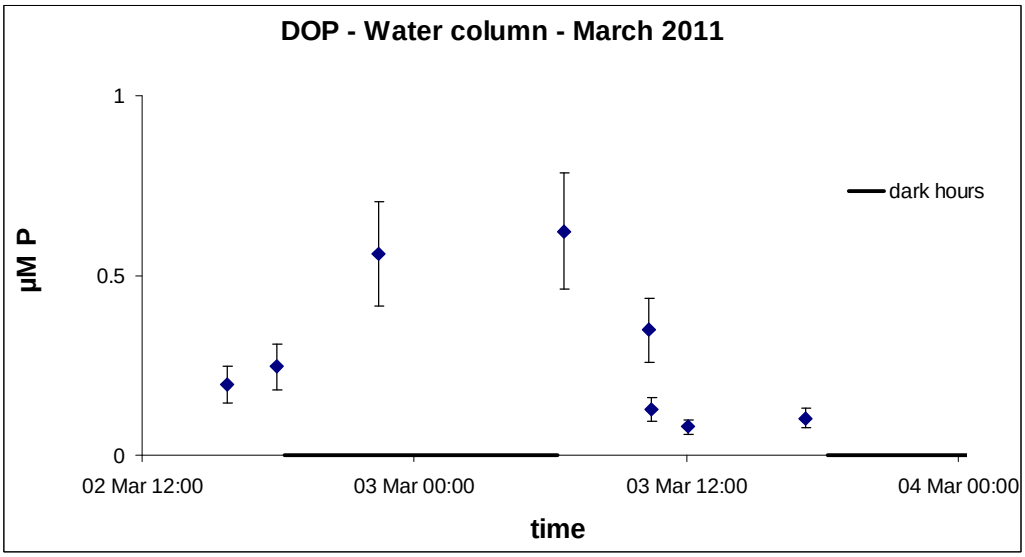


Figure 4-7: Concentrations of DOP through the inlet, for March and June, 2011. Error 26%, n=6.



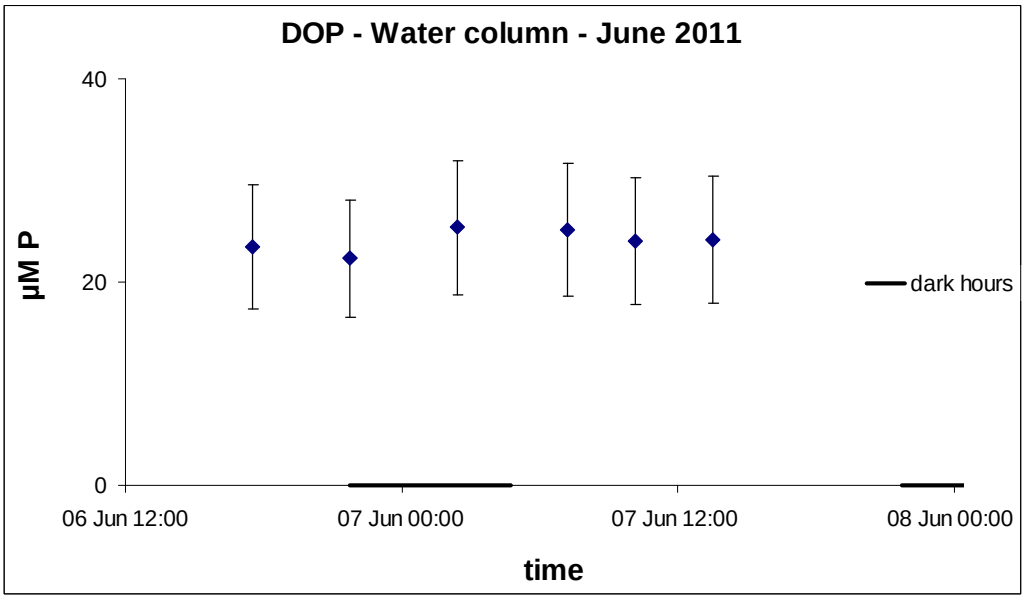


Figure 4-8: Concentrations of DOP in the water column, for March and June, 2011. Error 26%, n=6.

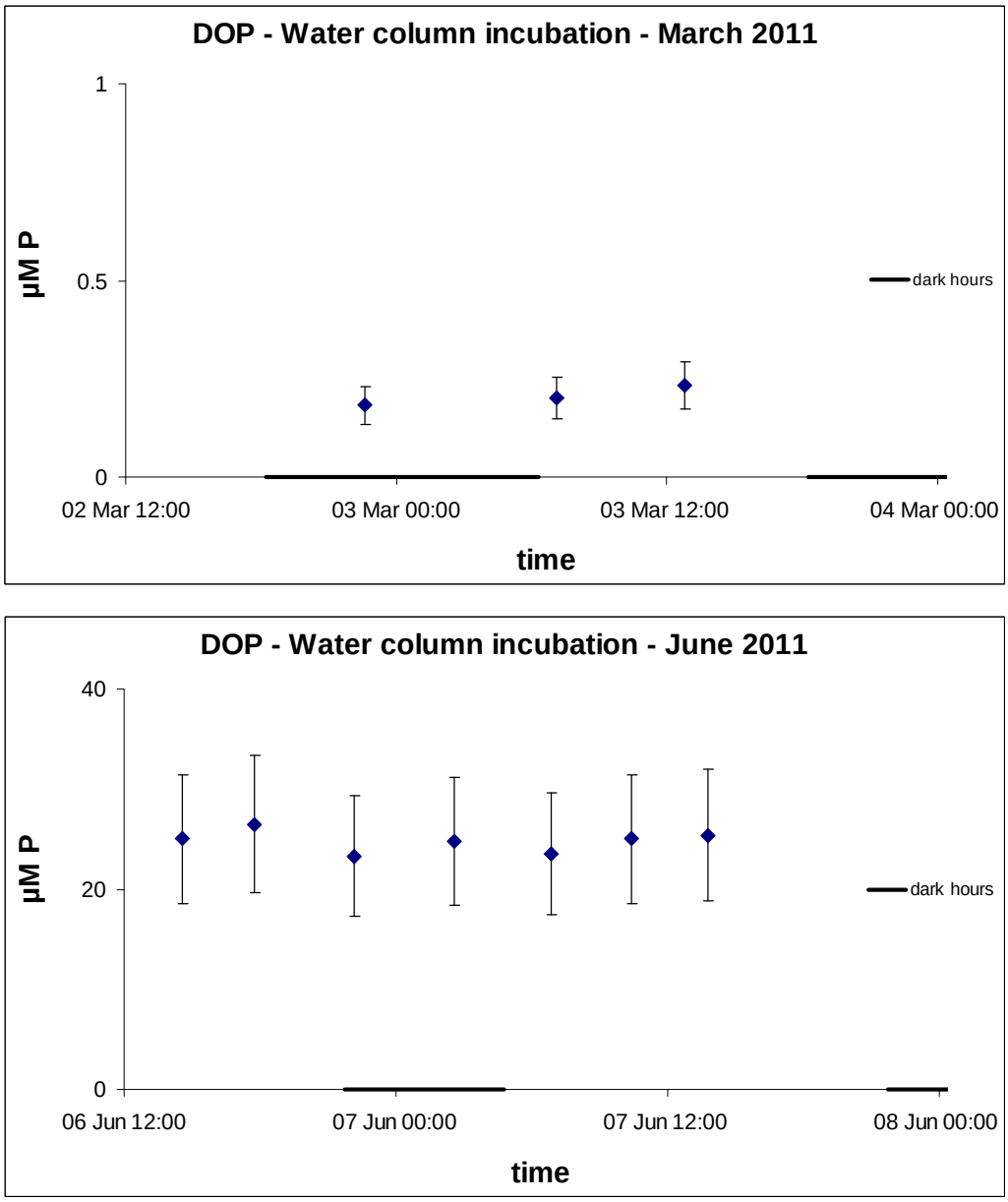


Figure 4.9: Concentrations of DOP inside the water column incubations, for March and June, 2011. Error 26%, n=6.

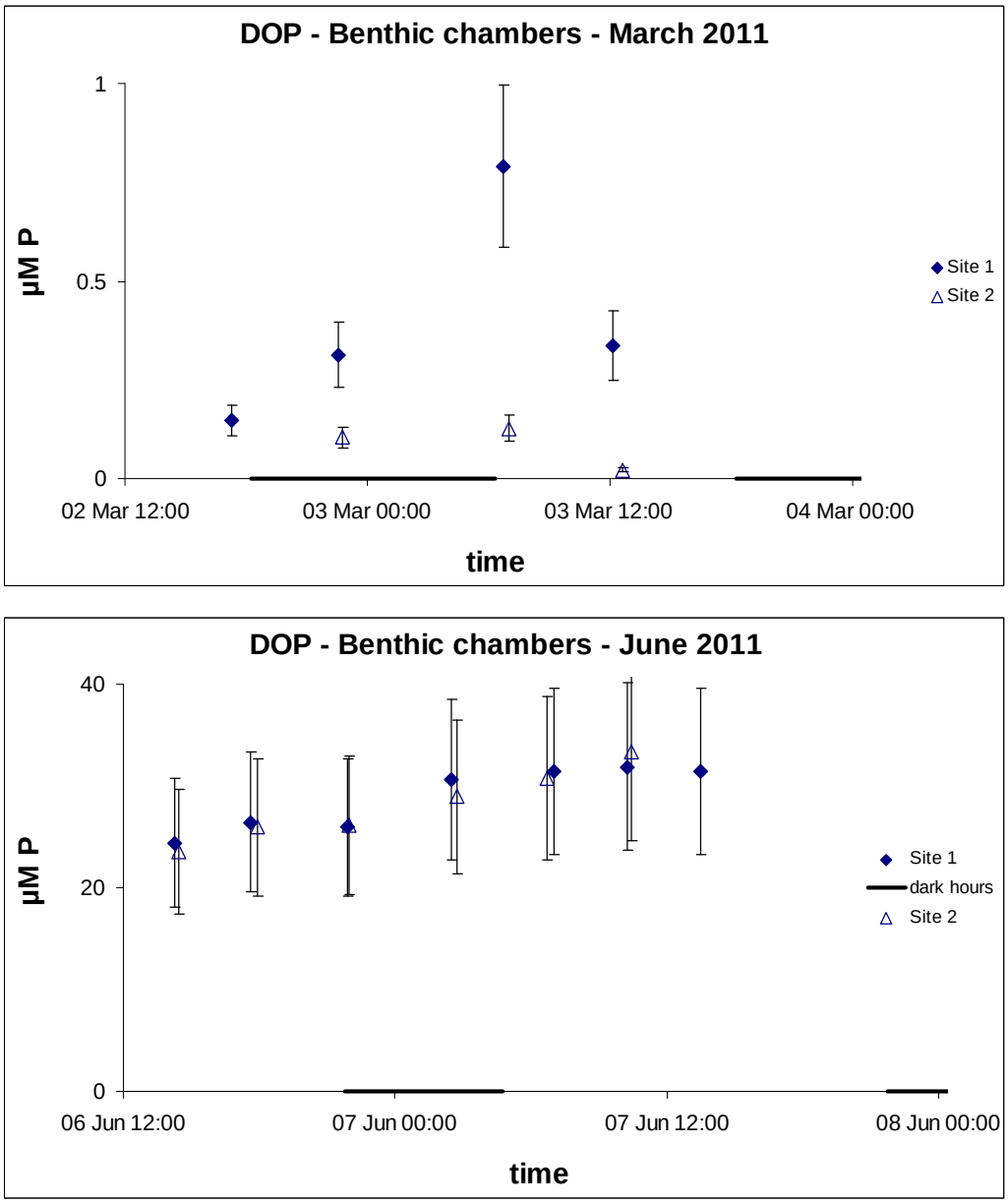


Figure 4-10: Concentrations of DOP inside the benthic chambers, for March and June, 2011. Error 26%, n=6.

4.2.4.3 Particulate P (Part P)

Particulate P coming through the inlet in March varied between 8 and 13 µM (see Figure 4.11), and in the settlement lagoon this decreased to concentrations between 8 to 10 µM P during the 24 hours of sampling (see Figure 4.12). Particulate P in the water column incubations decreased during the sampling period in March, from 7.8 to 6.3 µM P (see Figure 4.13).

During the June sampling, concentrations of Particulate P coming through the inlet were lower than in March, with values between 2 and 7 µM P (see Figure 4.11). These 4.12). Particulate P inside the water column incubations decreased steadily during the sampling period in June from 5.7 to 2.2 µM P (see Figure 4.13).

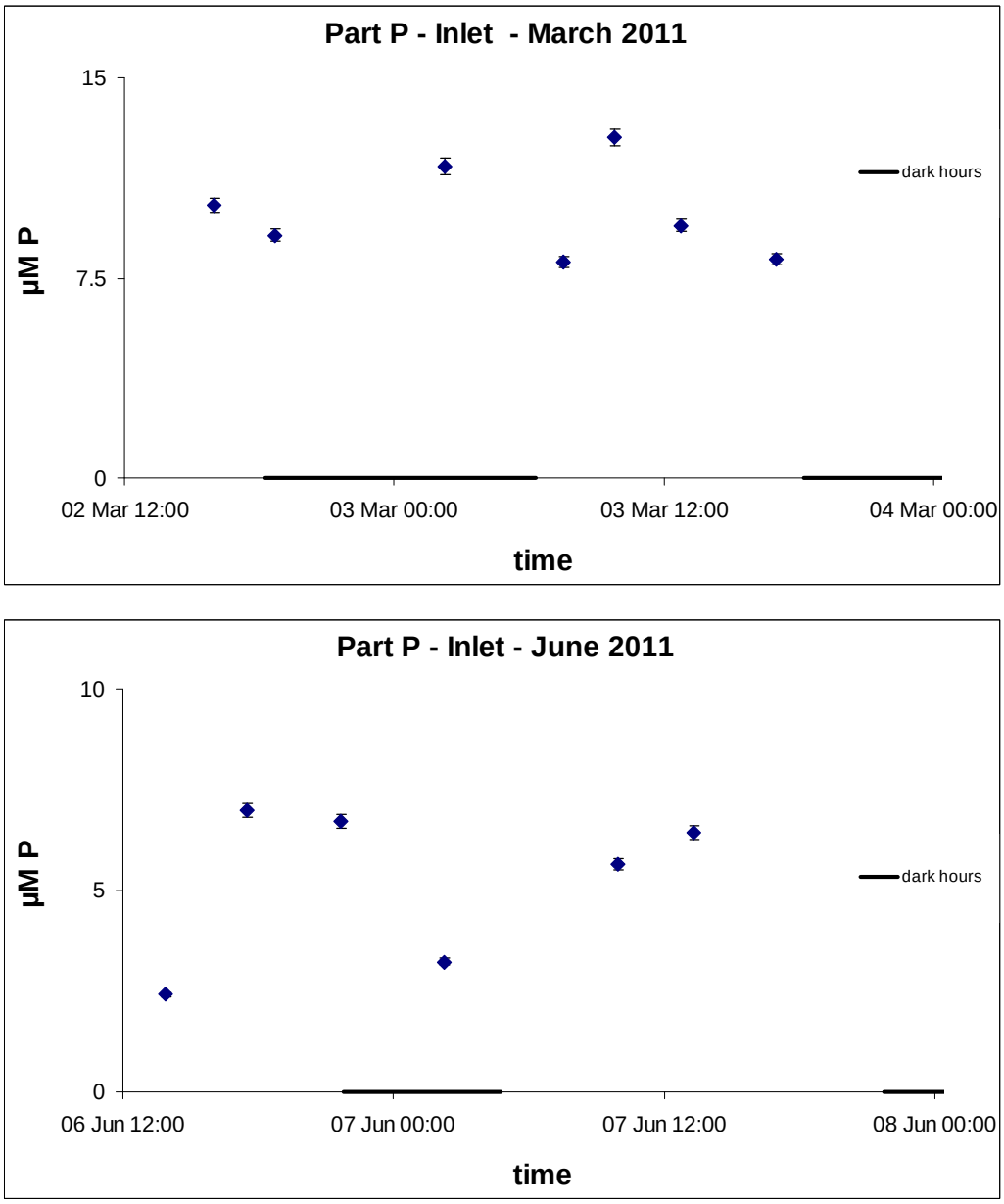


Figure 4-11: Concentrations of Part P through the inlet, for March and June, 2011. Error 3%, n=6.

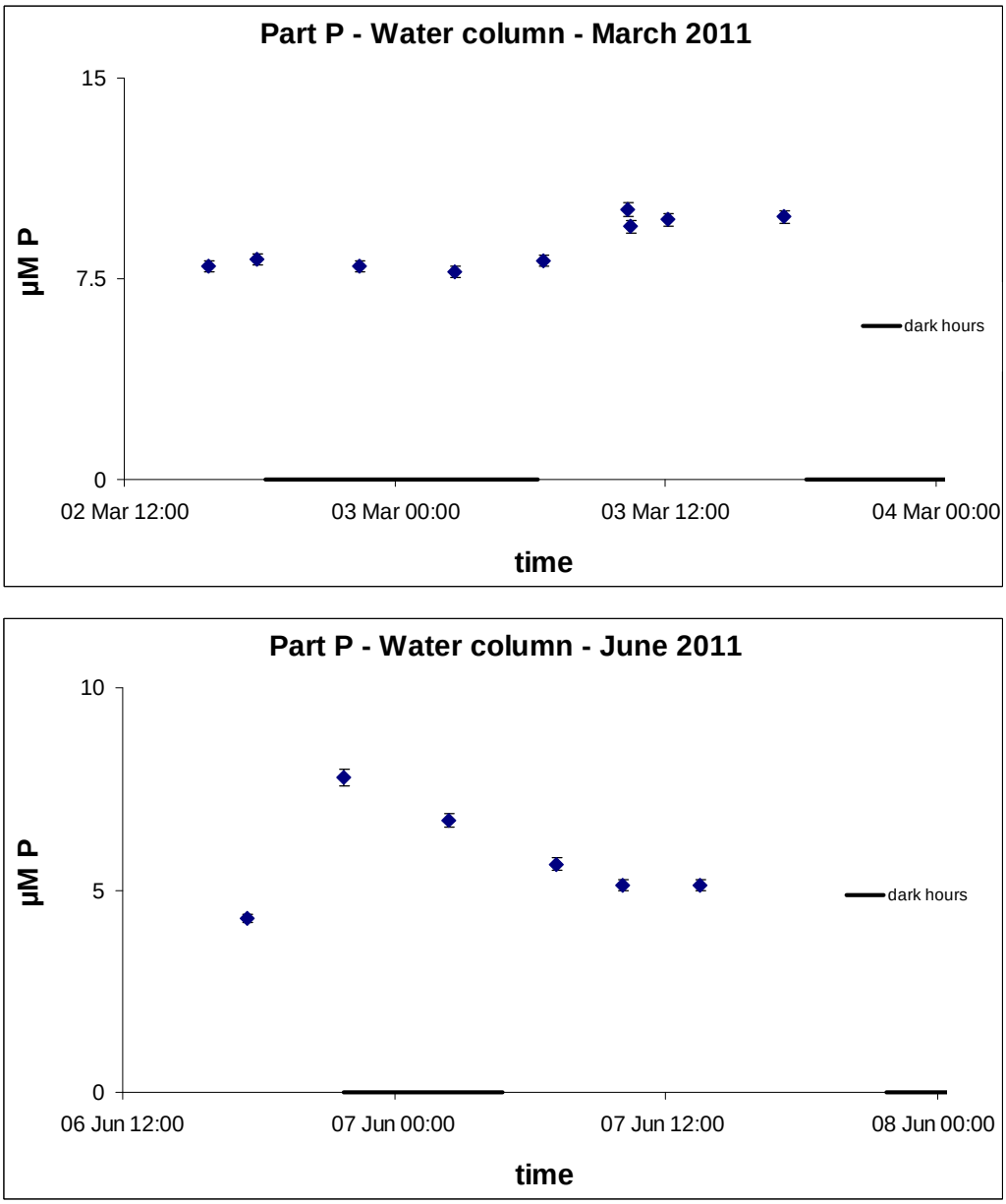


Figure 4-12: Concentrations of Part P in the water column, for March and June, 2011. Error 3%, n=6.

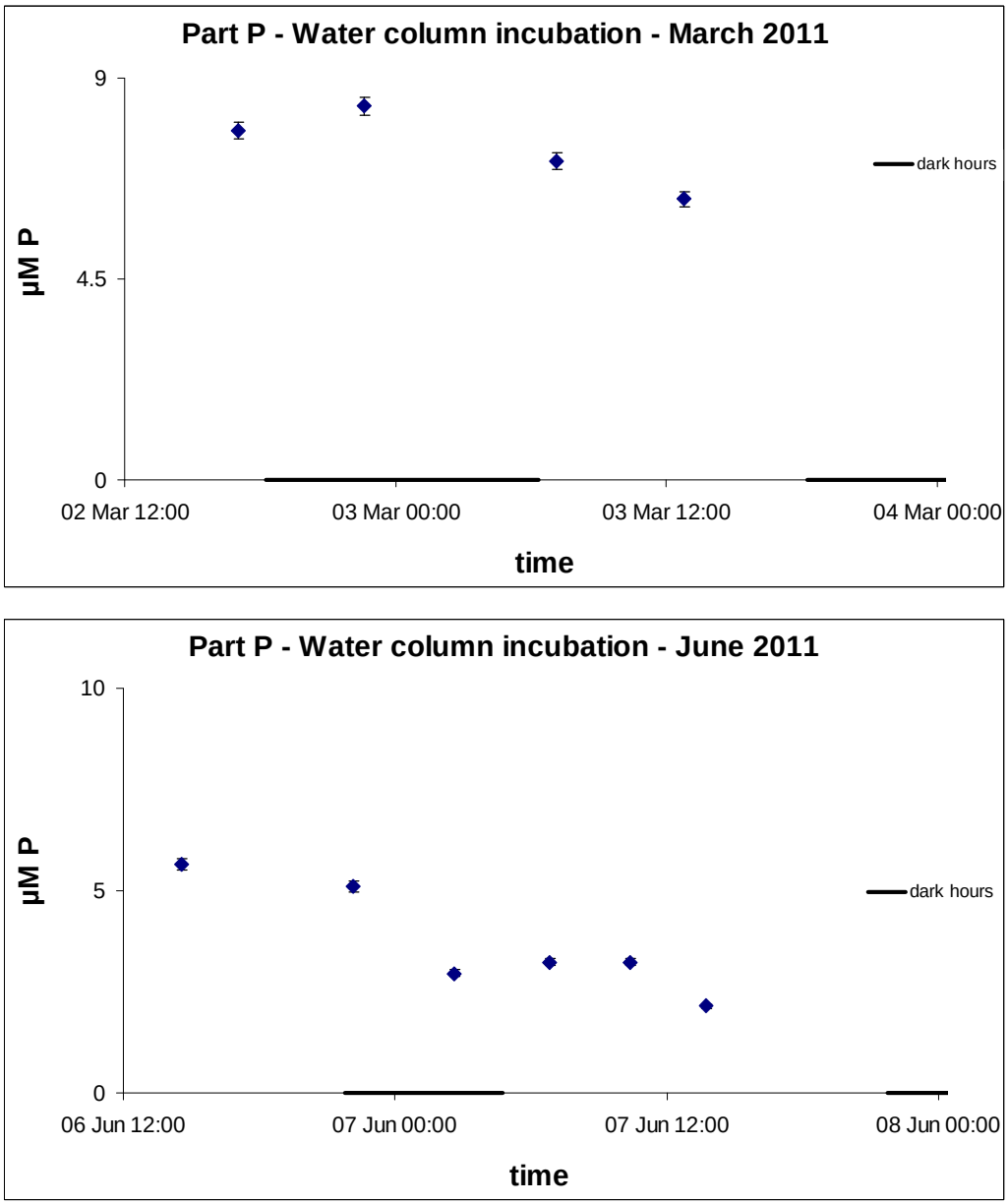


Figure 4-13: Concentrations of Part P inside the water column incubations, for March and June, 2011. Error 3%, n=6.

4.2.5 Biological activity indicators

4.2.5.1 Chlorophyll

Chlorophyll-a was analysed in samples taken from the settlement lagoon during the March and the June visits, and also from samples taken every two weeks between those two occasions (see Figure 4.14). Levels of Chl.a during March

sampling were 150 µg l^{-1}. Chorophyll.a peaked in mid-March, nearly reaching 450 µg l^{-1}. From then on, levels of Chl.a dropped consistently and by the time of the summer sampling they had decreased to 9 µg l-1.

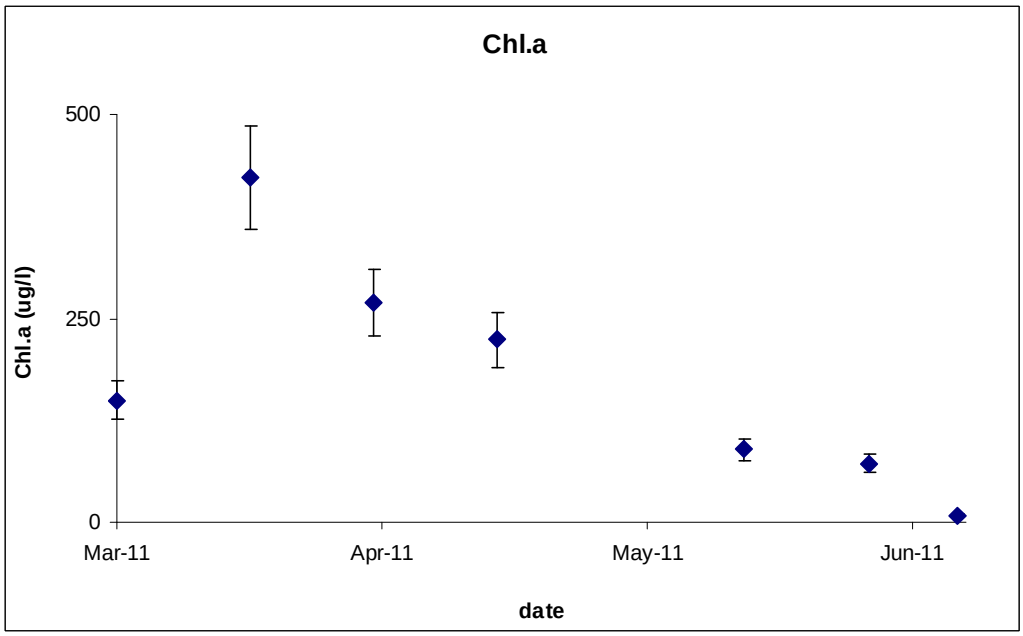


Figure 4-14: : Concentrations of chlorophyll in the water column of the settlement lagoon, every two weeks, between March and June 2011. Error: 15%, n=8

4.2.5.2 Dissolved oxygen

During the sampling of March, dissolved oxygen in the water column, measured 20 centimetres below the water surface, reached or surpassed saturation levels, but by the June sampling, dissolved oxygen had decreased to 35 % saturation and it went as low as 3 % during the night. See Figure 4.15.

Levels of DO next to the SWI were also at saturation levels in March, but in June they were at 28 and 20 % of saturation, at Sites 1 and 2 respectively. DO was completely depleted within millimetres under the SWI, both in March and June. See Figures 4.16 and 4.17.

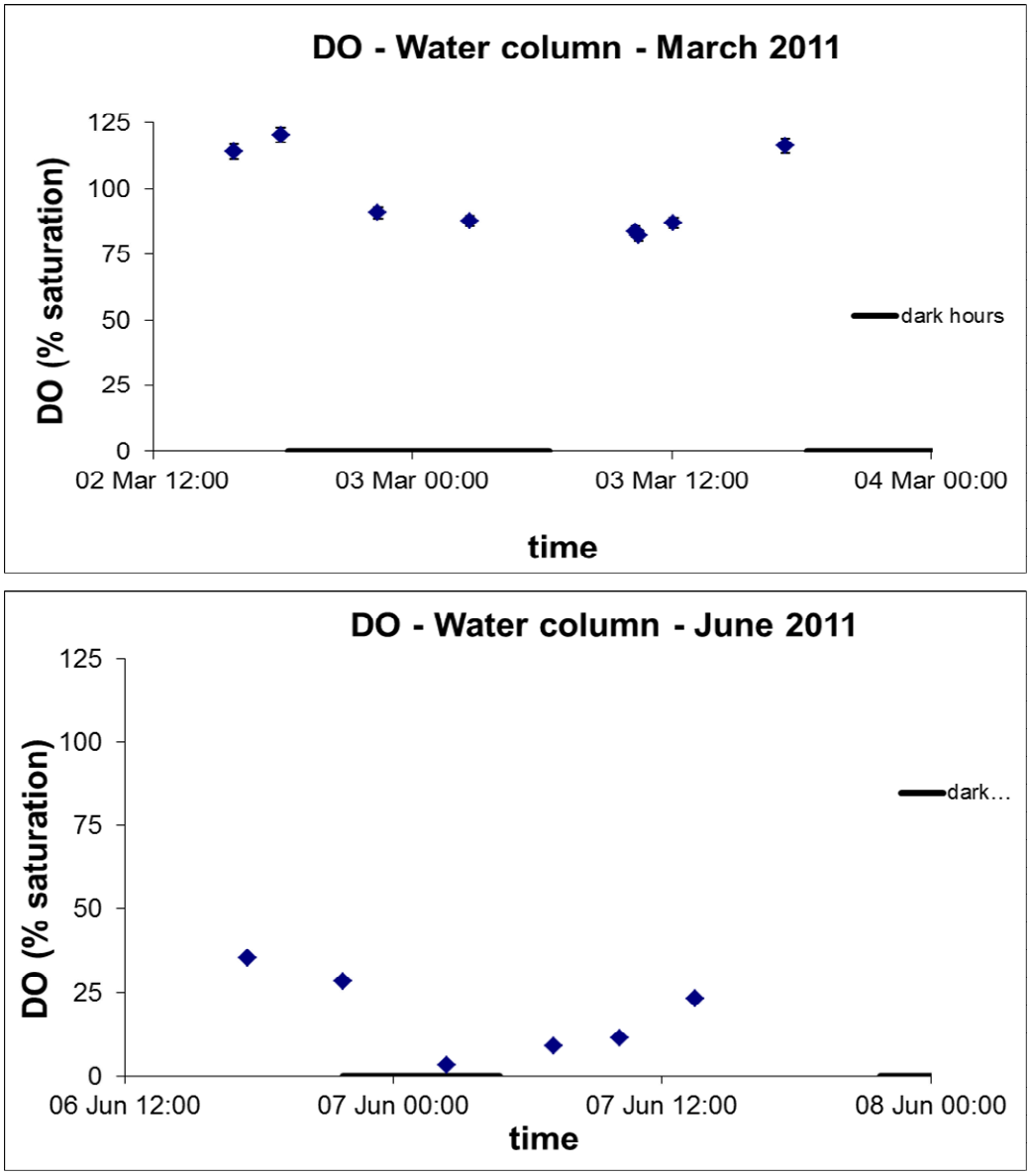
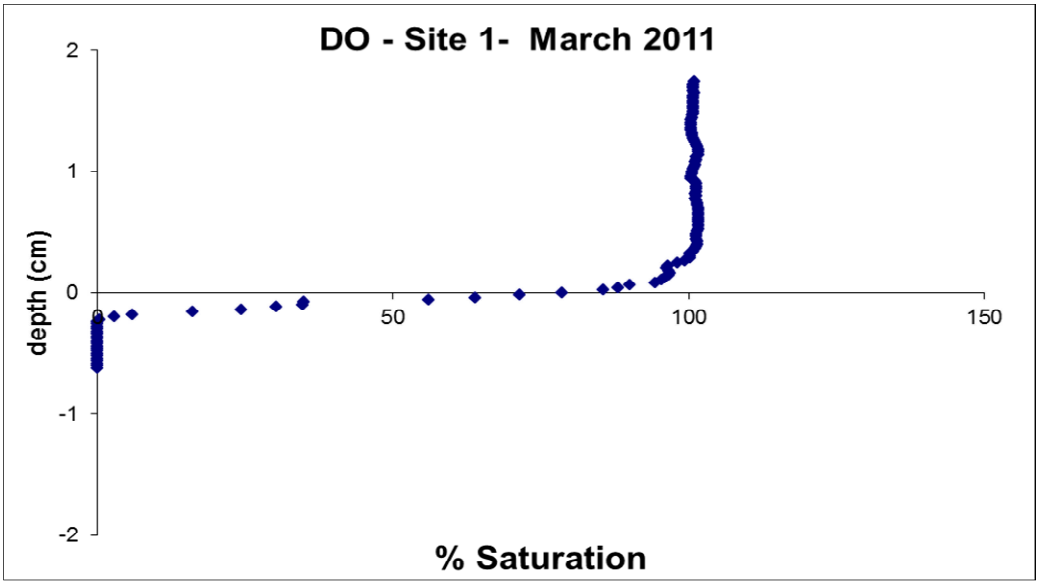


Figure 4-15: Concentrations of DO in the water column of the settlement lagoon, during the March and June 2011. Error 2%, n=6



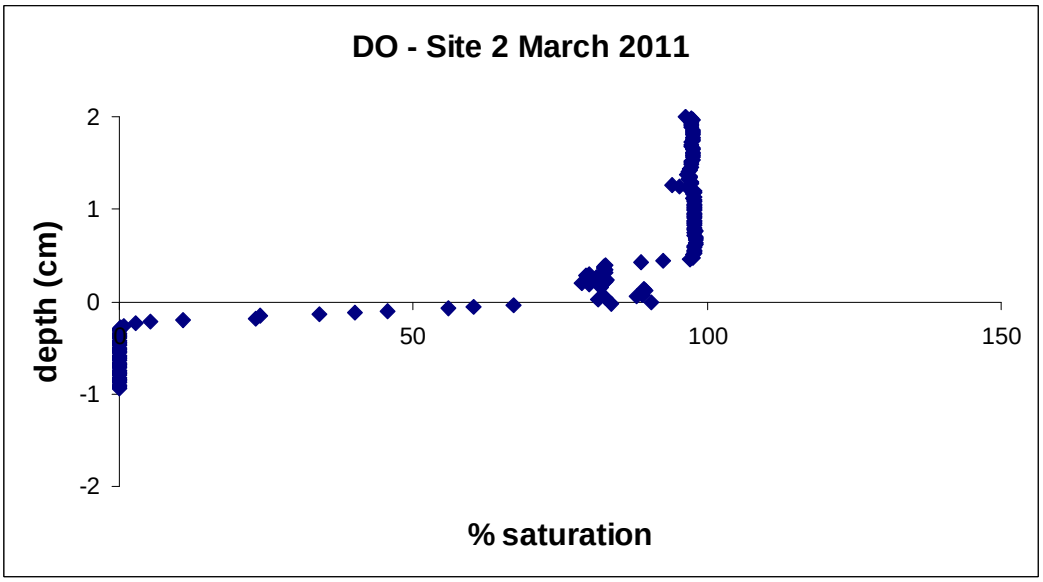


Figure 4-16: Concentrations of DO at the bottom of the water column and through the SWI, sites 1 and 2, during March 2011.

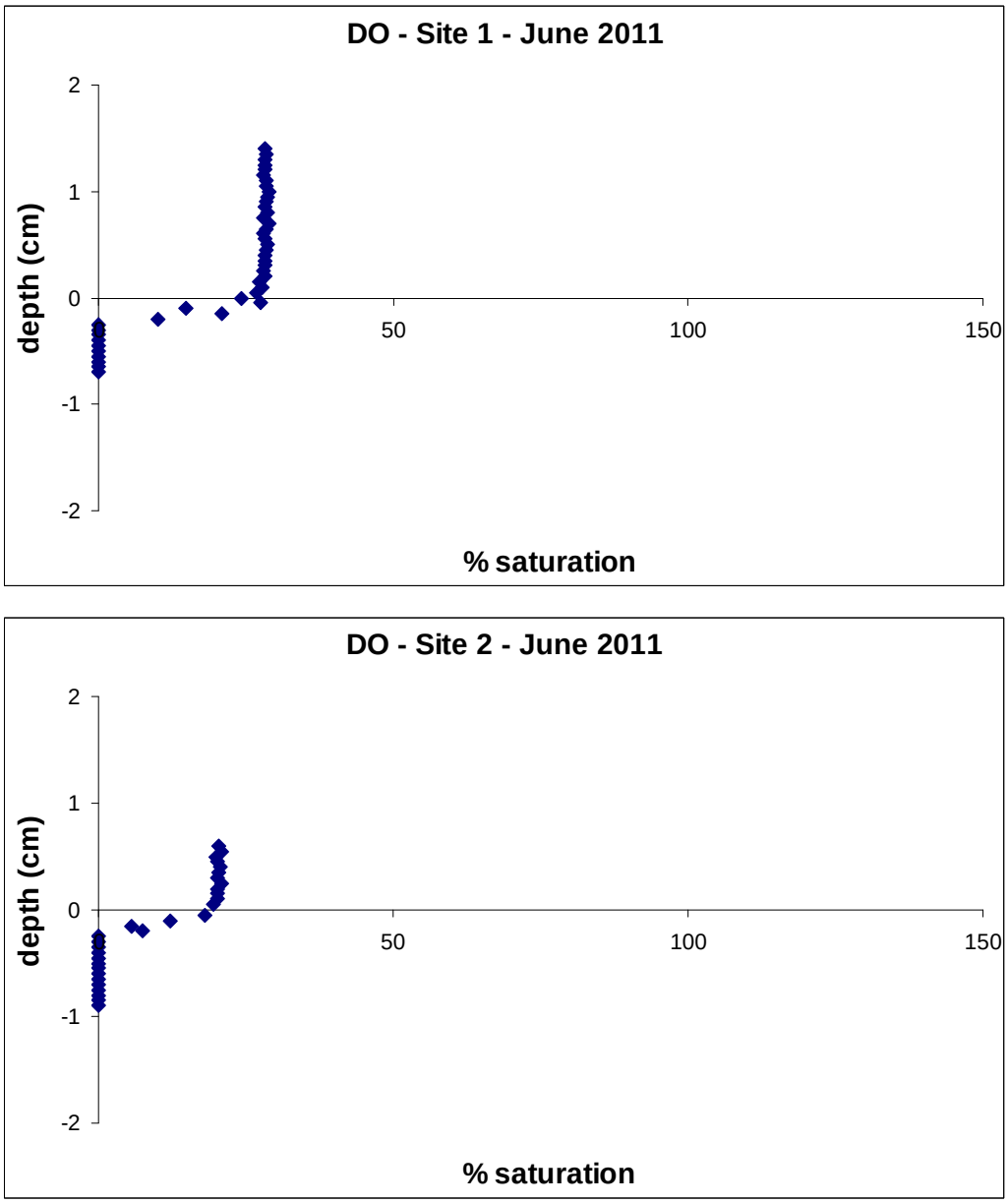


Figure 4-17: Concentrations of DO at the bottom of the water column and through the SWI, sites 1 and 2, during June 2011.

4.2.5.3 Ammonium

Levels of ammonium in the settlement lagoon varied between 34 and 38µM NH_4^+ (see Figure 4.18). Ammonium in the benthic chambers in March varied between 26 and 37 µM NH_4^+, without a clear trend (see Figure 4.19), while concentrations of ammonium in the pore waters just below the SWI were lower, at 4 µM NH_4^+, increasing downwards (see Figure 4.20).

During the sampling in June, ammonium in the water column varied between 228 and 264 µM NH_4^+ (see Figure 4.18). In June, concentration of ammonium increased slightly within the benthic chambers during the 24 hours of sampling, from about 196 to 209 µM NH_4^+. Pore waters ammonium in June peaked at the SWI, reaching values between 400 and 500 µM NH_4^+, deeper in the pore waters levels of ammonium varied between 200 and 400 NH_4^+. See Figures 4.18 and 4.19.

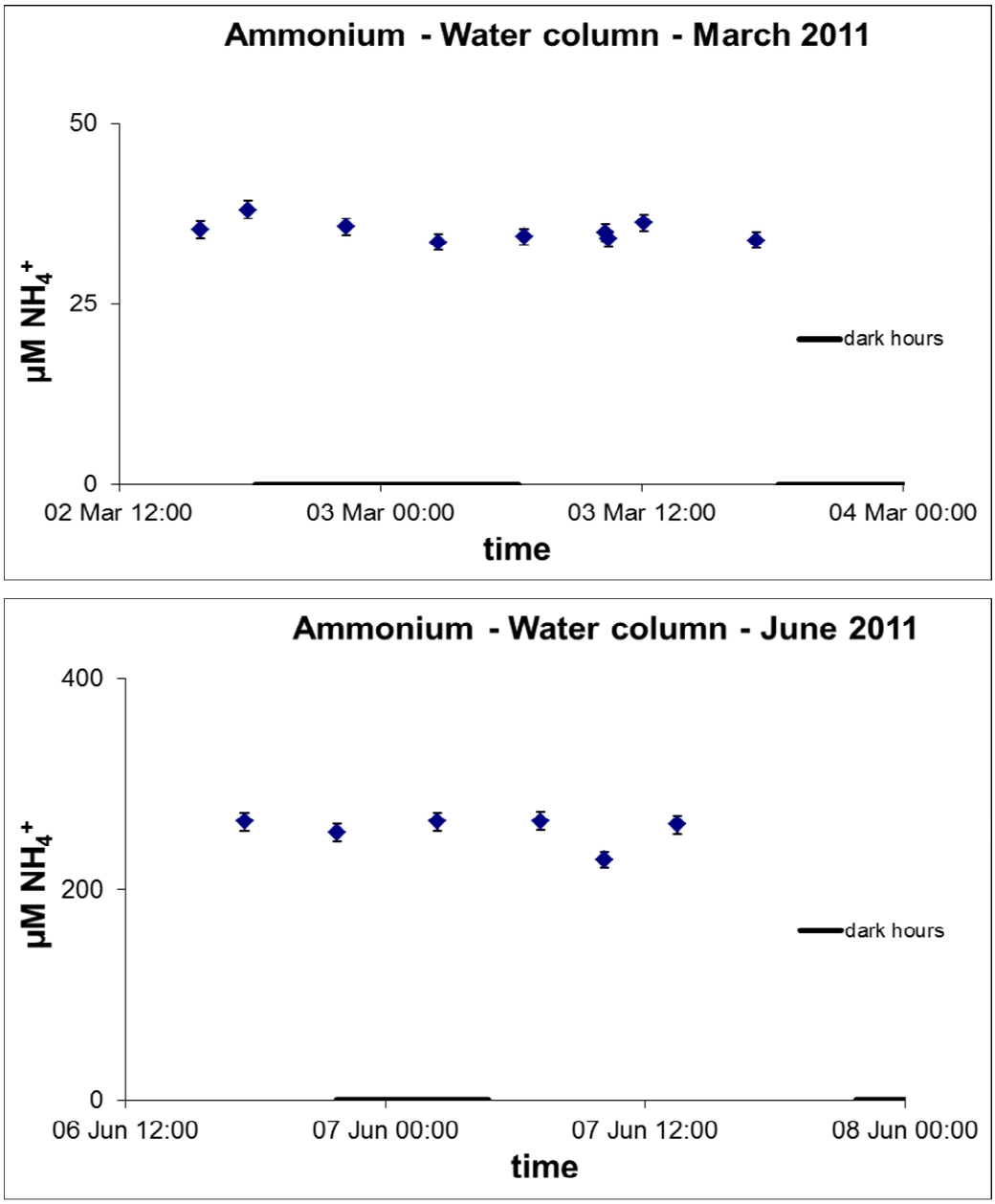


Figure 4-18: Concentrations of ammonium in the water column, for March and June, 2011. Error 3%, n=6.

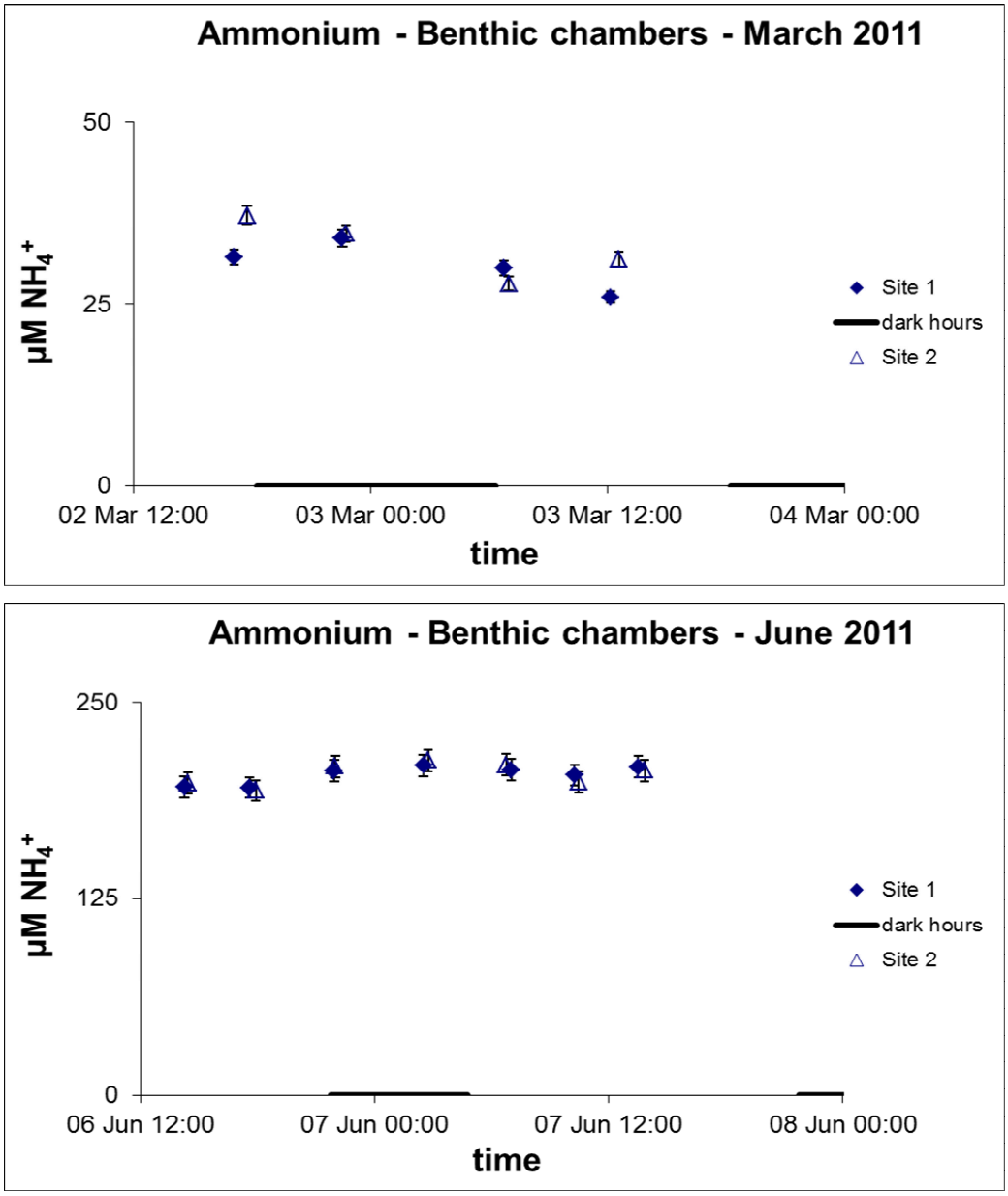


Figure 4-19: Concentrations of ammonium inside the benthic chambers, for March and June, 2011. Error 3%, n=6.

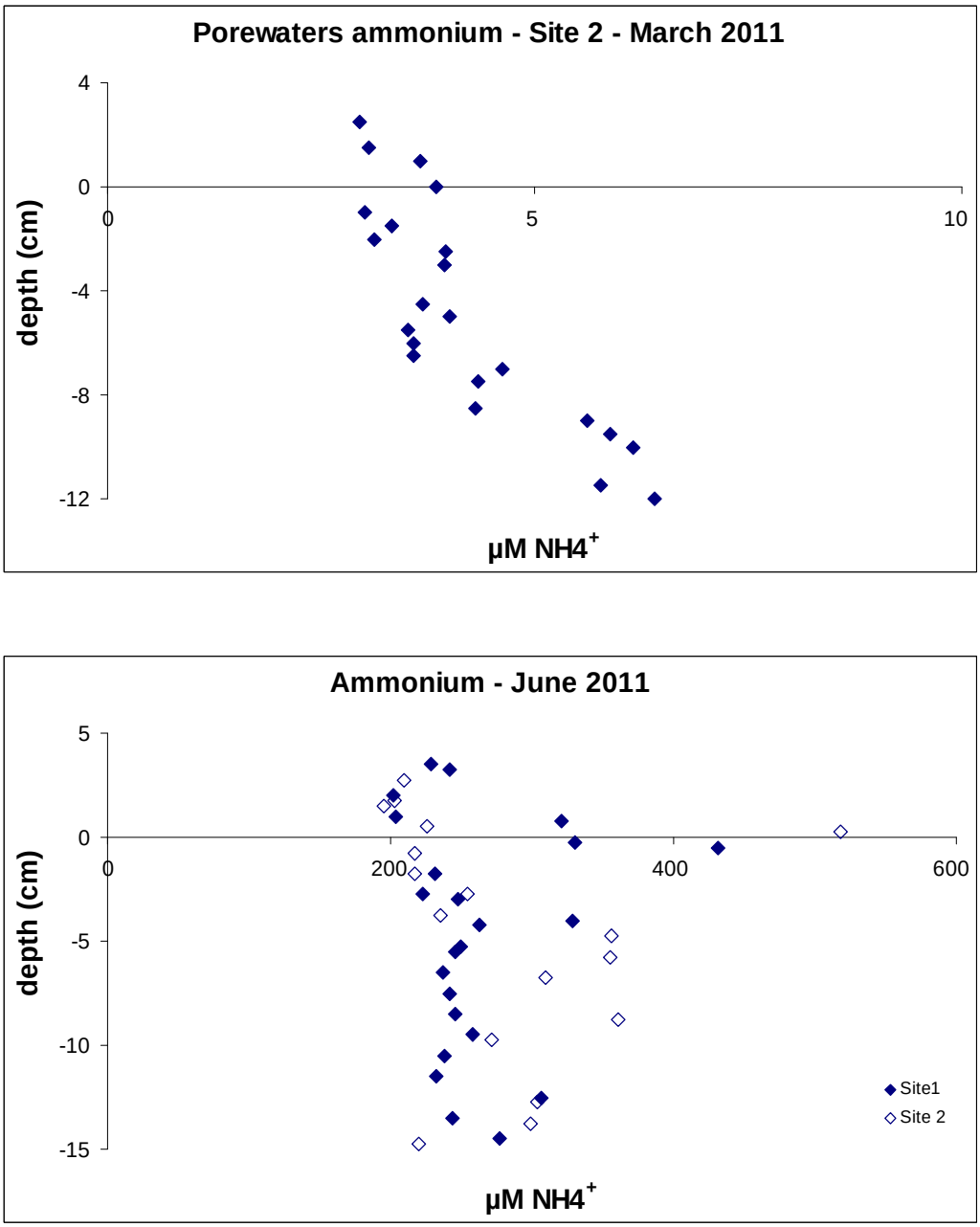


Figure 4-20: Concentrations of ammonium at the bottom of the water column and through the SWI, sites 2 for March, 2011, and sites 1 and 2 for June, 2011.

4.3 Discussion

In this section, the budgets of Part P, DOP and SRP in the settlement lagoon, together with other environmental factors are discussed in detail. This was carried out by testing the hypothesis stating that the sediments release P and are responsible for the excessive P leaving the lagon in summer

4.3.1 The budgets of P

The fluxes of P were calculated as explained in Sections 2.4 and subsections, and they have been integrated into the cycling of P model proposed in Figure 3.3.

4.3.1.1 Spring

During the March sampling, 25 moles P entered the settlement lagoon in 24 hours. During the same period, 21 moles P flowed through the outlets. The difference, 4 moles P, sank to the lagoon bottom as particulate P. The water in the settlement lagoon held an average of 18 moles P during the sampling period. The main species of P flowing in, passing through, and flowing out of the settlement lagoon was Particulate P (see Figure 4.21).

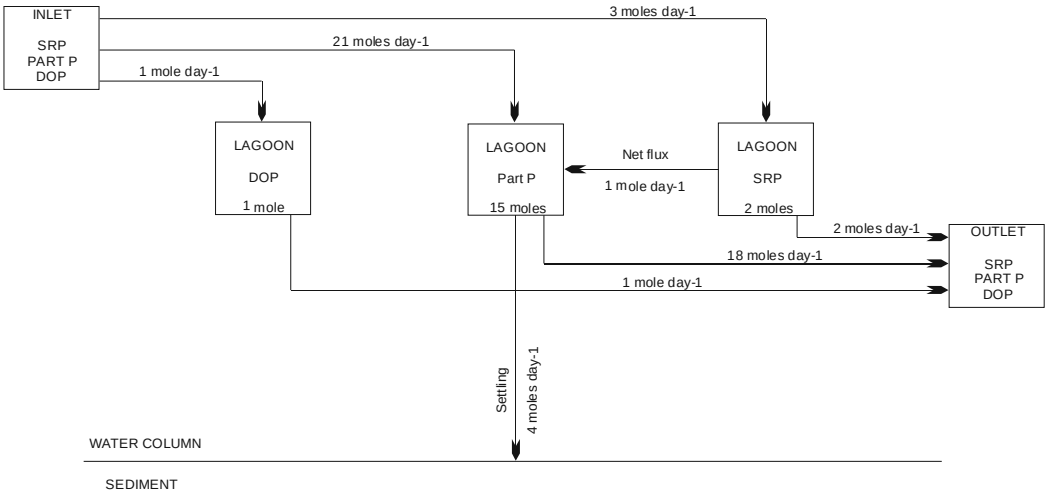


Figure 4-21: The daily cycling of P in the settlement lagoon, March 2011

4.3.1.2 Summer

During the June sampling, the flux of P through the settlement lagoon was one order of magnitude higher than in March, and the settlement lagoon exported P in summer. 118 moles P flowed in and 143 moles P flowed out of the lagoon. The

water column held an average of 85 moles of P during the sampling period. This coincided with previous observations (Strafford, 2010 and Palmer Felgate et al 2011b). The source of the excess P in June was the sediments, releasing both DOP and SRP. P also settled on the lagoon sediments as Particulate P, at a similar rate as that observed during the March sampling. See Figure 4.22.

The fluxes and diurnal variations of SRP and DOP in the water column incubations were minimal compared with their overall levels (see Figures 4.4 and 4.9). This signified that the cycling of P was dominated by the large influx from the inlet and P released from the sediments.

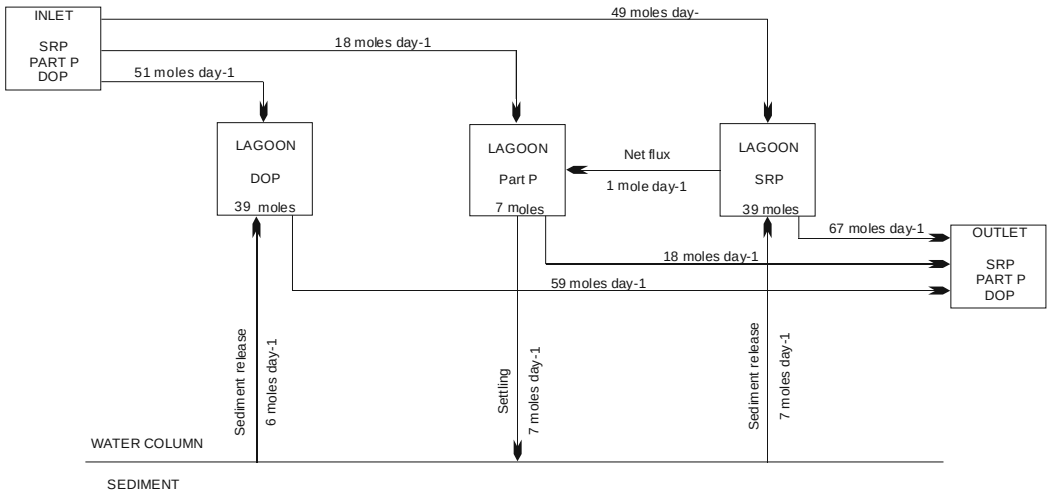


Figure 4-22: The daily cycling of P in the settlement lagoon, June 2011.

The described behaviour of P has been reported repeatedly for shallow lakes, where early spring algal blooms are often followed by internal loading of P in summer (Vollenweider and Kerekes 1982; Jeppesen et al. 2005, Istanovics, 1988). Processes that resulted in that behaviour are discussed in the following subsections.

4.3.2 Cycling of P in spring

4.3.2.1 Settling of particulate P

Figure 4.13 showed that concentrations of particulate P in the water column incubations decreased with time. This was interpreted as particulate P settling onto the bottom of the settlement lagoon, most likely within the bodies of algae. This assumption is supported by many studies of the cycling of P in shallow lakes. A study of the role of biota in the cycling of P observed that in shallow lakes there is a constant settling of algae and bacteria onto the bottom, transporting P in its particulate form, from the water column into the sediments (Istanovics, 1988). Another study noted that during algal blooms in shallow lakes algae reach the sediments before decomposing, supplying to the sediments a rich source of organic matter (Søndergaard et al 2003). A study of the shallow Lake Glaningen, Sweden, reached similar conclusions (Ryding 1985).

The settling of freshly produced organic matter is a fundamental step in the cycling of P in the settlement lagoon and it is the necessary mechanism for the release of dissolved species of P from the sediments, in summer. This is discussed in detail in Chapter 5.

4.3.2.2 Mineralisation of Particulate P over the SWI

Levels of DO in the water column in March were above saturation, but a few millimetres above the SWI these decreased to values around 80% (see Figure 4.16). Although temperatures were still low, these results suggested that recently deposited detritus from the algal bloom was feeding a population of microorganisms over the SWI. The evidence from ammonium, a by-product of respiration, from benthic chambers and from DET gels (see Figures 4.19 and 4.20, respectively) is inconclusive in this respect. The values of ammonium, from the DET gel for March shows a probable peak just above the SWI, but this is masked by the level of noise in the results.

A study of the eutrophic shallow Lake Vallentunasjön, in Sweden, also concluded that the early spring blooms of diatoms are consumed by microorganisms on deposition and that they never reach deeper sediments (Boström et al 1989). Other studies also concluded that fresh algal blooms are a rich source of organic matter for bacteria, and that these incorporate, store and release P, as long as oxygen or other oxidisers like nitrate are present (Søndergaard et al, 2003). More generally, other authors concluded that in shallow lakes, 50% of the primary production is mineralised above the sediments (Caraco et al 1990).

The proposed levels of respiration at the SWI of the settlement lagoon in March 2011 can explain some important differences between the observations made during this study and those made in 2009, detailed in Palmer-Felgate etal (2011b). Although in 2009, levels of chlorophyll were in general lower than those reported in this work, DO in 2009 was higher than in 2011. Also, ammonium in the water column in March 2009 was less than 10 µM , while in 2011 ammonium was around 40 µM.

DET gel profiles showed a peak in SRP above the SWI (see Figure 4.6) coinciding with the depth at which DO also decreased. Therefore, the microbial mineralisation of Particulate P from the fresh algae, occurring 2 or 3 centimetres above the sediments caused a localised peak in SRP and a decrease at DO in those depths. There is previous evidence of freshly deposited algae being consumed before they were incorporated into the sediments, and their Particulate P being mineralized into phosphate. The study of Lake Vallentunasjön concluded that the regeneration of the Particulate P contained in the freshly deposited algae, in the top 2 cm of sediments, accounted for all the P released during one season (Boström et al 1989). The studies of Lake Grevelingen and of the Loosdrecht Lakes in the Netherlands also concluded that the top few centimetres of sediments contained freshly deposited algae and their decomposition caused the P loading of the lakes (Marsden, 1989).

Although microbial activity may have caused the release of SRP above the SWI, the benthic chambers in March showed an overall decrease in concentrations of

SRP during the 24 hours sampling (see Figure 4.5). This was interpreted as the sediments and planktonic organisms rapidly taking up the SRP released during bacterial mineralisation of the recently deposited algae.

Molecular diffusion of phosphate from the water column into the sediments could have been driven by biotic or abiotic processes. Regarding abiotic processes, phosphate can co-precipitate with iron and manganese, or it can be sequestered by surfaces of clays, amorphous oxyhydroxides, and carbonates. (Boström 1988b). The sequestration of P by iron minerals occurs in oxygenated sediments (Carlton and Wetzel, 1988), and data from the oxygen probes (see Figure 3.9) shows that the top few millimetres of sediments were oxic in March. Organisms living within the sediments can also drive the diffusion of water column phosphorus if they are consuming phosphate from the pore waters (Boström, 1988b). For example, sediments of Lake Sodra Bergundasjön, in Sweden, are rich in both iron and humic matter and they were described as having a high capacity to capture P (Boström, 1984).

Another reason why the benthic chambers showed an overall decrease in concentration of SRP, even when P was being mineralised just above the SWI, could have been its immediate uptake by the planktonic organisms above the SWI. This mechanism probably removed the released phosphate more rapidly than the molecular diffusion through the SWI discussed in the previous paragraph. This suggestion is supported by comparing the calculated diffusion rates with the integrated fluxes of SRP in the benthic chambers. The fluxes calculated using data from the DET gels were in average 0.4 moles day^{-1}, for the whole of the pond area. On the other hand the decrease in SRP concentration within the benthic chambers was in average 1.2 moles day^{-1}, for the whole of the pond area. The uptake of SRP in the water above the SWI happened in dark conditions because the benthic chambers had been obscured. Dark uptake of phosphate could have been performed by bacterioplankton to satisfy their metabolic demands, and also by algae accumulating excess P.

4.3.3 Cycling of P in summer

4.3.3.1 The dissolved species of P

Average levels of SRP in the water column increased by one order of magnitude since March. These were maintained by a large influx from the sediments (7 moles P day^{-1}), and principally by a main flux from the inlet (49 moles P day^{-1}) (see Figure 4.22). Therefore the release of P from settlement lagoon observed during the June field work originated in the sediments.

This behaviour is common in shallow lakes in temperate regions and has been reported to have occurred, for example, in the shallow Lake Blankensee, in Germany (Ramm and Scheps, 1997). A study of Loch Leven, in Scotland reached similar conclusions and that study proved that the excess P in summer was released from the sediments (Spears et al 2007). The examples are numerous in the literature and have been discussed, among others by Søndergaard et al (2003), Ryding (1985) and Marsden (1989). An in depth discussion of the mechanisms that produced the release of SRP from the sediments into the water column of the settlement lagoon in June 2011 is presented in Chapter 5.

Concentrations of DOP in the water column were also one order of magnitude higher than in March, and as with SRP, the main source of DOP was the inlet, while the sediments also contributed to DOP, but in a smaller degree (see Figure4.22). The high statistical errors calculated for this species of P, made it impossible to make reliable inferences about the diurnal cycling of DOP, based on diurnal variations within the water column incubations. Typically in the water column, concentrations of DOP increase as the algal bloom decays, due to increased rates of excretion from bacteria, and the breaking down of the ageing biomass. It was unlikely that any of the released DOP was consumed as a source of P in the water column because that would happen in systems limited in inorganic P (Selig et al, 2002).

DOP release through the SWI indicated that the breakdown of organic matter within the sediments was intense (Zhang et al, 2012). DOP is an intermediate species of P between the enzymatic hydrolysis of organic matter and the dissolution into SRP (Zhang et al, 2012). If the rate of breakdown or organic matter is higher than the subsequent dissolution into SRP, DOP appears as a large proportion of TDP (Coveney et al 1977).

4.3.3.2 Settling of particulate P

The settling rate of Particulate P is directly related to its concentration in the water column and to the settling velocity of the bodies containing the Particle P (Brett and Benjamin, 2008). The calculated sedimentation flux of Particulate P in the water column incubation in June was higher (7 moles P day-1) than in March (4 moles P day-1), even when in June the concentration of Particulate P in the lagoon was lower than in March. Therefore the sinking velocity of the particles containing the Particulate P should have been significantly higher in June than in March 2011.

High sedimentation fluxes of Particulate P, even when its concentration is low in the water column, can be driven by settling grazers when these die. The large size of grazers increases their sinking velocities and therefore the sedimentation rate of Particulate P (Sarnelle, 1992). The effect can be the opposite if the reduction in concentrations of Particulate P from the water column by grazing exceeds the effect of the increased settling velocities (Sarnelle, 1992).

The fact that unusual densities of grazers were not recorded during the fieldwork carried out in 2009 (Palmer-Felgate et al 2011b) was not unexpected. Dense populations are usually unsustainable in shallow eutrophic lakes and collapse within one or two weeks after their peak, due to exhaustion of the algae or by the growth of a fish population (Scheffer et al 1997). Therefore, it could have happened that the fieldwork of June 2009 was carried out during one of the periods in between peaks.

In lakes where fish are absent, like the settlement lagoon of the South Finger wetland, algae and grazers can have several peaks during spring and summer, with the consecutive periods of growth and collapse of the two populations, by grazing or lack of food. This was observed, among others, in Lake Aydat in France (Lair and Ayadi 1989) and in Lake Grosser Binnensee in Germany (Lamper and Rothhaupt, 1991), which experienced four cycles of algae and daphnia peaks in one season.

4.3.3.3 Evidence of resuspension of Particulate P

The study carried out in 2009 showed, by sampling the settlement lagoon every two weeks, that concentrations (although not fluxes) of Particulate P followed the levels of chlorophyll, and they decreased by one order of magnitude between the bloom in March and the collapse in June (Palmer-Felgate et al 2011b). However, in 2011 there was not a significant difference between the fluxes of Particulate P into and out of the lagoon, measured in March and June.

The discrepancy was attributed to the occurrence of a resuspension event during the evening of the 6th June 2011. Figure 4.12 shows a sudden increase in Particulate P values in the water column taking place on the evening of the 6th, which coincided with an increase in the strength of winds (see Section 4.2.1). It was noted in the field book that on the 7th the water was 4.12), also coinciding with a drop in wind strength. Palmer-Felgate et al (2011b) demonstrated that the settlement lagoon is susceptible to resuspension caused by heavy rain and / or strong winds. Similarly, rain and wind have been reported to cause resuspension in shallow lakes elsewhere, e.g. Kristensen et al (1992) and Bengtsson & Hellström (1992).

The water within the incubations was not in contact with the lagoon water and bottom sediments, and it was better sheltered from the wind than the open water of the rest of the settlement lagoon. Therefore, water within the incubations was not affected by sediment resuspension or water turbulence. For that reason, the concentrations of Particulate P from the water column incubation deployed in

June (see Figure 4.13) did not show a peak during the night of the 6th – 7th, but instead Particulate P decreased steadily, due to settling, during the 24 hours sampling. The calculated fluxes of Particulate P for June did not balance (see Figures 4.22) because the calculated settling flux using data from the water column incubations did not represent the real conditions of the lagoon.

If the sudden increase of concentration of Particulate P in the water column in the evening of the 6th June were multiplied by the volume of water of the lagoon, it would have represented a flux of 6 moles P from the sediments into the water column. This flux was included in Figure 4.23 as a dotted line because it has to be considered with some reservations given that it was calculated using data from the water column, probably skewed by the constant supply of Particulate P from the flux through the inlet.

Even with reservations, the calculation described in the previous paragraph seems to explain the apparent imbalance in Particulate P for June. Accordingly, the 6 moles of Particulate P were resuspended during the evening of the 6th June, and the majority settled back by the afternoon of the 7th June, 2011 (see Figure 4.12). Other, studies of shallow lakes with highly organic sediments reported similar settling velocities: 24 hours for a 2 to 4 meters deep Lake Arresø, in Denmark (Kristensen et al 1992), and 10 to 20 hours for the 1.5 meters deep Lake Tämnaren in Sweeden (Bengstsson and Hellström, 1992).

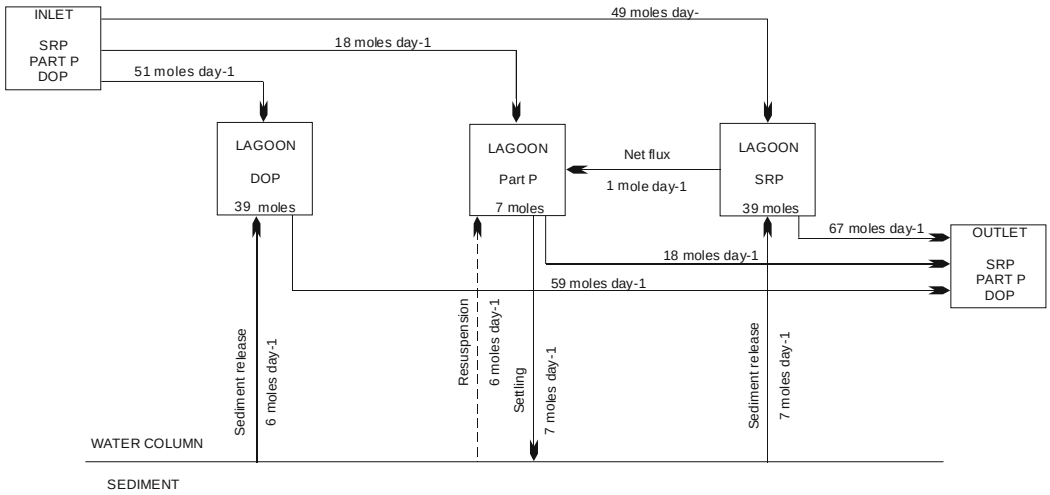


Figure 4-23: The cycling of P in the settlement lagoon, June 2011, including the resuspension of Particulate P that probably occurred during the night of the 6th – 7th. The flux was denoted as a broken line because it has to be considered with some reservations given, that it was calculated using data from the water column, probably skewed by the constant supply of Particulate P from the flux through the inlet.

Disturbance of bottom sediments of shallow lakes have been reported to bring pore water into contact with the water column, increasing concentrations of SRP (Cheng and Sheng, 2003, and Boström 1982). However, the increase of Particulate P in the evening of the 6th June was not accompanied by an increase in SRP in the water column, which remained almost unchanged (see Figure 3.17)

Søndergaard et al (1992) stated that resuspension can increase, decrease or have no effect on the water column SRP. The resuspension of particulate matter can sequester or release dissolved P from the water, depending in the equilibrium between the resuspended particles and the water column (Boström, 1988b) and the redox conditions in the sediments and in the water column. For example, organic rich sediments are usually consumed by anaerobic bacteria at slow rates within the anoxic layers, and mineralised P is released slowly through diffusion into the water column. But when those sediments are resuspended, they can be consumed more rapidly by aerobic microorganisms of the water column and the resulting phosphate is released directly into the water (Søndergaard et al, 1992). Also, iron would sequester P from the surrounding water if the ratio Fe:P is above 15. Accordingly, at low ratios of Fe:P, P will be released until an

equilibrium is reached between the solid phase and the surrounding water (Jensen et al 1992). Boström (1988b) and Søndergaard et al (1992) explained how an increase in the circulation of water produced by high winds can induce the release of SRP from the pore water, even with no sediment resuspension. The constant renewal of the bottom waters keeps steep gradients of SRP between the pore waters and the water column, increasing the rates of diffusion.

5 BURIAL AND REGENERATION OF P IN THE SEDIMENTS OF THE SETTLEMENT LAGOON

5.1 Introduction

5.1.1 Relevance of sediments for the budgets of P in the settlement lagoon

In Chapter 4 it was demonstrated that Particulate P is carried from the ponds of the WWT reserve upstream and deposited in the settlement lagoon, and it is also created within the settlement lagoon during its eutrophic and hypereutrophic states, between March and June. Of the Particulate P that enters the settlement lagoon or that is synthesised within it, approximately 20 to 40% is deposited onto the lagoon bed. It was shown in Chapter 4 that part of the settled material undergoes some kind of biogeochemical changes in June that mineralise part or all of the Particulate P before it is finally buried. The liberated inorganic P is then transported back into the water column.

These mechanisms probably occur in all the ponds of the wetland centre, and that results in a 25 fold increase in the influx of dissolved P into the settlement lagoon in June compared to March, and the flow of dissolved P in June is 5 times larger than that of Particulate P. This mass of dissolved P, plus what it is released by the sediments of the settlement lagoon, constitutes the load of P into the reed beds, which ultimately fail to contain. Therefore the sediments of the settlement lagoon and probably of the whole wetland centre are the source of the excessive mass of P in summer, which results in the failure of the treatment wetland.

5.1.2 Aim

The aim of the work presented in this chapter was to identify which processes cause the retention and the release of P from the sediments of the settlement lagoon, in spring and in summer, in order to provide to the management of management of WWT the most complete picture of the behaviour of P in the settlement lagoon, and by inference in other ponds of the wetland centre. This was carried out by studying two main hypotheses (see section 1.5):

Hypothesis 2) the minrealisation of organic matter within the sediments is the mechanism by which large amounts of P are released through the sediments in June.

Hypothesis 3) the organic matter that releases P in June is a combination of recently deposited primary productivity and particulate matter that has been being accumulated in the sediments for a long time.

5.1.3 Background

The retention of particulate matter (i.e. Particulate P) in the sediments of shallow lakes depends on the shape of the lake, water retention time, and size and density of the particles (Håkanson & Jansson, 1983), also on weather conditions and bioturbation. P in the sediments is present in the following forms (Boström 1988b):

- Adsorbed onto surfaces of particles, such as clays and oxyhydroxides.
- Co-precipitatated with iron particles.
- Co-precipitated with calcium minerals, such as apatite.
- Inorganic particles containing P derived from the watershed.
- Organic matter containing P.

The capacity of shallow lakes to retain P varies depending on the quality of their sediments and on the intensity and the quality of the P load at which they are exposed (Pettersson 1986). Boström (1988b) summarised the principles of exchange of phosphorus between sediments and water column of lakes, by

describing the processes taking place in different Swedish lakes. The sediments of Lake Södra Bergundasjön are rich in iron and they have a high retention capacity of iron bound-P during periods of intense loading. Conversely, the sediments of Lake Erken were calcareous, and had a high capacity of retaining P from the runoff of farmland nearby, as P was co-precipitated together with calcium minerals (Boström, 1988b).

On the other hand, sediments of Lake Vallentunasjön in Sweden are rich in freshly produced and deposited organic matter, and an important part of the organic matter within the sediments consists of living microorganisms. When the lake received sewage, the binding sites for P were few and the rate of mineralisation of P was high. For those reasons, the lake had a low capacity to retain P. Lake Stora Hastevatten, in Sweden, does not retain P. The little P in the sediments is mainly refractory organic P, while inorganic P is extremely low. This was attributed to the acidity of the sediments (Boström, 1998b).

5.1.3.1 Iron bound P

Gonsiorczyk et al (2001) showed that the depth of penetration of oxygen into the sediments influences the release of P, coinciding with the research performed by Einsele (1936) and Mortimer (1941). The oxic top layer of the sediments contain particulate ferric iron that sorbs P, which would dissolve into ferrous iron if that layer goes anoxic, releasing the sorbed P (Penn et al 2000). This occurs frequently in shallow lakes during short periods of anoxia (Søndergaard et al, 2003). Iron can be maintained in its oxidised form also by nitrate. For example, the high levels of P release from sediments of Lake Mügalsee, in Germany, were attributed to the low input of nitrate (Kozerski et al, 1999). On the other hand, the presence of nitrate can promote the release of P from sediments as it stimulates respiration of anoxic bacteria and the mineralisation of Organic P (Søndergaard et al, 2003).

The retention of P by iron oxides and hydroxides responds to a dynamic equilibrium with the pore waters, and it has been suggested that there is a threshold above which iron minerals will not retain further P, even in oxic

conditions (Søndergaard et al, 2003). Jensen et al (1992) demonstrated that the threshold is reached when the Fe:P ratio of the particles is 15:1 (weight by weight), and P is retained by iron particles when the ratio is higher, and as long as the sediments are kept oxidised. At lower ratios, pore water P may diffuse through the oxidised layer into the water column (Søndergaard et al, 2003). Accordingly, Caraco et al (1993) demonstrated that the ratio Fe:P should exceed 10:1.

High pH can stimulate the release of P bound to iron particles, because OH- ions compete with phosphate ions for sites on the surfaces of the particles (Lijklema, 1976). This effect has been described during intense photosynthesis in eutrophic lakes (Søndergaard, 1988 and Istvánovics and Pettersson, 1998).

5.1.3.2 Calcium bound P

Calcium minerals containing P, either within their structure or adsorbed onto surfaces, can be imported or precipitated within shallow lakes. The in situ precipitation of calcium minerals usually has an impact in the cycling of P of the lake. It was determined in laboratory studies that the co-precipitation of calcium and phosphorus occurs at pH between 8 and 10 (Otsuki and Wetzel, 1972). High temperatures also favour the precipitation of calcium minerals, by decreasing the solubility of both $CaCO_3$ and CO_2. Concordantly, water temperatures and levels of CO_2 are directly related to biological activity, and the precipitation of calcium minerals is usually mediated by microorganisms (Boström, 1988b).

Calcium minerals within the sediments sequester further phosphorus, given that the concentrations of P in the pore waters are normally much higher than in the water column (Dobolyi and Herodek, 1980). Similarly, hydroxyapatite is precipitated within the pore waters (Stumm and Leckie, 1970), and the concentration of calcium bound P increases with depth (Williams and Mayer, 1972). The main factor controlling the retention capacity of calcium bound P in sediments is pH, while redox levels do not seem to affect the retention or release of this type of sediment P (Christophoridis and Fytianos 2006). Intense bacterial

activity in the sediments can result in excessive production of CO_2, which in turn will inhibit the formation of Ca-P minerals (Boström 1988b).

5.1.3.3 Organic P

Spring and summer are the seasons when the cycle of P becomes most active, due to higher rates of insolation and to higher temperatures. The better light conditions of the spring result in an increase in water column productivity and the synthesis of Particulate P during photosynthesis. Particulate P is subsequently transported to the sediments during deposition (Istvánovics and Pettersson, 1998). Higher temperatures, in turn, are associated to the release of P from sediments of shallow lakes (e.g. Jensen and Andersen, 1992, Boers et al, 1998, or Søndergaard etal, 1999). Increasing temperatures stimulate the mineralisation of organic matter by microorganisms and the subsequent release of dissolved P (Boström and Pettersson 1982, and Jeppensen et al 1997). Increasing respiration in the sediments, in turn, reduces the redox conditions of these, and this can cause the release of P from iron particles (Jensen and Andersen, 1992).

Sediment microorganisms have a significant role in the cycling of P in lakes with the characteristics of the settlement lagoon of the South Finger wetland. In these shallow eutrophic lakes, the organic matter from the algal blooms reaches the sediments before being decomposed, fuelling the activity of sediment bacteria, and increasing their rate of mineralisation of P (Pettersson, 1998). This depends also in the depth of penetration of oxidisers like oxygen, nitrate or sulphate. Typically, oxygen is exhausted within the top millimetres of sediments, while nitrate can penetrate several centimetres, depending on the rates of consumption and input (Søndergaard et al, 2003). If bioavailable organic matter is present and concentrations of nitrate are low, sulphate reduction and sulphur cycling can become important (Holmer and Storkholm, 2001). The reduction of sulphate can derive into the formation of hydrogen sulphide and then iron sulphide. If this happens, the capacity of iron to retain P decreases and this can be released into the pore waters (Kleeberg and Schubert, 2000).

It has been demonstrated that some species of cyanobacteria and bacteria found on sediments store polyphosphates (Boström 1988b), and that these are synthesised under aerobic conditions and dissolved under anaerobic conditions (Fleischer, 1986). The formation of polyphosphates chains consumes P from the pore waters, while the destruction of the chains releases P back to the pore waters (Boström 1988b). The dissolution of polyphosphate chains in anaerobic conditions is primarily associated with the utilisation of the energy stored in the bonds of the polyphosphate chains (Wentzel et al 1986). This results in a competitive advantage, for systems where shifts between aerobic and anaerobic conditions are frequent (Boström 1988b), like the sediments of shallow lakes. Polyphosphates, in turn, can lead to the permanent sink of P. It has been suggested that polyphosphates can nucleate the growth of apatite minerals, locking P permanently (Diaz et al, 2008).

Another factor controlling the capacity to retain P of sediments of shallow lakes is related with the turbidity of the overlying water, which is closely associated to its ecology. The settlement lagoon is a turbid system, with frequent algal blooms. Turbidity can also occur through the constant sediment resuspension by a dense population of fish (Søndergaard et al, 2003). Turbid waters are related to shallow lakes that release P from their sediments, whereas clear water lakes are related to systems with a better capacity to retain P within their sediments (Beklioglu et al, 1999).

There are several mechanisms that result in the behaviour described above. For example, the absence of algal blooms reduces the transport of organic matter and P onto the sediments through sedimentation. This in turn consumes less oxygen and keeps higher redox conditions at the sediments surface, both factors enhance the retention of P by sediments (Søndergaard et al, 2003). Better light conditions at the bottom of shallow lakes promote benthic primary production through the development of algal mats and the oxidation of sediments and their uptake of P (van Luijn et al, 1995). Better light conditions in shallow lakes can also promote the development of submerged macrophytes, with the benefits described above,

and the added advantage that their roots would drive oxygen deeper into the sediments (Søndergaard et al, 2003).

Clear water lakes can be achieved by managing the shallow lakes intensely. For example, by having the right equilibrium between algae, zooplankton and fish. Sediments of Lake Engelsholm enhanced their capacity to retain P after 2/3 of the fish population was removed (Søndergaard et al., 2002a).

5.2 Results

5.2.1 Weather

The spring sampling in 2011 coincided with the field work described in Chapter 3. This was carried out on the 2nd and 3rd of March. Weather was dry and temperatures varied between 2ºC near midnight and 6ºC at around noon. On the 2nd ,weather remained clear and calm, but on the 3rd the sky stayed overcast almost continuously, and winds had risen to 20 mph from the SW. Daylight started at 6:20 hours and it became dark at 18:15 hours.

The sampling in the spring of 2012 was carried out on the 6th and 7th March. There was intermittent drizzle during the first day, and the second day remained overcast, but dry. Temperatures varied between 4 ºC before midnight and 10 ºC at around noon.

The summer sampling of 2011 was carried out between the 6th and 7th June, as reported in Chapter 3. Temperatures varied between 8 ºC at midnight and 21ºC in the afternoon. It was overcast and windy on the 6th; it rained during the night, and on the 7th winds increased further with intermittent showers.

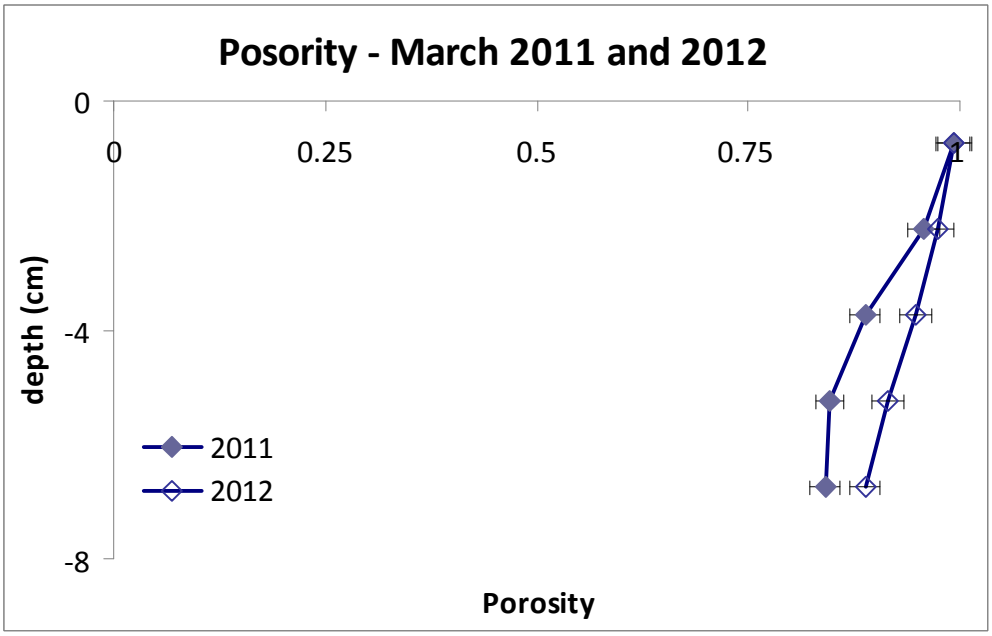
The sampling in the summer of 2012 was carried out on the 27th and 28th June. It rained during the whole duration of the field work, and most intensely during the night. Wind velocities during the night were estimated between 10 and 20 mph.

This affected the quality of the water of the settlement lagoon, which was noticeably more turbid on the morning of the 28th than it had been the previous evening. Temperatures were high, with 17 ºC during the night and 27 ºC in the early afternoon.

Water temperatures in the settlement lagoon in 2011 ranged between 3.6 to 7.2 ºC in March and 16.0 and 18.0 ºC in June. In 2012, water temperatures ranged between 6.5 and 7 ºC in March, and 17 to 21 ºC, in June.

5.2.2 Porosities

The porosity of the sediments decreased from 1 at the SWI to approximately 0.86, 5 centimetres below it. From this depth downwards, porosities remained at 0.86. During June 2011, porosities remained high down to 3 centimetres below the SWI. See Figure 5.1.



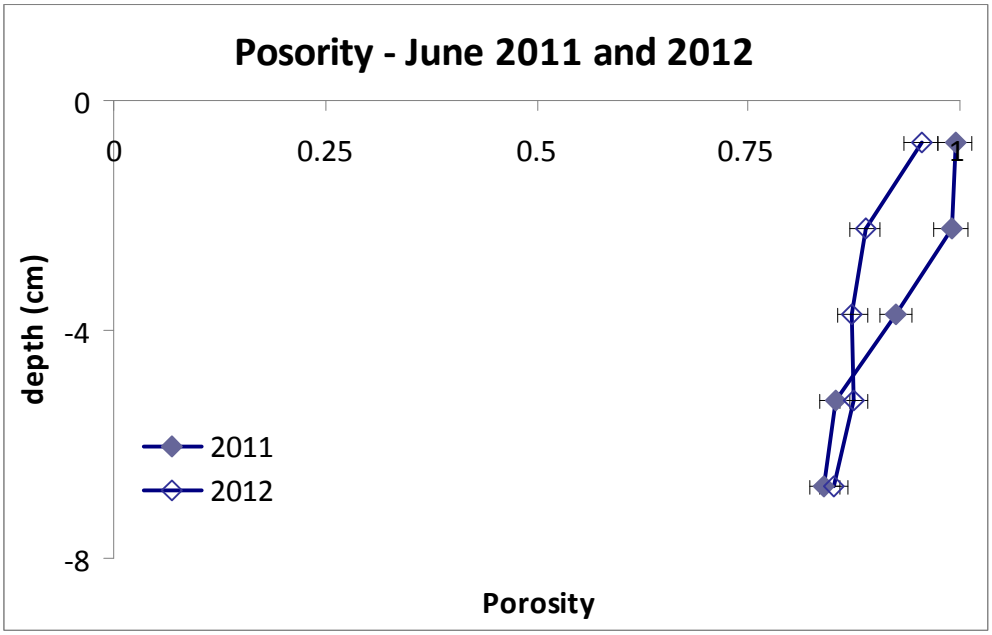


Figure 5-1: Porosities between 0 and 7 centimetres of sediments of the settlement lagoon, March and June, 2011 and 2012. Error 2%, n=4

5.2.3 Pore water DO

Levels of DO in the pore waters were measured in March and June 2011. Levels of DO next to the SWI were at saturation levels in March, but in June they were at 28 and 20 % of saturation, at Sites 1 and 2 respectively. DO was completely

depleted within millimetres under the SWI, both in March and June. See Figures 5.2 and 5.3.

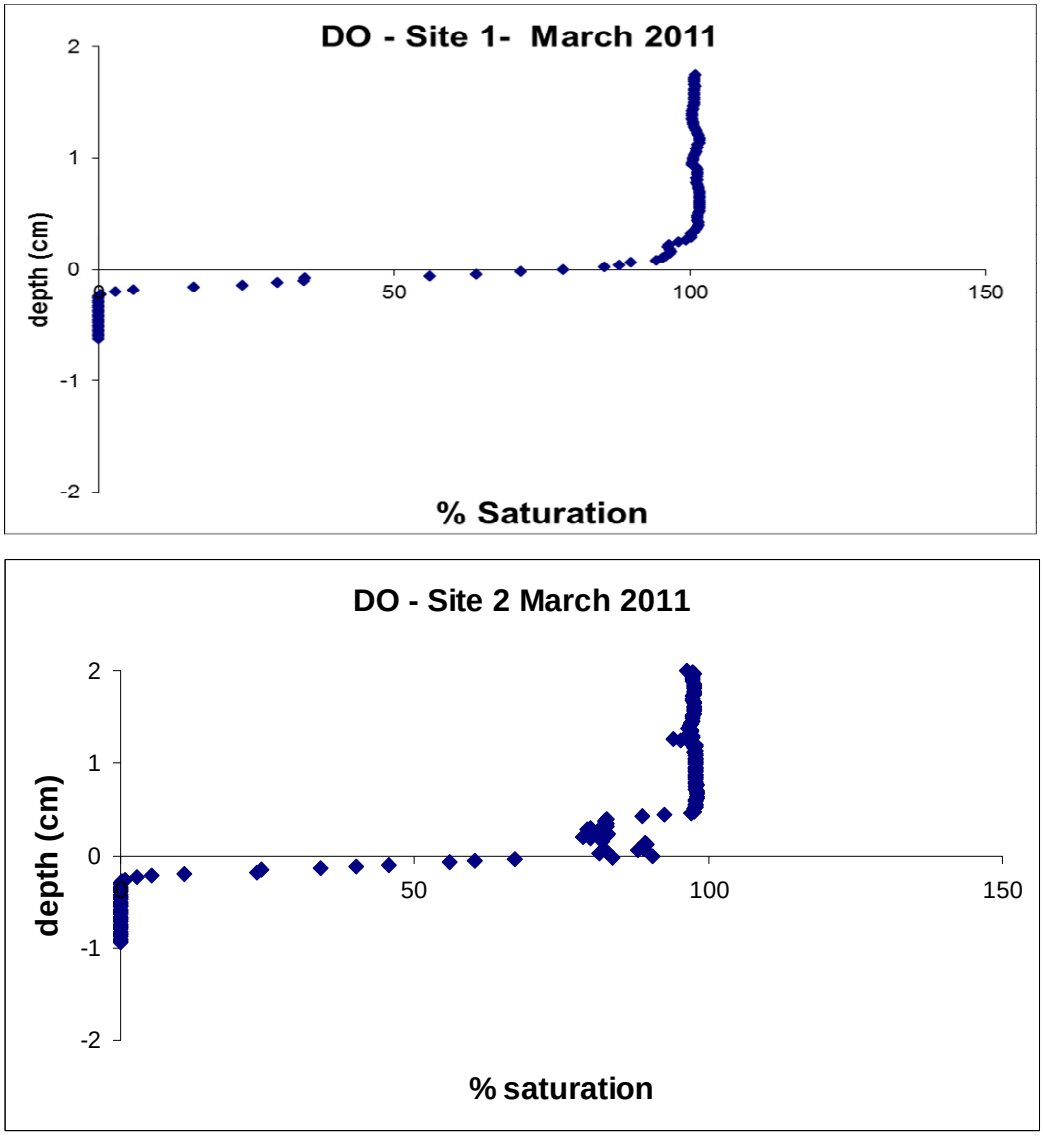


Figure 5-2: DO concentrtions in the bottom waters of the settlement lagoon and the porewaters between the SWI and 1 centimetre below it, March 2011.

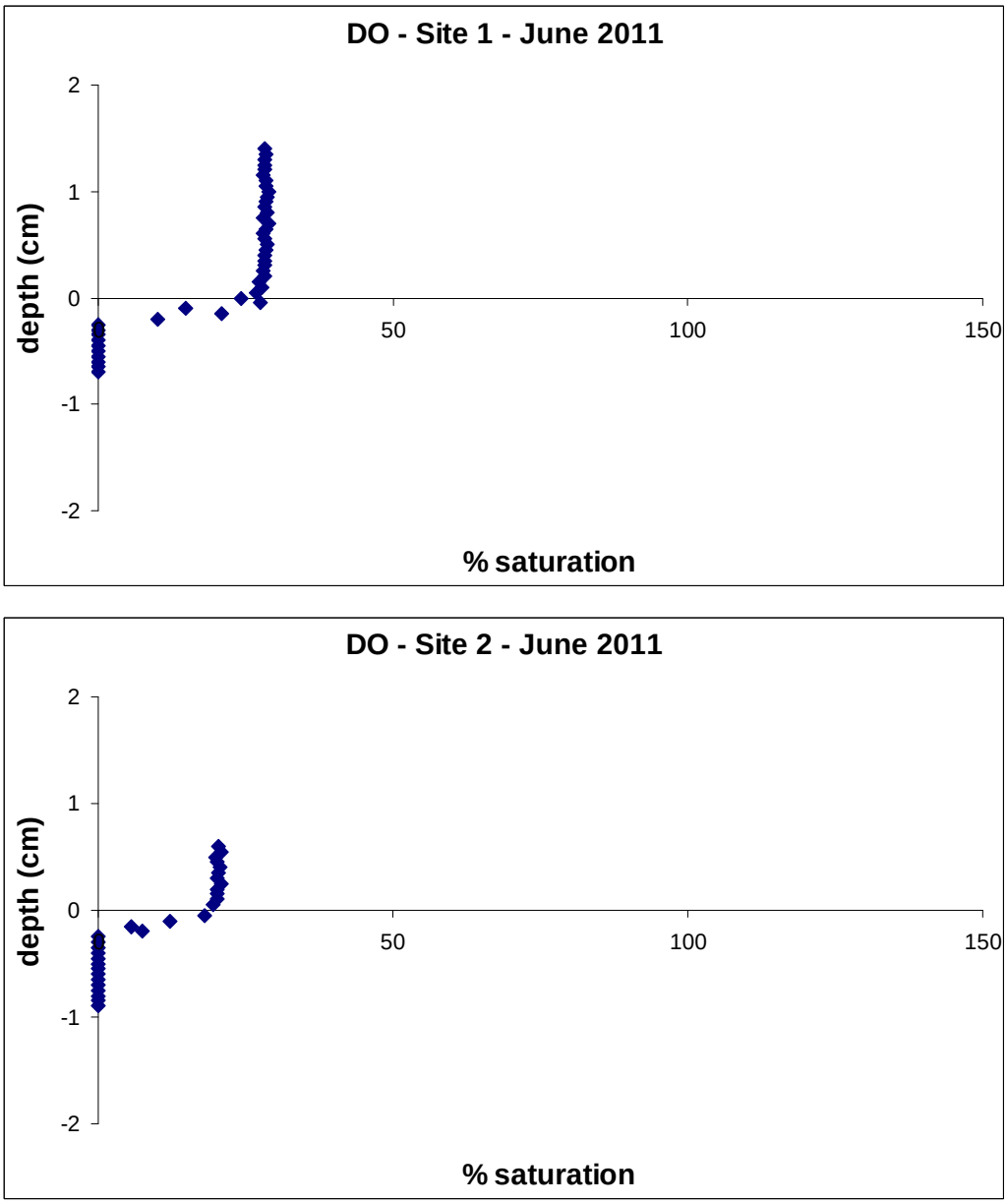


Figure 5-3: DO concentrtions in the bottom waters of the settlement lagoon and the porewaters between the SWI and 1 centimetre below it, June 2011.

5.2.4 Ammonium

Concentrations of pore water ammonium in March 2011 varied between sites 1 and 2. At site 1 concentrations of ammonium peaked at the SWI, at 2µM NH_4^+, they decreased to 1µM NH_4^+, at 1.5 centimetres below the SWI and from there they increased to 2µM NH_4^+ again at 7.5 cm below the SWI. At site 2, concentration of pore water ammonium was 4µM NH_4^+ at the SWI, it decreased

to 3µM NH_4^+, 1 cm below the SWI and then they increased to 5µM NH_4^+, at 7 cm below the SWI (see Figure 5.4).

Levels of ammonium in March 2012 varied between 154 and 205 µM NH_4^+, between the SWI and 7 cm below it. Concentrations decreased slightly downwards first and then they increased again (see Figure 5.5).

In June 2011, concentrations of ammonium peaked near the SWI, at 330 µM NH_4^+ at site 1 and 430 µM NH_4^+ at site 2. Concentrations decreased rapidly downwards, to levels around 200 µM NH_4^+. A smaller peak occurred between 4 and 6 cm below the SWI, with values between 330 and 350 µM NH_4^+, at site 1 and 2 respectively (see Figure 5.6).

In June 2012, levels of ammonium showed a small peak at the SWI and then they increased slightly downwards. At site 1 concentrations varied between 220 and 260 µM NH_4^+, while at site 2, concentrations varied between 340 and 390 µM NH_4^+(see Figure 5.7)

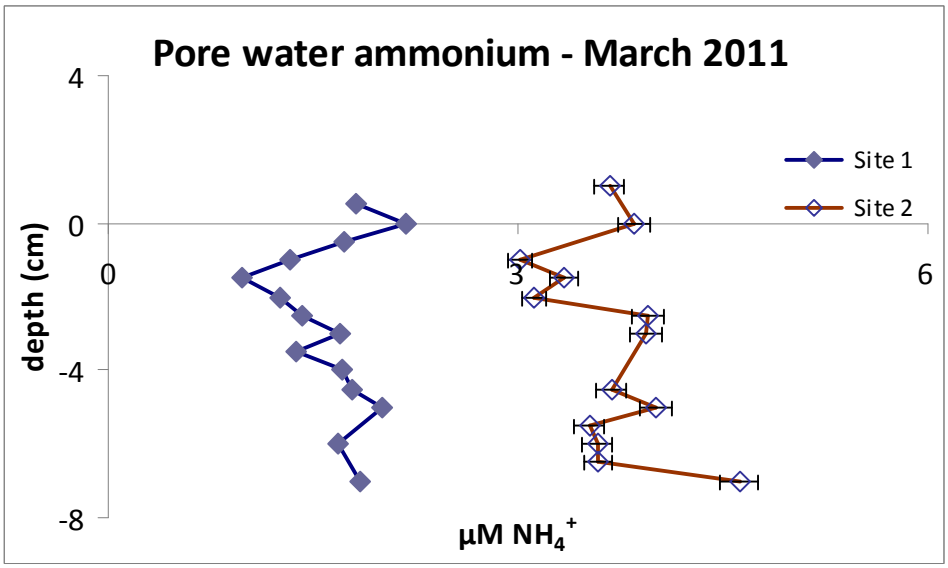


Figure 5-4: Concentrations of ammonium at the bottom of the water column and through the SWI, at sites 1 and 2, for March 2011. Error: 3%, n=6.

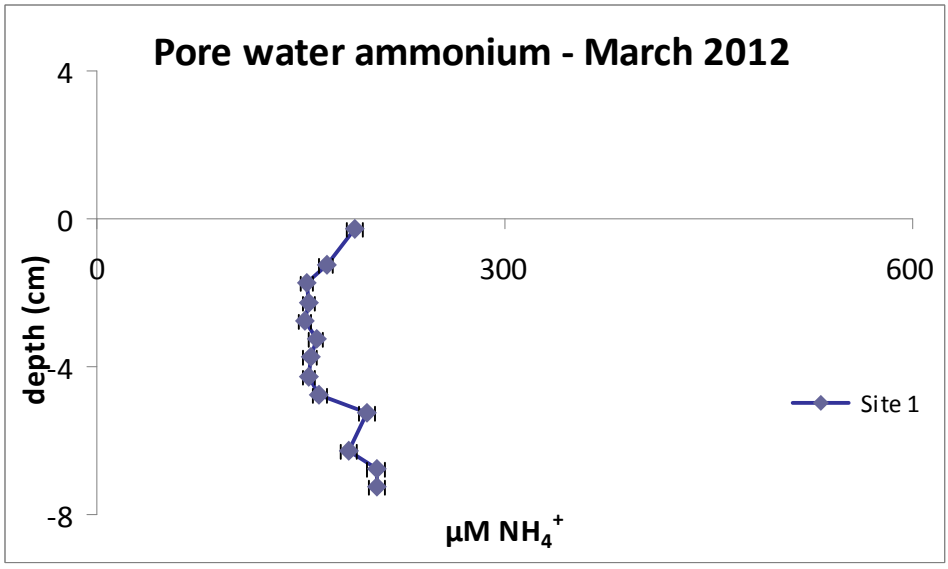


Figure 5-5: Concentrations of ammonium at the bottom of the water column and through the SWI, at site 1 for March 2012. Error: 3%, n=6.

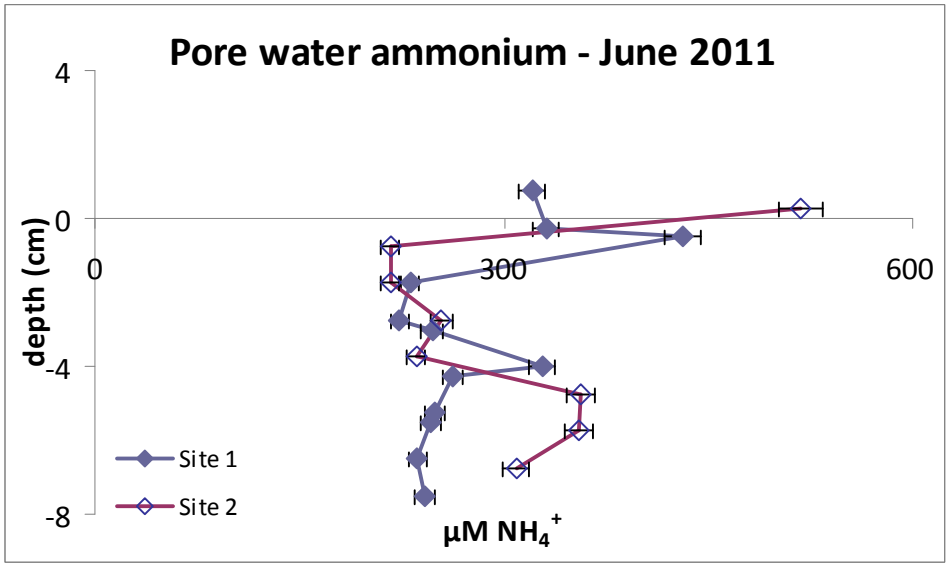


Figure 5-6: Concentrations of ammonium at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2011. Error: 3%, n=6.

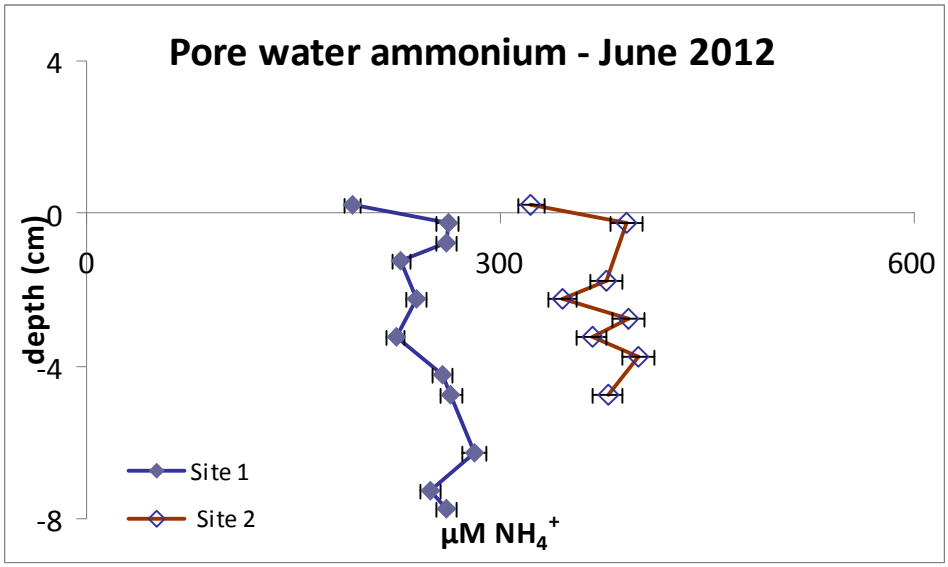


Figure 5-7: Concentrations of ammonium at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2012. Error: 3%, n=6.

5.2.5 Pore water nitrate

In March 2011 concentrations of pore water nitrate were maximum, at 175 µM $NO3^-$ just below the SWI, and nitrate became exhausted at 2 centimetres below the SWI (see Figure 5.8).

In March 2012, pore water nitrate were maximum just below the SWI, with 142 µM $NO3^-$ at site 1 and 144 µM NO3- at site 2. Nitrate was still present at 4 centimetres below the SWI (see Figure 5.9).

In June 2011, nitrate was almost exhausted above the SWI, with concentrations as low as 0.6 µM NO_3^- , and at the SWI, it had been completely consumed (see Figure 5.10).

In June 2012, concentrations of pore water nitrate peaked just below the SWI, at 139 µM NO3- , then they decreased rapidly downwards, but without being completely exhausted at al least 5 centimetres below the SWI (see Figure 5.11).

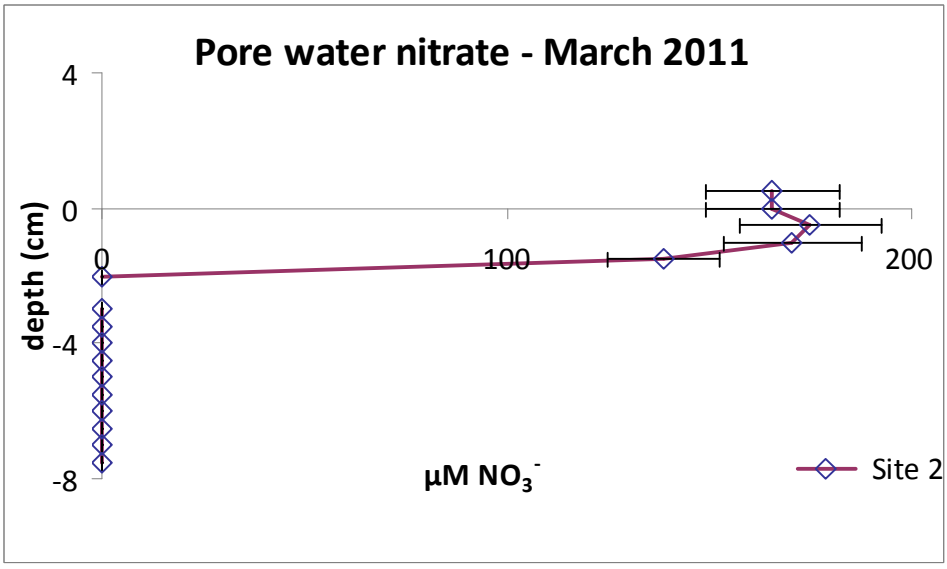


Figure 5-8: Concentrations of nitrate at the bottom of the water column and through the SWI, at site 2 for March 2011. Error: 10%, n=8.

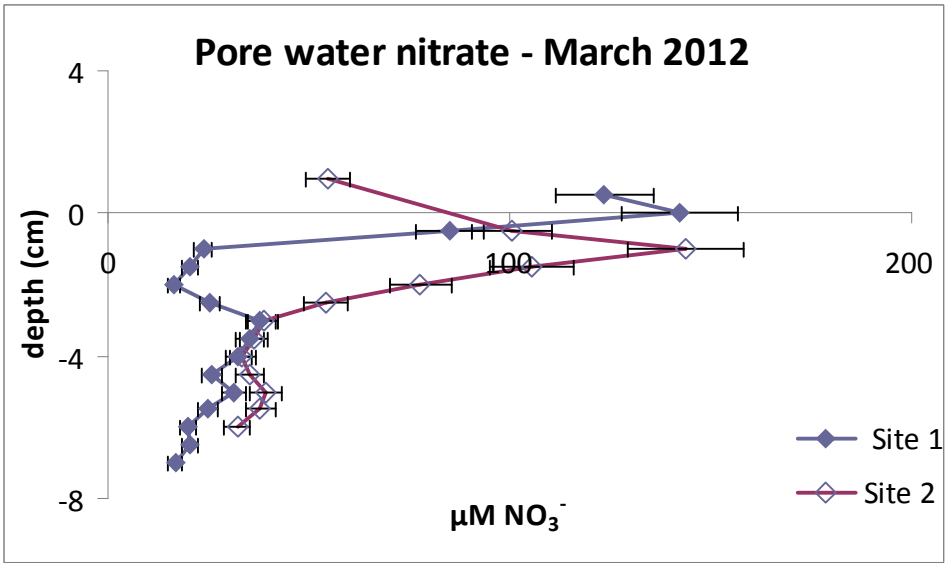


Figure 5-9: Concentrations of nitrate at the bottom of the water column and through the SWI, at sites 1 and 2 for March 2012. Error: 10%, n=8.

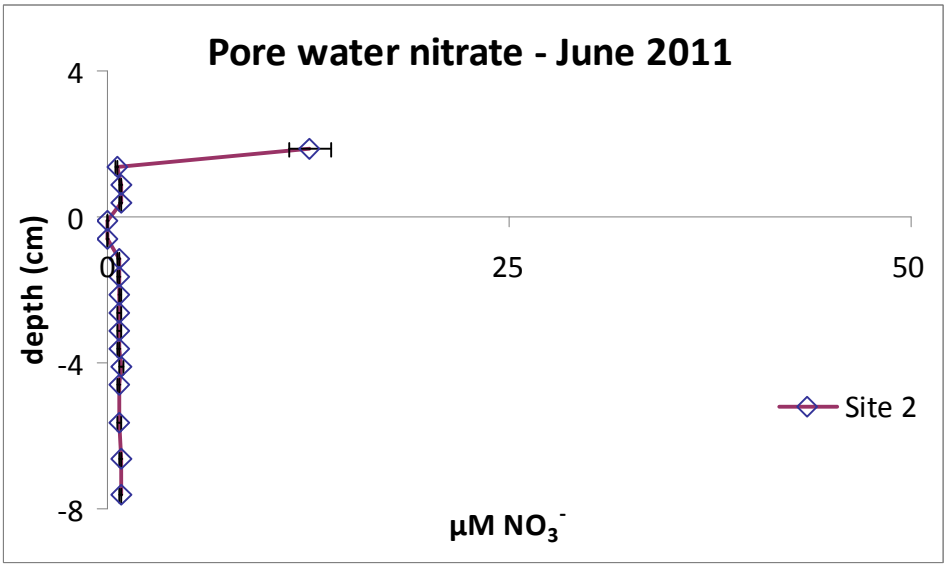


Figure 5-10: Concentrations of nitrate at the bottom of the water column and through the SWI, at site 2 for June 2011. Error: 10%, n=8.

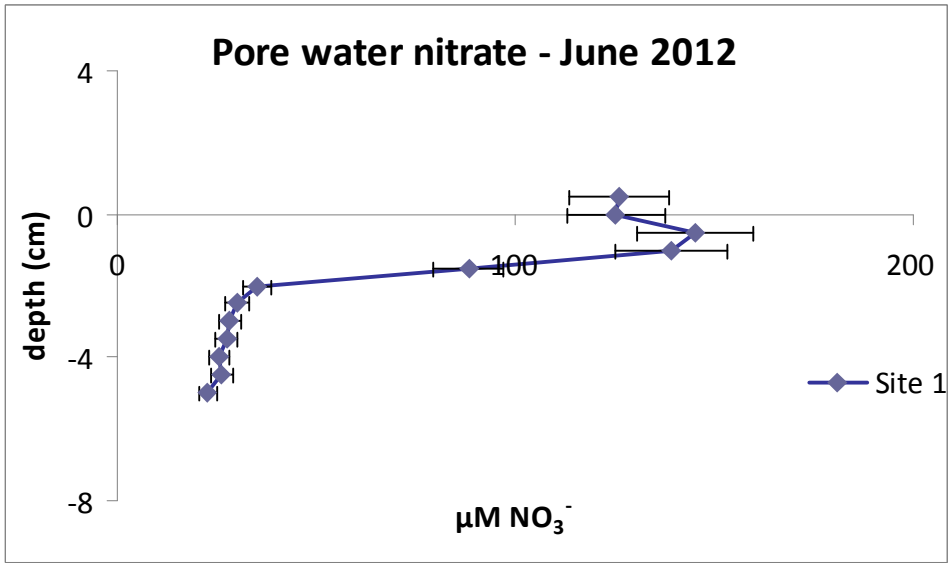


Figure 5-11: Concentrations of nitrate at the bottom of the water column and through the SWI, at site 1 for June 2012. Error: 10%, n=8.

5.2.6 Pore water sulphate

In March 2011, concentrations of pore water sulphate varied between 566 and 630 µM SO_4^{2-}, without a clear tendency of decrease or increase along the profile (see Figure 5.12).

Concentrations of sulphate in March 2012, at site 1, peaked at the SWI at 753 µM SO_4^{2-}, and then they decreased rapidly to levels between 624 and 687 µM SO_4^{2-}. At site 2, concentrations of sulphate remained between 805 and 837 µM SO_4^{2-} down to 2 centimetres below the SWI. At that depth, sulphate decreased to 721 µM SO_4^{2-}, and then it increased again downwards (see Figure 5.13).

In June 2011, at site 1, pore water sulphate decreased downward from 597 to 250 µM SO_4^{2-} in the top 1.5 centimetres of sediments and then it decreased further but at a slower rate. At site 2, sulphate decreased downwards from 677 to 226 µM SO_4^{2-} in the top 3.5 centimetres of sediments, and it kept decreasing downwards also at a slower rate. By June 2012, levels of pore water sulphate peaked at the SWI, at 525 µM SO_4^{2-}, and it decreased downwards to 382 µM SO_4^{2-}, 3 centimetres below the SWI. From there downwards, sulphate increased rapidly, reaching 710 µM SO_4^{2-} 9.5 centimetres below the SWI (see Figures 5.14 and 5.15).

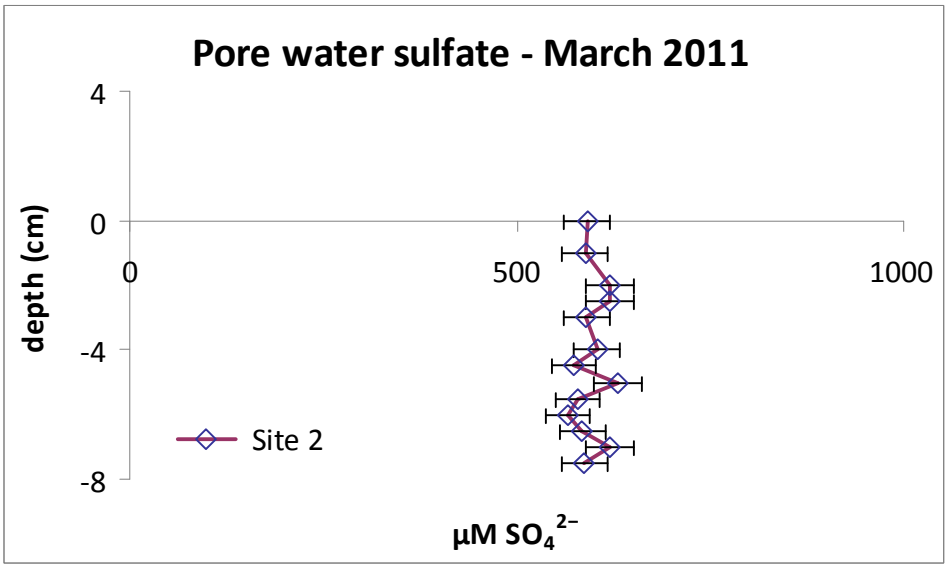


Figure 5-12: Concentrations of sulphate at the bottom of the water column and through the SWI, at site 2 for March 2011. Error: 5%, n=5.

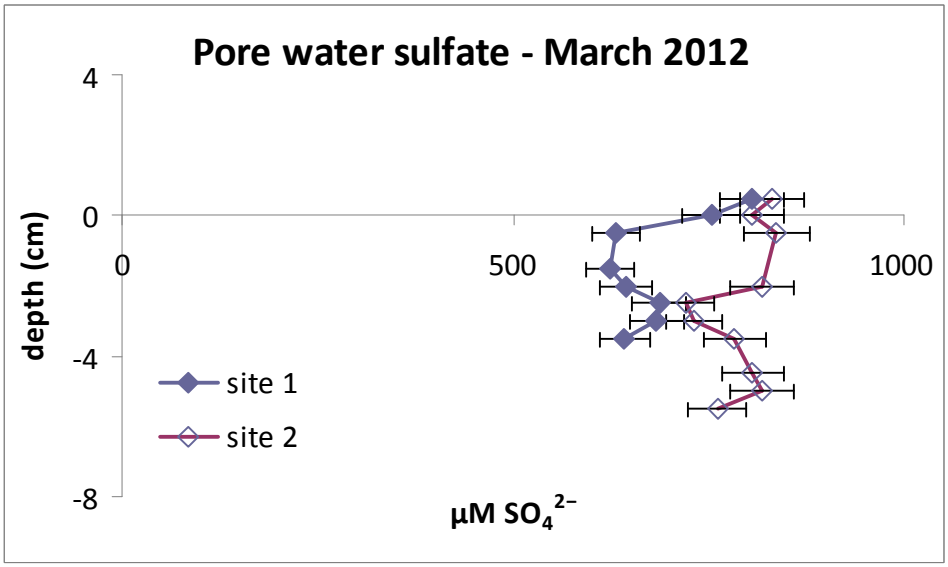


Figure 5-13: Concentrations of sulphate at the bottom of the water column and through the SWI, at sites 1 and 2 for March 2012. Error: 5%, n=5.

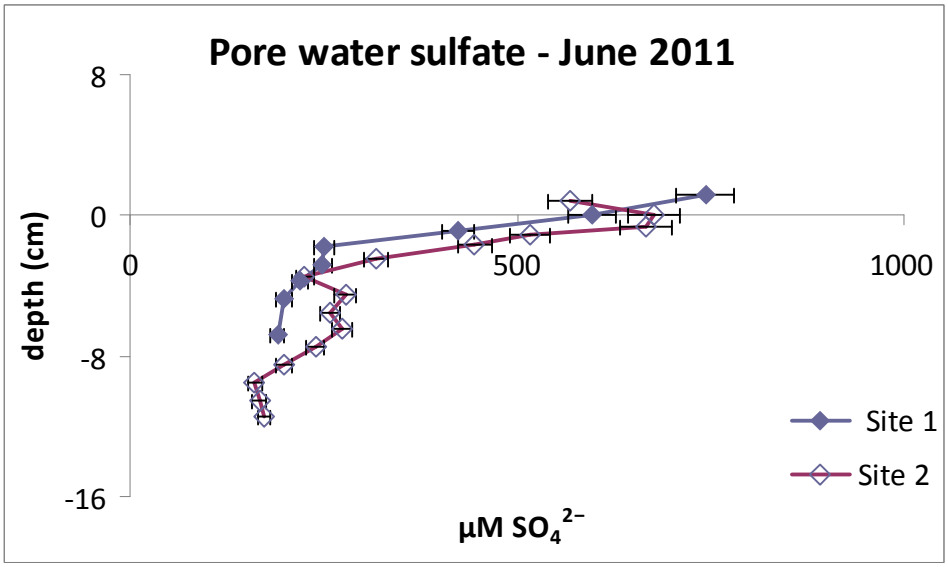


Figure 5-14: Concentrations of sulphate at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2011. Error: 5%, n=5.

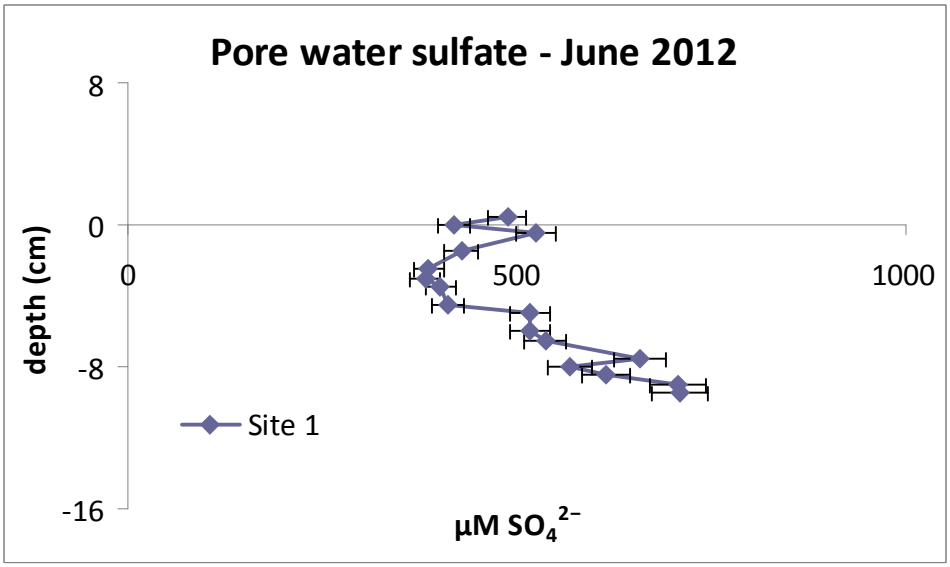


Figure 5-15: Concentrations of sulphate at the bottom of the water column and through the SWI, at site 1 for June 2012. Error: 5%, n=5.

5.2.7 Pore water iron

Concentrations of total dissolved iron in the pore waters, in March 2011 decreased downwards at the SWI, and levels varied between 30 and 131 µM Fe at site 1 and 80 and 144 at site 2 (see Figure 5.16).

In March 2012, total dissolved Fe in pore waters decreased downwards, rapidly, at the SWI. At site 1, Fe was exhausted between 2.5 and 4.5 centimetres below the SWI, and from there it increased rapidly downwards. At site 2, levels of total dissolved iron peaked 2.5 centimetres below the SWI, at 2 µM Fe, it became exhausted 4.5 centimetres below the SWI, and then it kept increasing downwards (see Figure 5.17).

Levels of total dissolved Fe in pore waters varied between sites 1 and 2, in June 2011. At site 2, it decreased slowly downwards, ranging from 26 to 245 in the top 5.5 centimetres of sediments. At site 1, total dissolved P reached 860 µM Fe at the SWI, and decreased rapidly to 600 µM Fe in 0.5 centimetres. From there downwards, Fe increased to 2200 µM Fe at 5.5 centimetres below the SWI (see Figure 5.18).

Concentrations of total dissolved iron in pore waters, in June 2012 varied between sites 1 and 2. Dissolved Fe in site 1 increased rapidly from 29 µM Fe at the SWI to 750 µM Fe 2.5 centimetres below the SWI. Then it decreased rapidly to 250 µM Fe at 7.5 centimetres below the SWI. Levels of dissolved Fe increased slowly downward at site 2, from 70 µM Fe at the SWI, to 290 µM Fe, 6 centimetres below the SWI (see Figure 5.19).

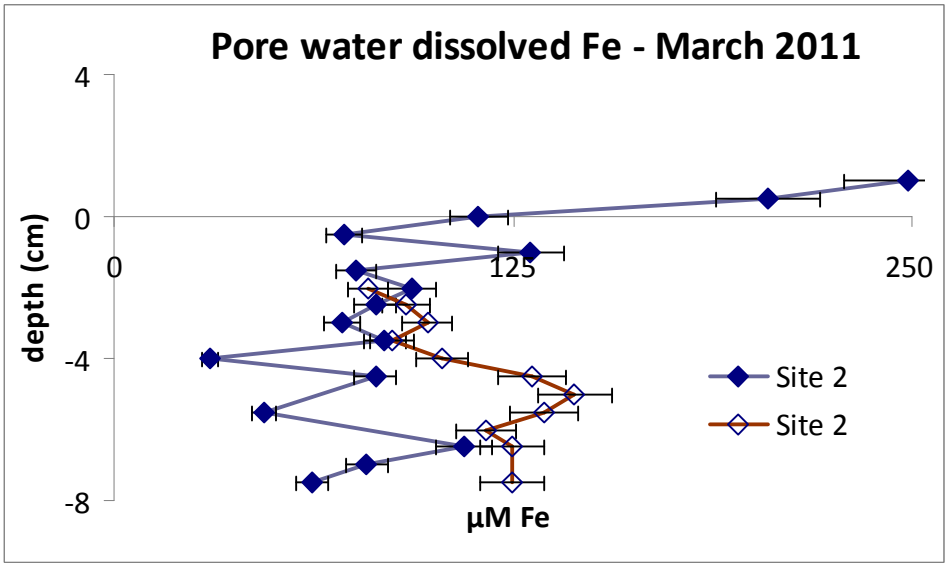


Figure 5-16: Concentrations of iron at the bottom of the water column and through the SWI, at sites 1 and 2 for March 2011. Error: 8%, n=6.

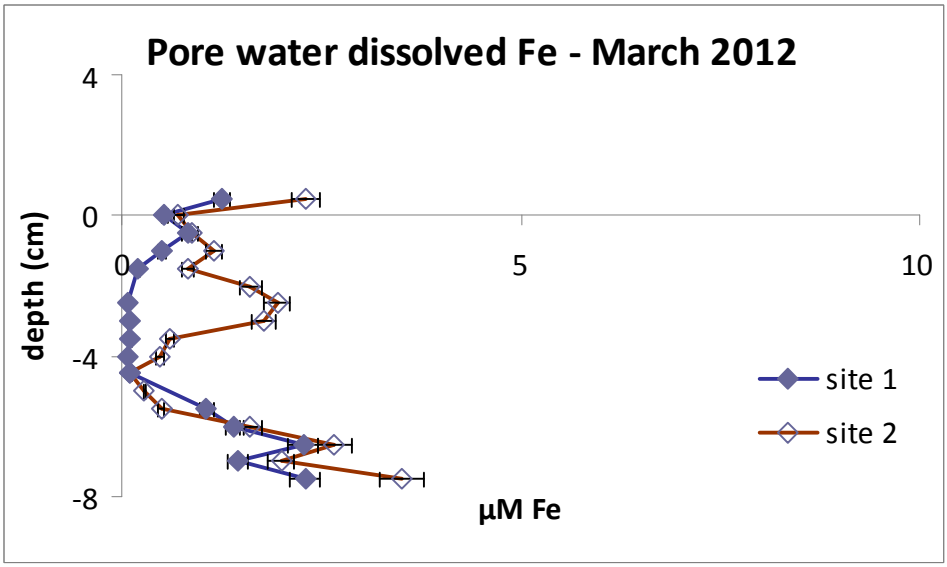


Figure 5-17: Concentrations of iron at the bottom of the water column and through the SWI, at sites 1 and 2 for March 2012. Error: 8%, n=6.

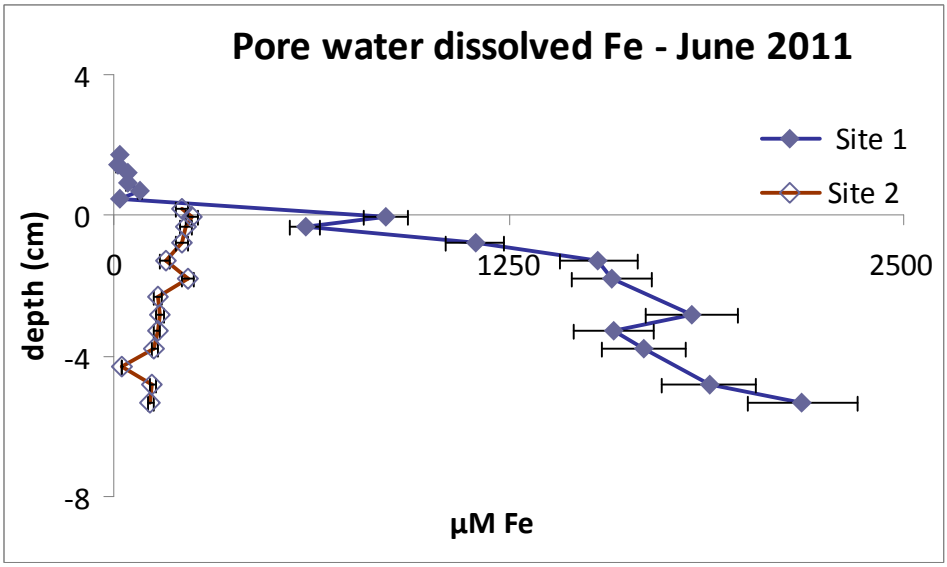


Figure 5-18: Concentrations of iron at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2011. Error: 8%, n=6.

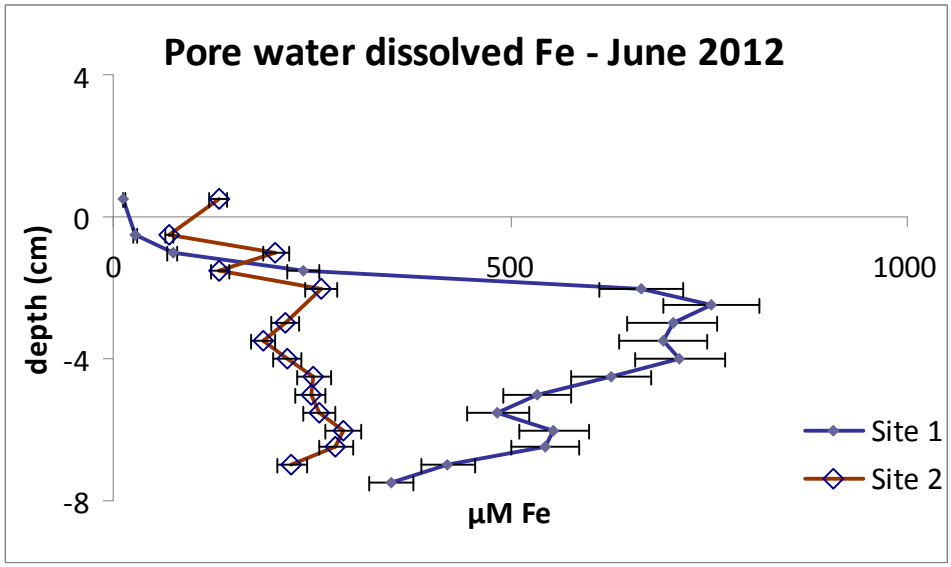


Figure 5-19: Concentrations of iron at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2012. Error: 8%, n=6.

5.2.8 Pore water calcium

Pore water cacium in March 2011 varied between 2400 and 2900 µM Ca^{2+}. It peaked 5.5 centimetres below the SWI and from there it decreased slightly upwards and rapidly downwards (see Figure 5.20).

Pore water calcium in March 2012 varied between 2100 and 2600 µM Ca^{2+} at site 1 and between 1900 and 2300 µM Ca^{2+} at site 2. Both profiles decreased from the SWI downwards to 2 centimetres below the SWI and from there the concentrations of Ca^{2+} peaked at 4 centimetres below the SWI (see Figure 5.21).

Concentrations of Ca^{2+} in pore waters in June 2011 varied between 1900 and 3100 µM Ca^{2+} at site 1 and between 1200 and 2100 µM Ca^{2+} at site 2. Ca^{2+} peaked within the top 2 centimetres of pore waters and then it decreased downwards (see Figure 5.22).

Pore water Ca^{2+} in June 2012 varied between 1900 and 2300 µM Ca^{2+} at site 1 at site 1 and between 2200 and 2900 at site 2. The concentrations of Ca^{2+} decreased downwards slightly at the SWI. Concentrations of Ca^{2+} at site 2 stayed without

significant changes along the profile, while those concentrations at site 2 increased downwards (see Figure 5.23).

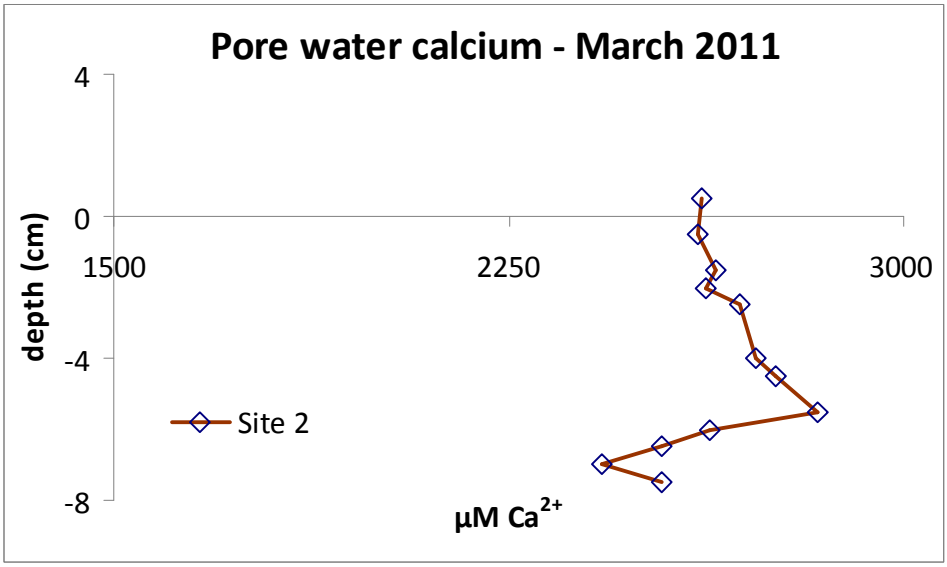


Figure 5-20: Concentrations of calcium at the bottom of the water column and through the SWI, at site 2 for March 2011. Error: 0%, n=6.

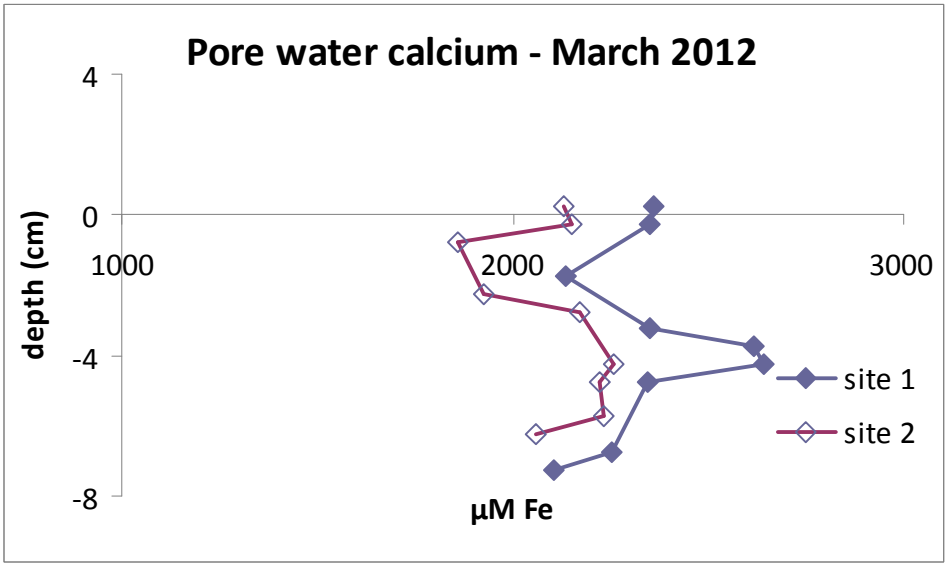


Figure 5-21: Concentrations of calcium at the bottom of the water column and through the SWI, at sites 1 and 2 for March 2012. Error: 0%, n=6.

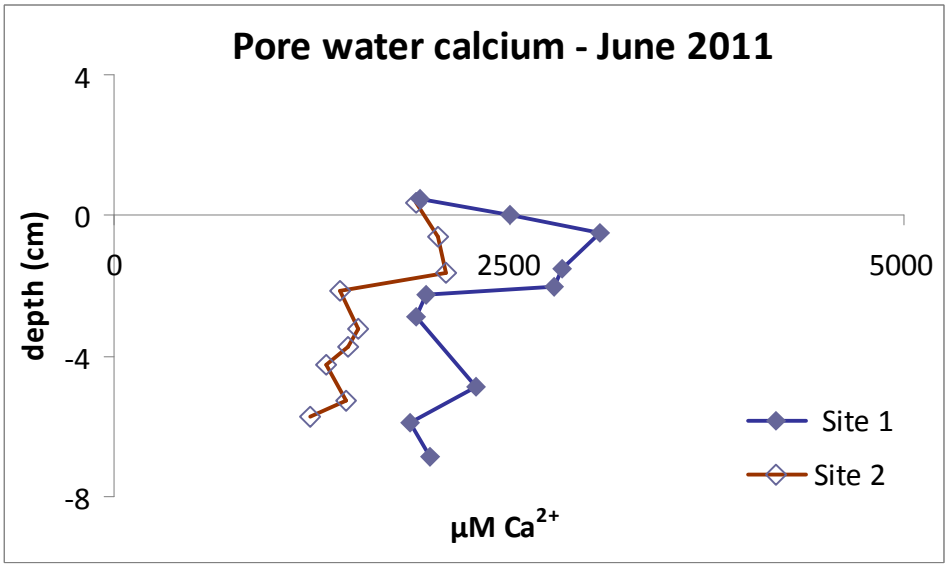


Figure 5-22: Concentrations of calcium at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2011. Error: 0%, n=6.

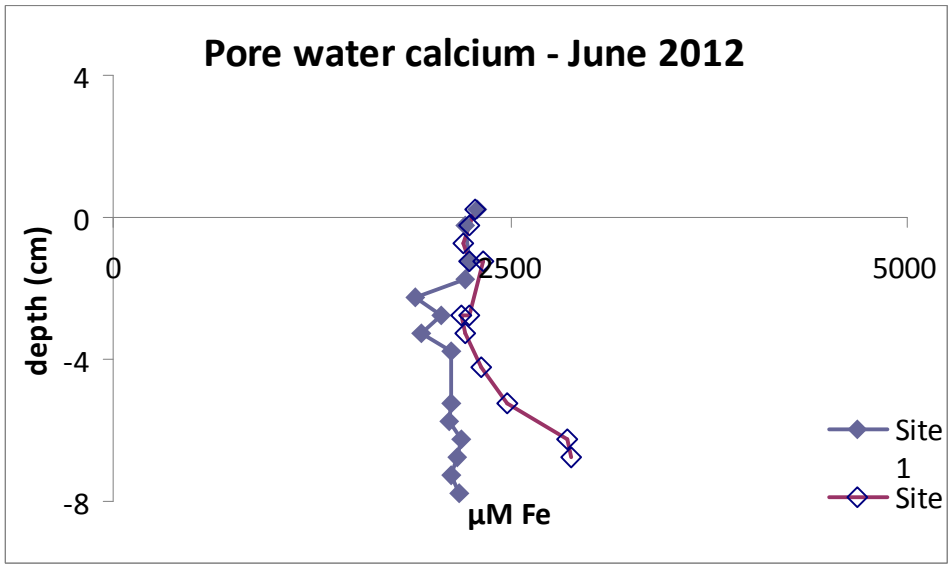


Figure 5-23: Concentrations of calcium at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2012. Error: 0%, n=6.

5.2.9 Pore water SRP

Pore water SRP in March 2011 ranged from 5 to 40 µM P at site 1, and from 11 to 22 µM P at site 2. Concentrations were highest at the SWI and decreased rapidly downwards (see Figure 5.24).

Pore water SRP in March 2012 varied between 13 and 62 µM P at site 1 and between 11 and 62 at site 2. Concentrations of SRP increased downwards at the SWI and they peaked between 2 and 3 centimetres under the SWI, below which they decreased again (see Figure 5.25).

Pore water SRP in June 2011varied between 330 and 360 µM P at site 1, and between 200 and 390 µM P at site 2. Pore water SRP peaked near the SWI and it decreased downwards (see Figure 5.26).

Pore water SRP in June 2012 varied between 35 and 170 µM P at site one, and between 110 and 240 µM P at site 2. Concentrations of SRP were highest at the SWI and decreased downwards (see Figure 5.27).

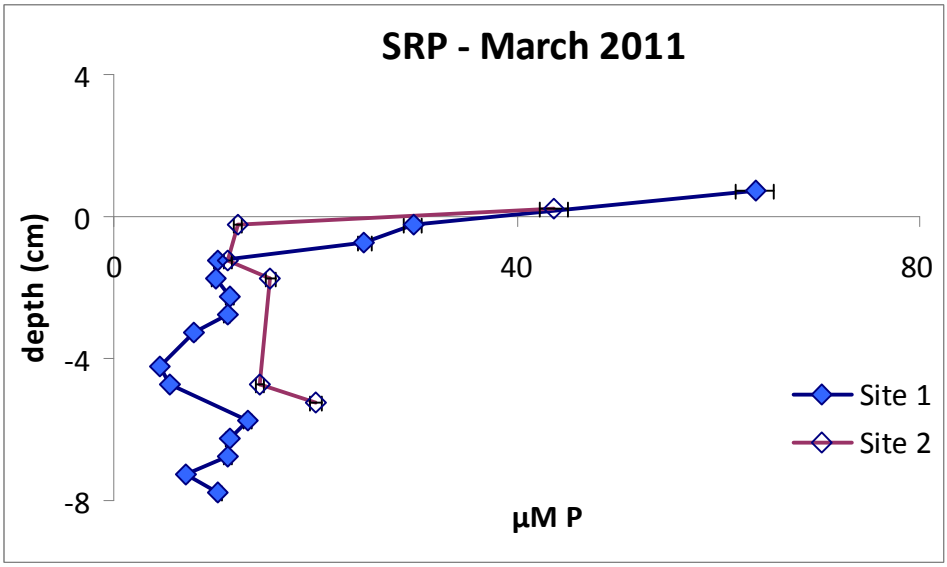


Figure 5-24: Concentrations of SRP at the bottom of the water column and through the SWI, at sites 1 and 2 for March 2011. Error: 3%, n=6.

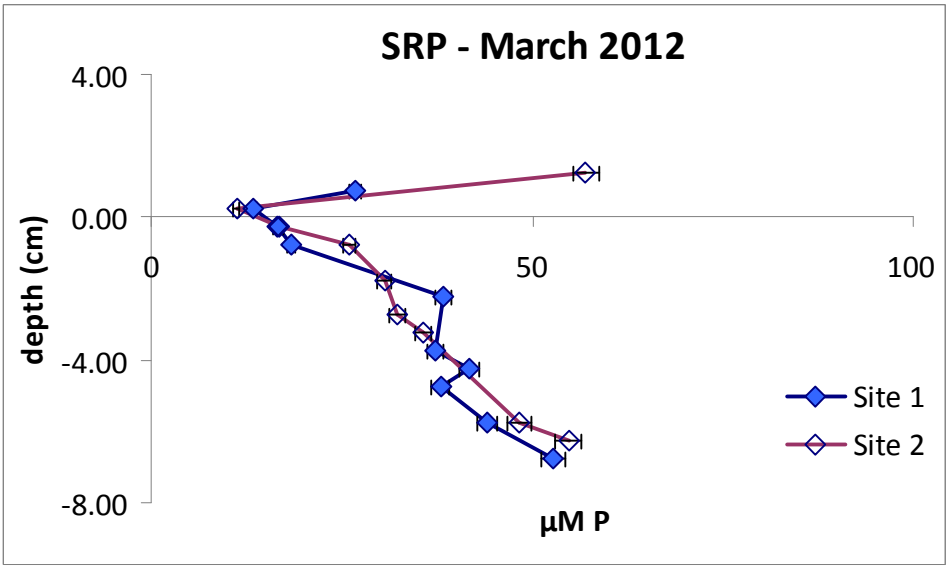


Figure 5-25: Concentrations of SRP at the bottom of the water column and through the SWI, at sites 1 and 2 for March 2012. Error: 3%, n=6.

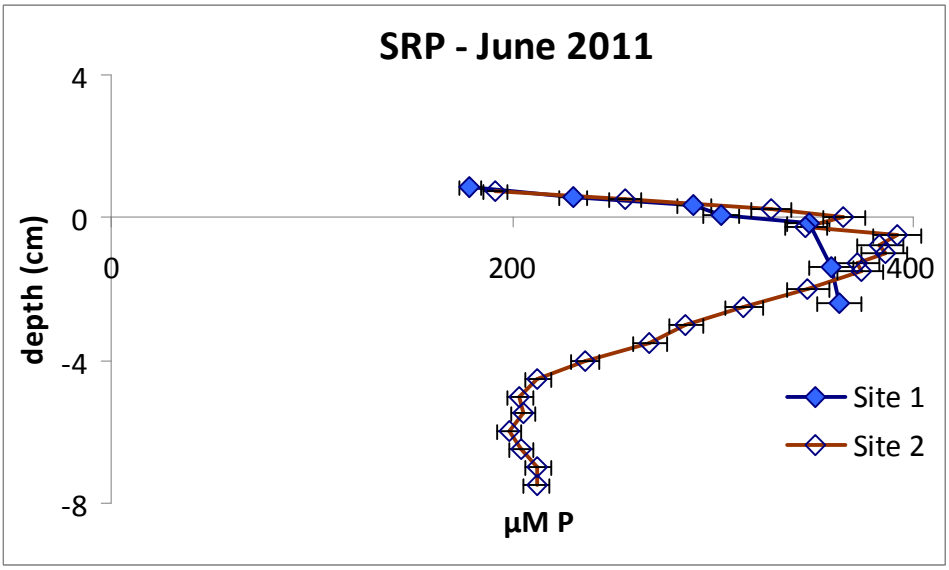


Figure 5-26: Concentrations of SRP at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2011. Error: 3%, n=6.

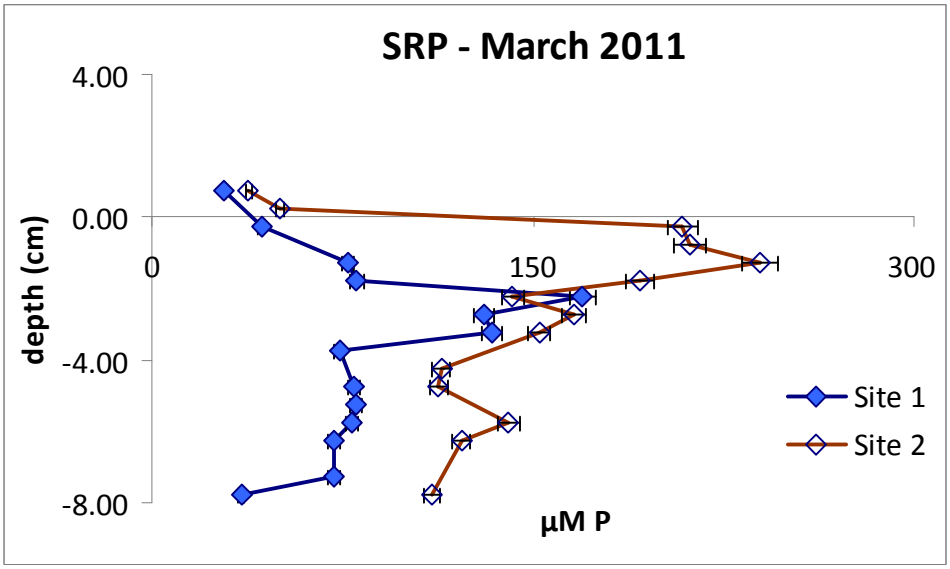


Figure 5-27: Concentrations of SRP at the bottom of the water column and through the SWI, at sites 1 and 2 for June 2012. Error: 3%, n=6.

5.2.10 P speciation (SEDEX)

5.2.10.1 Readily available P

Concentrations of readily available P in sediments in March 2011 varied between 0.7 and 2.9 µmole P / gram dry sediment, at site 1, and from 0.7 and 2.4 µmole P / gram dry sediment at site 2. Concentrations peaked at 2 centimetres below the SWI and they decreased downwards from there (see Figure 5.28).

In March 2012, concentrations of readily available P in the sediments varied between 1 and 3.6 µmole P / gram dry sediment at site 1 and between 0.6 and 5.5 µmole P / gram dry sediment at site 2. Concentrations were maximum at the SWI and decreased downwards, at the same rate for both sites (see Figure 5.29).

In June 2011, levels of readily available P in sediments were between 0.4 and 2.9 µmole P / gram dry sediment at both sites 1 and 2. They peaked at the SWI and decreased downwards, doing this at a slightly faster rate at site 1 than at site 2 (see Figure 5.30).

In June 2012, concentrations of readily available P peaked at the SWI, but with different values at the different sites. At site 1, readily available P reached 3.5 µmole P / gram dry sediment at the SWI, while at site 2 it only reached to 1.4 µmole P / gram dry sediment. The concentrations of readily available P decreased downwards to a baseline level of 0.4 µmole P / gram dry sediment, 6 centimetres below the SWI (see Figure 5.31).

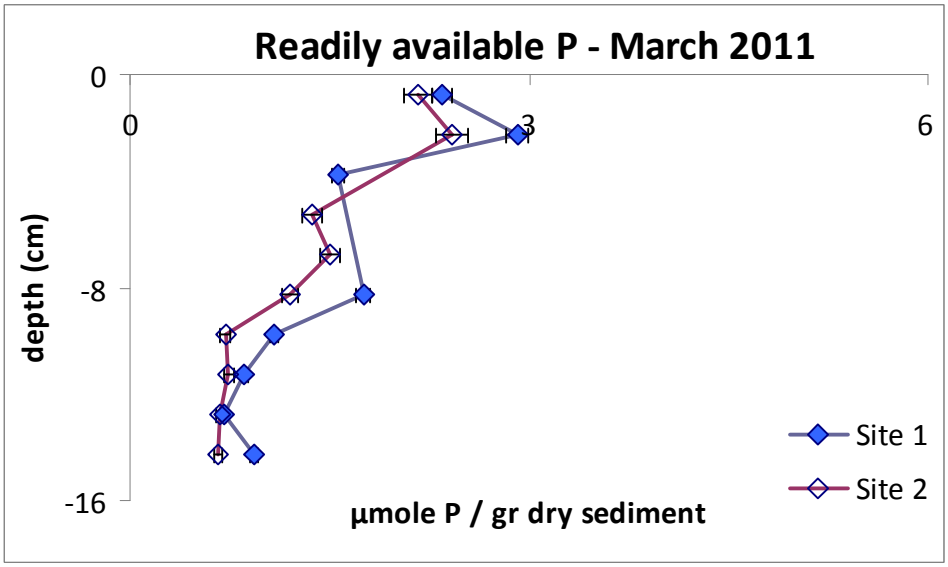


Figure 5-28: Concentrations of readily available P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2011. Error: 3%, n=6.

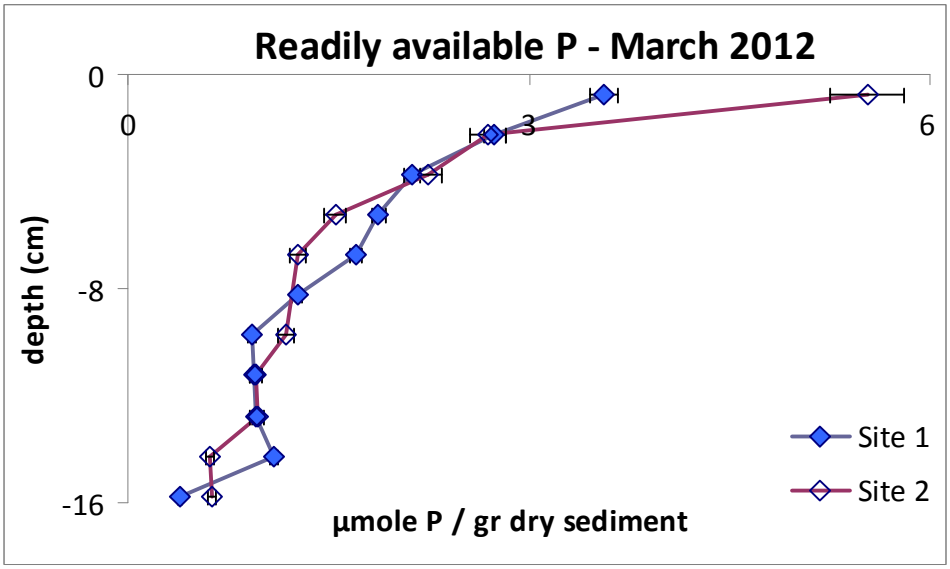


Figure 5-29: Concentrations of readily available P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2012. Error: 3%, n=6.

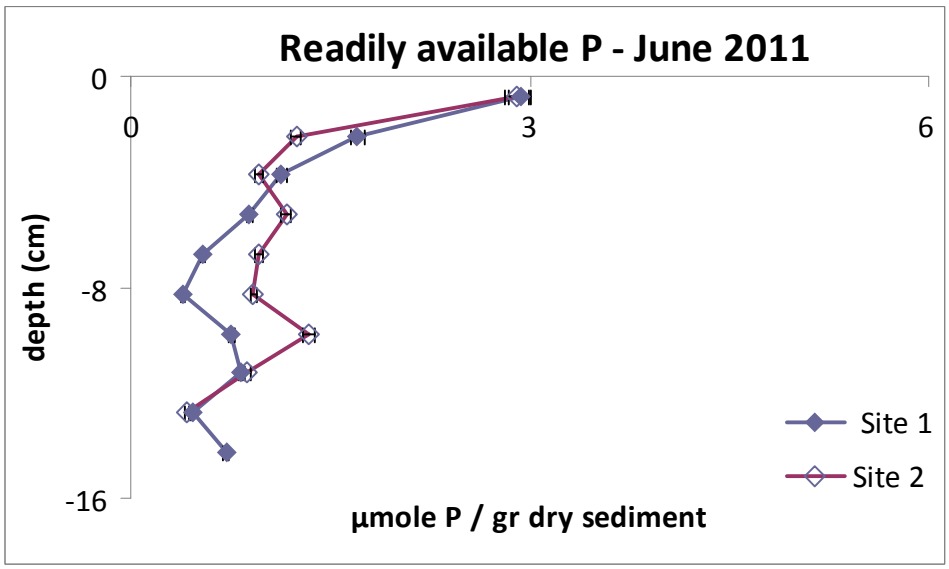


Figure 5-30: Concentrations of readily available P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2011. Error: 3%, n=6.

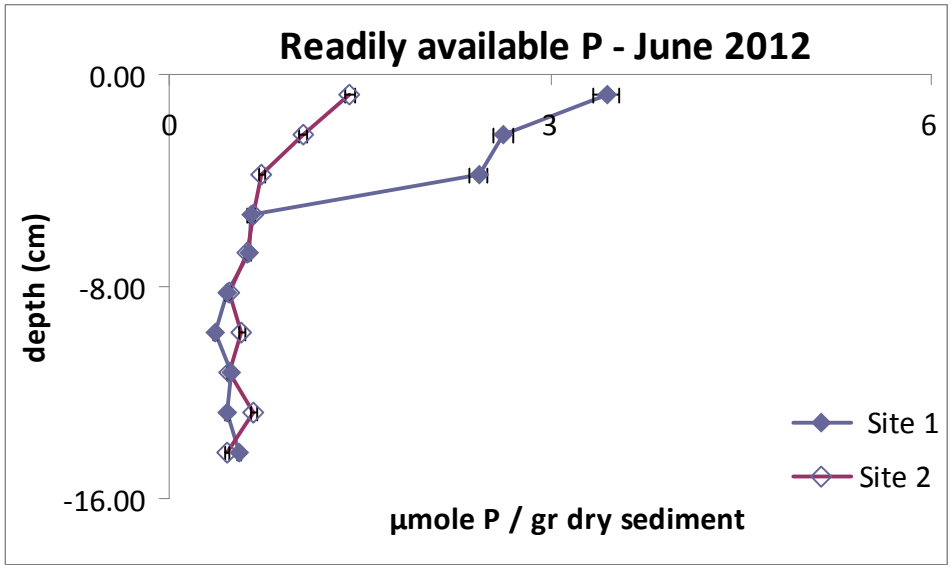


Figure 5-31: Concentrations of readily available P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2012. Error: 3%, n=6.

5.2.10.2 Iron bound P

Concentrations of iron boun P in sediments, in March 2011, were between 9 and 26 µmole P / gram dry sediment at site 1 and between 7 and 25 for site 2. Concentrations peaked 5 below the SWI at site 1 and 5 centimetres below the SWI at site 2 (see Figure 5.32).

In March 2012, concentrations of iron P in sediments varied between 6 and 29 µmole P / gram dry sediment at site 1 and between 5 and 28 µmole P / gram dry sediment at site 2. Levels of iron P were highest between 4 and 5 centimetres below the SWI (see Figure 5.33).

Levels of iron bound P in sediments, in June 2011, varied between 8 and 30 µmole P / gram dry sediment at site 1, and between 9 and 24 µmole P / gram dry sediment at site 2. Concentrations were highest in the top 2 centimetres of sediments. Levels of iron bound P decreased faster with depth at site 1 than at site 2 (see Figure 5.34).

In June 2012, levels of iron bound P varied between 13 and 25 µmole P / gram dry sediment at site 1, and between 6 and 28 µmole P / gram dry sediment at site 2. In general, concentrations decreased downwards, although they showed some variability at site 1 (see Figure 5.35).

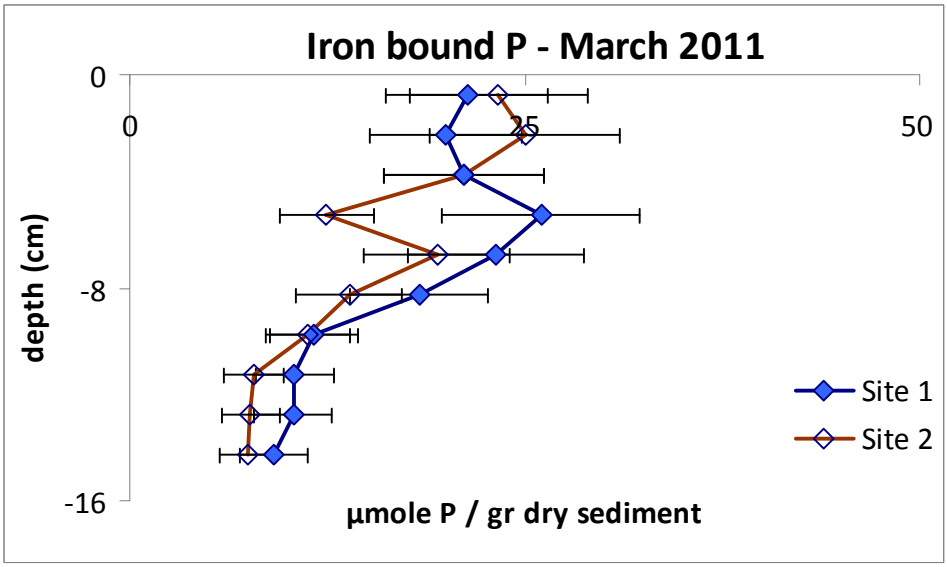


Figure 5-32: Concentrations of iron bound P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2011. Error: 24%, n=6.

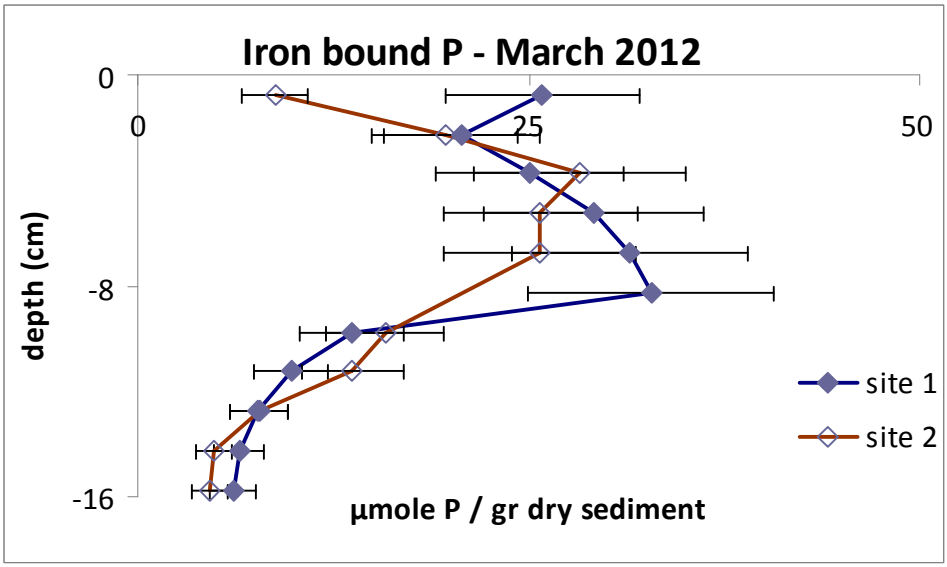


Figure 5-33: Concentrations of iron bound P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2012. Error: 24%, n=6.

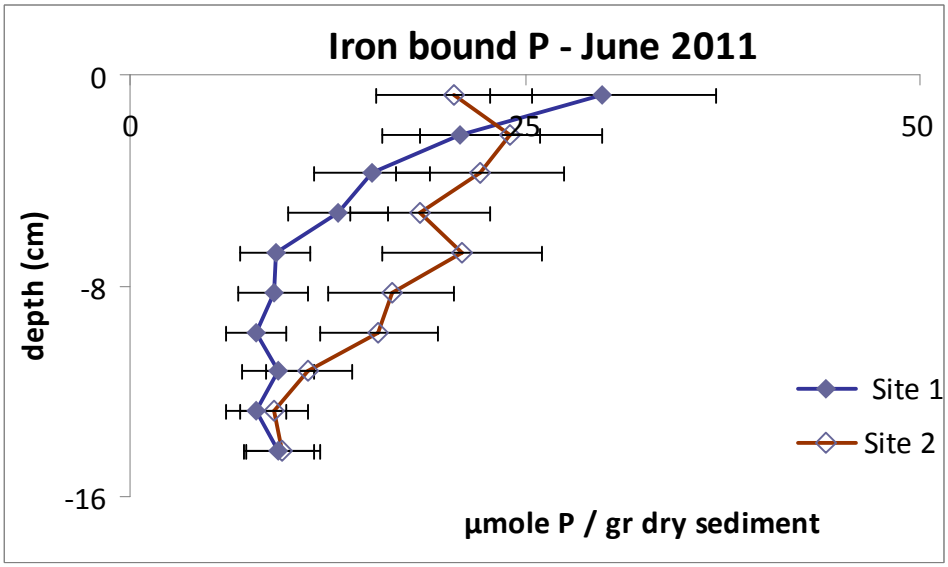


Figure 5-34: Concentrations of iron bound P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2011. Error: 24%, n=6.

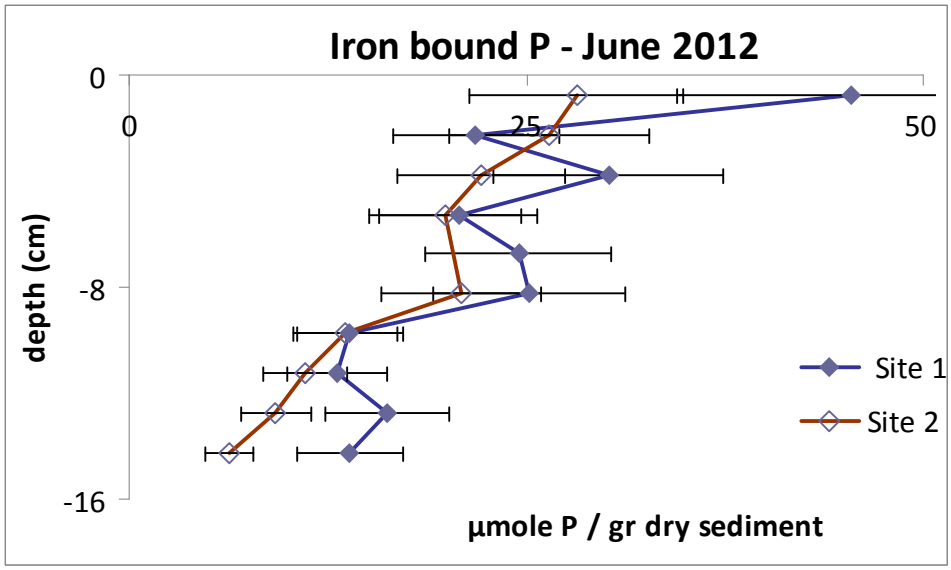


Figure 5-35: Concentrations of iron bound P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2012. Error: 24%, n=6.

5.2.10.3 Apatite P

Concentrations of apatite P in the sediments, in March 2011 showed similar values for sites 1 and 2. In the top 7 centimetres of sediments, levels of apatite P stayed between 10 and 11 µmole P / gram dry sediment. At that depth,

concentrations at both sites shifted to values between 16 and 19 μmole P / gram dry sediment (see Figure 5.36).

Concentrations of apatite P in the sediments, in March 2012, varied between 12 and 18 μmole P / gram dry sediment at site 1, and between 11 and 18 μmole P / gram dry sediment at site 2. Values increased downwards from the SWI and peaked at 5-6 centimetres below it. From that depth down, concentrations decreased (see Figure 5.37).

In general, concentrations of apatite in the sediments, in June 2011, decreased downwards, although with an elevated degree of variability. Concentrations at site 1 varied between 14 and 20 μmole P / gram dry sediment, and at site 2, between 13 and 21 μmole P / gram dry sediment (see Figure 5.38).

In June 2012, concentrations of apatite P in sediments decreased downwards from the SWI to 10-11 centimetres below it, where they started to increase again. At site 1, concentrations varied between 20 and 32 μmole P / gram dry sediment, while at site 2 they varied between 17 and 34 μmole P / gram dry sediment (see Figure 5.39).

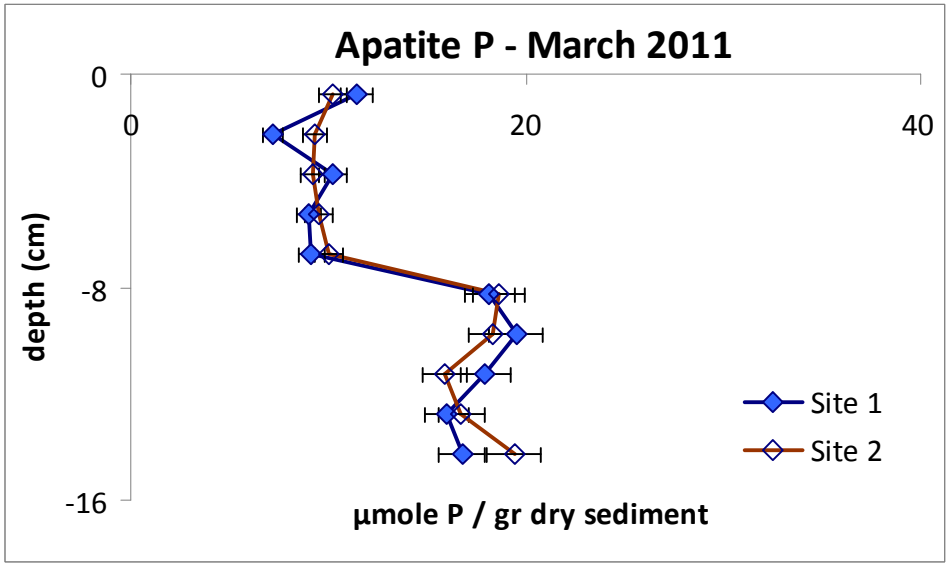


Figure 5-36: Concentrations of apatite P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2011. Error: 7%, n=6.

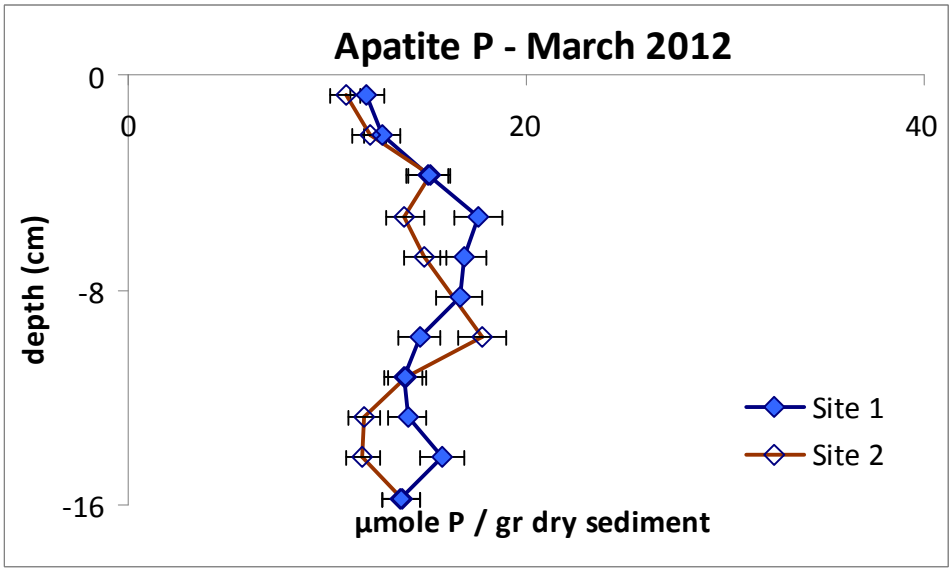


Figure 5-37: Concentrations of apatite P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2012. Error: 7%, n=6.

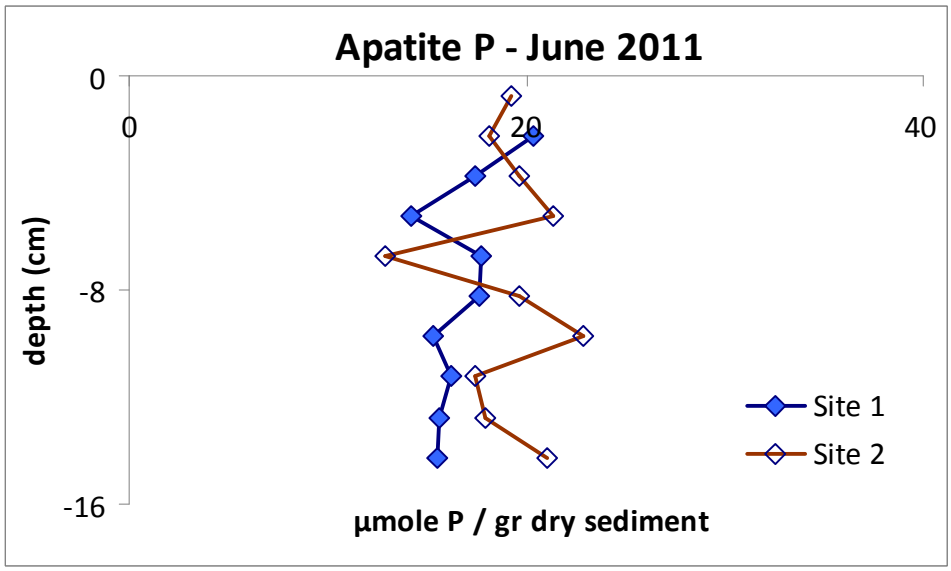


Figure 5-38: Concentrations of apatite P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2011. Error: 7%, n=6.

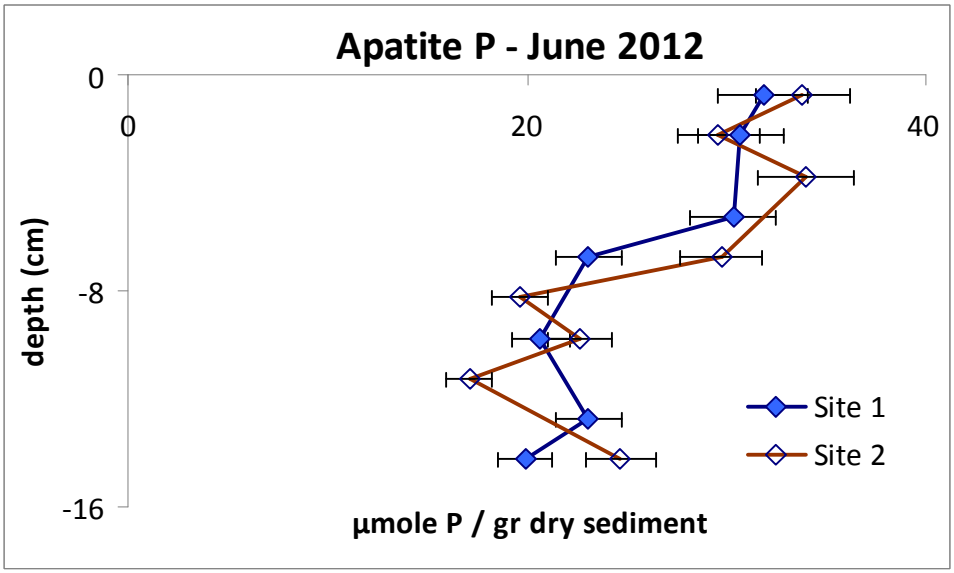


Figure 5-39: Concentrations of apatite P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2012. Error: 7%, n=6.

5.2.10.4 Other inorganic P

Levels of other inorganic P in sediments in March 2011 varied between 4 and 8 µmole P / gram dry sediment at site 1 and between 3 and 8 at site 2. Concentrations increased downwards from the SWI to 5-6 centimetres below, and then they decreased downwards (see Figure 5.40).

Levels of other inorganic P in March 2012 varied between 4 and 8 µmole P / gram dry sediment at site 1 and between 1 and 7 at site 2. Concentrations peaked 11 centimetres below the SWI (see Figure 5.41).

In June 2011, other inorganic P decreased downwards at site 1, from 8 to 5 µmole P / gram dry sediment. At site 2, it increased downwards from the SWI, from 4 to 8 µmole P / gram dry sediment, 5 centimetres below the SWI. From there it decreased downwards to 5 µmole P / gram dry sediment (see Figure 5.42).

In June 2012, other inorganic P increased downwards from the SWI, from 10 to 12 µmole P / gram dry sediment at site 1, 4 centimetres below the SWI. From there it decreased to 5 µmole P / gram dry sediment, 14 centimetres below the

SWI. At site 2, other inorganic P decreased consistently from the SWI, from 9 to 7 µmole P / gram dry sediment, 14 centimetres below the SWI (see Figure 5.43).

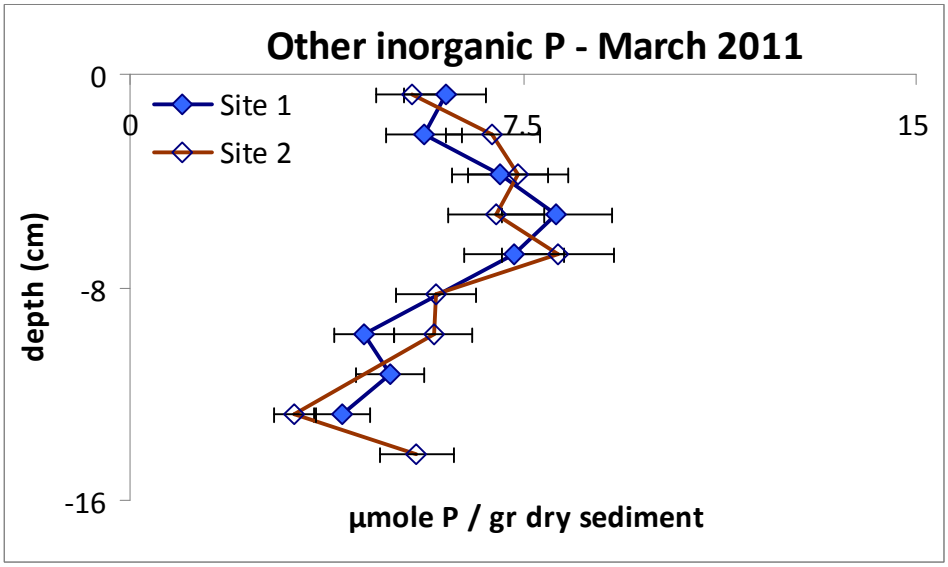


Figure 5-40: Concentrations of other inorganic P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2011. Error: 13%, n=6.

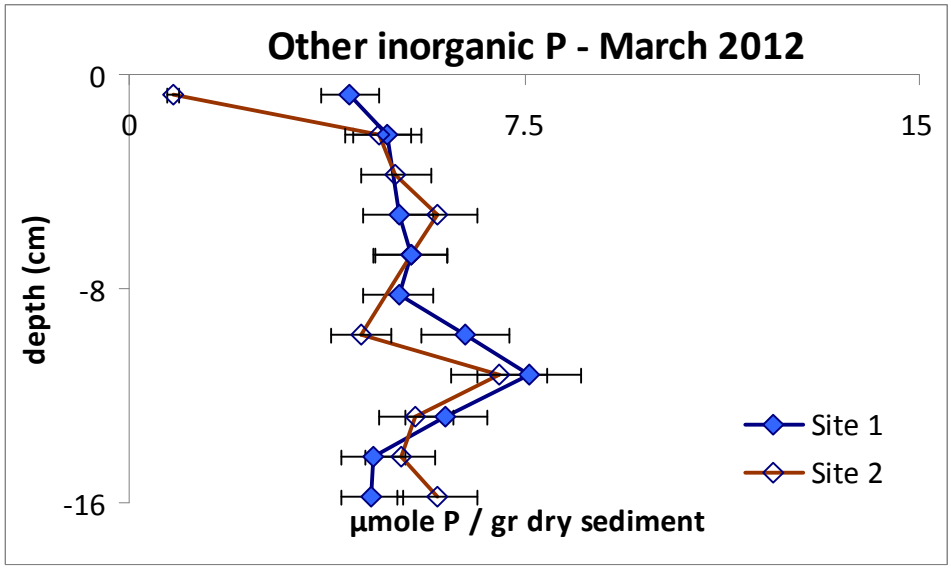


Figure 5-41: Concentrations of other inorganic P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2012. Error: 13%, n=6.

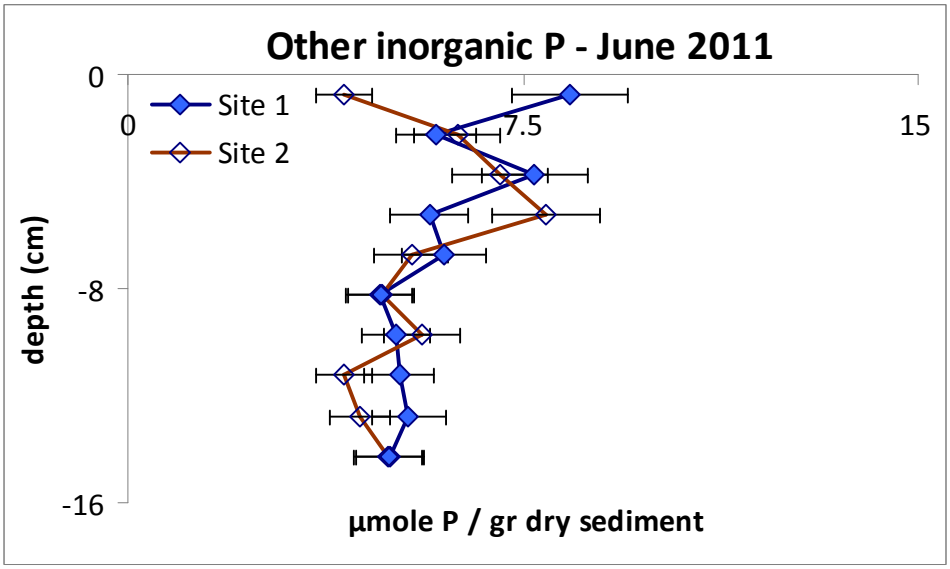


Figure 5-42: Concentrations of other inorganic P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2011. Error: 13%, n=6.

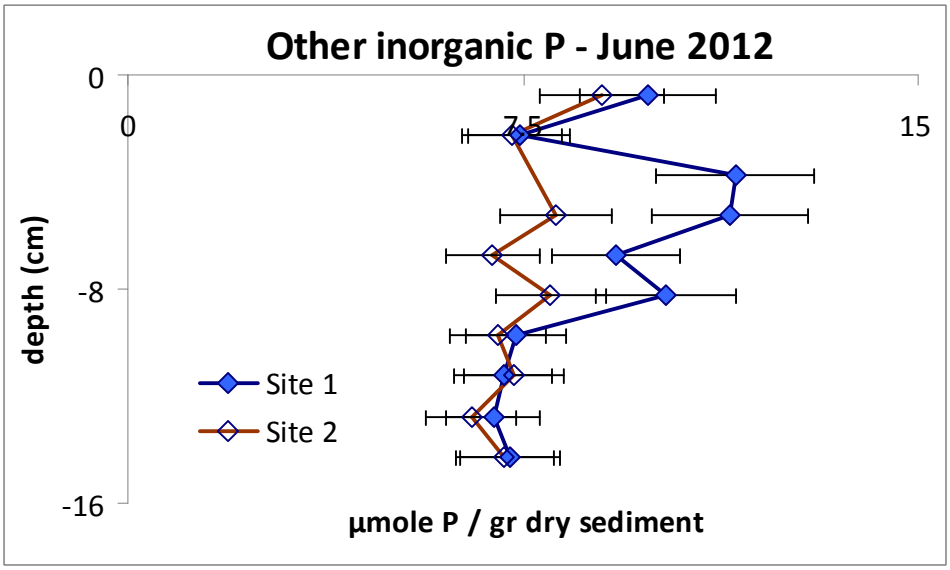


Figure 5-43: Concentrations of other inorganic P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2012. Error: 13%, n=6.

5.2.10.5 Organic P

Organic P between the SWI and 8 centimetres below it, varied between 34 and 46 µmole P / gram dry sediment at site 1 and between 32 and 43 µmole P / gram

dry sediment at site 2. At that depth levels of organic P shifted to values between 19 and 27 μmole P / gram dry sediment (see Figure 5.44).

Concentrations of Organic P in March 2012 increased downwards between the SWI and 5 centimetres below it. They increased from 20 to 23 μmole P / gram dry sediment at site 1 and from 16 to 21 at site 2. From that depth, concentrations decreased downwards to 16-17 μmole P / gram dry sediment (see Figure 5.45).

Levels of organic P in June 2011 remained between 10 and 13 μmole P / gram dry sediment for both sites 1 and 2 (see Figure 5.46).

At site 1, levels of organic P in June 2012 increased downwards from 14 to 17 μmole P / gram dry sediment, between the SWI and 5 centimetres below it. From there down, they decreased to 14 μmole P / gram dry sediment. At site 2, concentrations of organic P decreased consistently downwards, from 21 to 15 μmole P / gram dry sediment (see Figure 5.47).

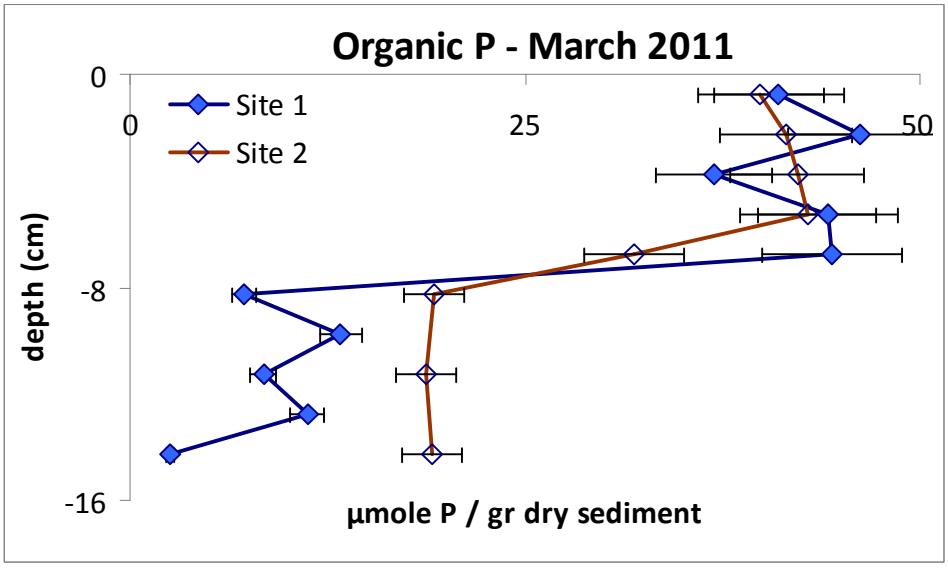


Figure 5-44: Concentrations of other organic P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2011. Error: 10%, n=6.

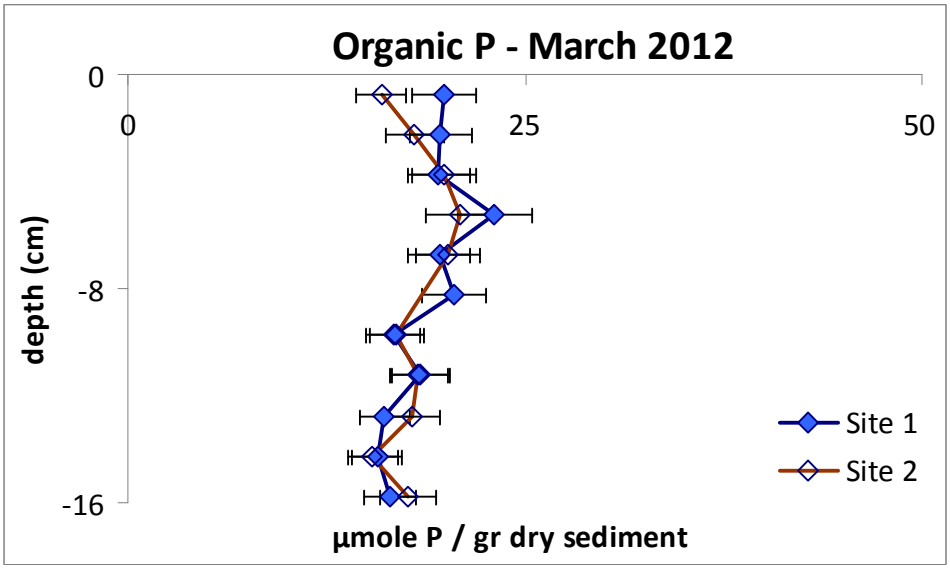


Figure 5-45: Concentrations of other organic P in the sediments of the settlement lagoon, at sites 1 and 2 for March 2012. Error: 10%, n=6.

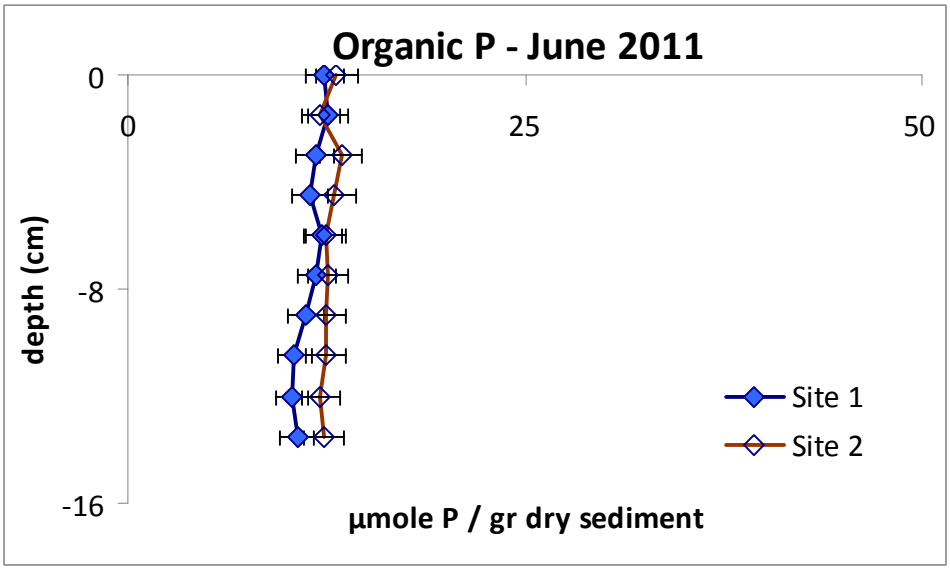


Figure 5-46: Concentrations of other organic P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2011. Error: 10%, n=6.

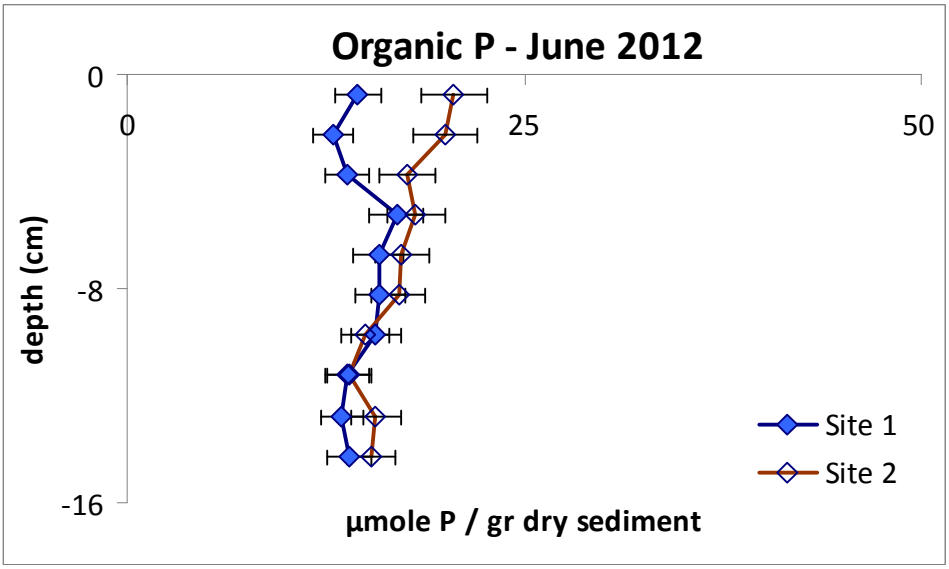


Figure 5-47: Concentrations of other organic P in the sediments of the settlement lagoon, at sites 1 and 2 for June 2012. Error: 10%, n=6.

5.2.11 Pore water SRP from sediment incubations

The initial SRP concentration in the pore waters was 78 µM P, similar to that measured by using DET gels. Concentrations of SRP in the pore water increased steadily during days 1 and 2. The rates of increase were higher at higher temperatures.

Concentrations of SRP stabilised on day 3 for the incubations at 20ºC, on day 4 for incubations at 15 ºC, and they were still rising when the experiment was stopped at day 5, in the incubations at 4ºC. The concentrations tended to converge around 300 µM P (see Figure 5.48).

The calculated Q10 coefficient for the increase of SRP concentrations in pore waters was 1.6.

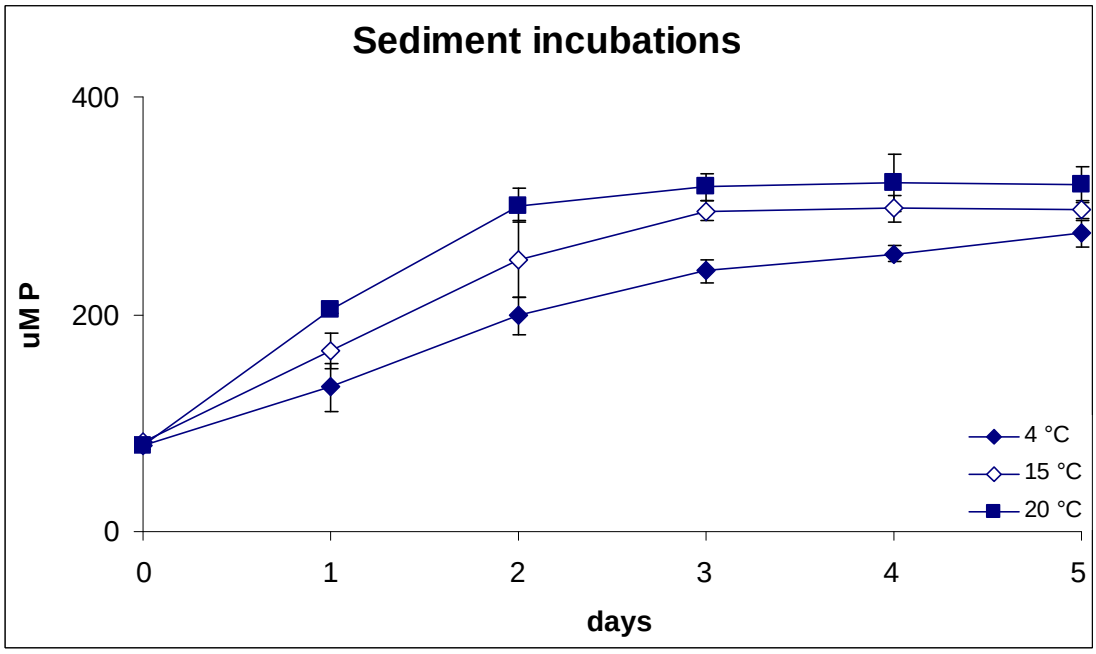


Figure 5-48: Concentrations of SRP in pore water of sediment incubations, between time=0 and time=5 days. Each sample was incubated, sampled and analysed in triplicate. Therefore, the error bars represent one standard deviation (n=3).

5.3 Discussion

5.3.1 March 2011

5.3.1.1 Water chemistry near the SWI

SRP peaked above the SWI in March and it was demonstrated in Section 4.3.2.2 that this resulted from the rapid oxic mineralisation of labile organic matter present in the falling algae, before it reached the sediments. The peak of SRP above the SWI is not corresponded by a peak of ammonium, which is also released during the degradation of organic matter and it is a waste product of microbial respiration (Kadlec and Knight, 1996). However, the lack of clear peaks of ammonium in conjunction with the peak of nitrate immediately below the SWI suggested that ammonium was being consumed during nitrification. This coincides with the depth of penetration of oxygen into the sediments (see

Figure 5.2), and with the levels of nitrate in the water column (115 µM NO_3^-) against those at the peak below the SWI (175 µM NO_3^-).

5.3.1.2 The solid phase

The solid phase in March 2011 showed that the dominant species of solid P in the sediments were Iron bound P, Apatite P and Organic P. However, while Iron Bound P showed a steady decline in concentrations with depth, Organic P and Apatite P showed steep changes of concentrations 6 centimetres below the SWI.

The average sedimentation rate at the settlement lagoon is 5-6 centimetres a year. This was estimated by dividing the depth of the recently deposited silt (appox. 75-90 cm) by the age of the pond (15 years). Organic P peaked between the SWI and 6 centimetres below this. This indicated that the peak was caused by material deposited during the previous year. This also indicated that the material responsible for the peak in Organic P could not have been falling algae from the algal bloom, because this had only been significant for 2-3 weeks before the time of sampling. Also freshly produced algae are very reactive and they are usually mineralised before they are buried into the sediments of shallow lakes. During an incubation experiment described in Hansen and Blackburn (1992), the addition of dead algae to the incubated sediment cores caused the immediate consumption of oxygen and nitrate from the water column and the release of ammonium from the sediments. 91% of the algal carbon was released within 5 days as CO2, and the algal material was completely mineralised within 2 to 3 weeks (Hansen and Blackburn, 1992). Boström et al (1989) concluded that the dead algae that fell over the sediments of the eutrophic shallow Lake Vellentunasjön, in Sweden, was consumed over the SWI, and that they never reached deeper sediments (Boström et al, 1989). More generally, other studies concluded that algae are a rich source of organic matter for bacteria, as long as electron receptors are present (Søndergaard, et al, 2003, and Caraco et al 1990).

Given the characteristics and function of the settlement lagoon, an important fraction of the organic matter supplied to the sediments was likely to have been bird faces, which tend to sink quickly (Pettigrew et al, 1998). The diet of herbivores waterfowl consists in a high fibre, low energy diet (Hahn et al 2008), that generates partly digested organic matter (Kear, 1963). The organic matter contained in bird faeces is therefore constituted by a) a not digested material that will be relatively refractory and that will take time to be decomposed; b) readily available particulate organic matter; and c) dissolved organic matter (Bazely and Jefferies, 1985, and Pettigrew et al, 1998). The last two types are easily assimilable for heterotrophic organisms (Ganning and Wulff 1969).

The different bio availability of the bird faeces coincided with the shape of the profiles of Organic P, which therefore represented a relatively more labile organic matter made predominantly of bird faeces, which was deposited in the previous year, and that had not started to be mineralised significantly by March 2011. Below 5-6 centimetres, the lower concentrations of organic P represented the background level of refractory organic matter, which the sediment microorganisms were not able to mineralise efficiently (Jansson, 1987 and Golterman, 2001).

The labile organic matter on the top 6 centimetres of sediments was being mineralised at a slow rate, limited by temperature. The effects on temperature on the rate of mineralisation of Particulate P was demonstrated by the sediment incubations (see Figure 5.48), which yielded a Q10 of 1.4 to 1.8. Nitrification taking place at the SWI and the exhaustion of nitrate 2 centimetres below the SWI indicated that the mineralisation of organic matter, although at slow rate, was carried out through nitrification-denitrification coupling. These processes were triggered by the production of ammonium above the SWI, during the oxic mineralisation of falling alge. The ammonium was oxidised to nitrate, in the presence of oxygen; and nitrate finally was used up by denitrifiers immediately below.

Nitrification was also observed to take place during early spring in the shallow eutrophic Lake Müggelsee, in Germany (Dudel and Kohl, 1992). The authors found a strong positive correlation between the amount of organic matter in the sediments and the rates of denitrification. Although, in that case the collapse of the algal bloom in late spring-early summer supplied the largest amount of readily available organic matter into the sediments and therefore the consumption of nitrate and the release of ammonium were maximum at that time. The authors also measured that rates of denitrification increased with temperature, and the corresponding Q10 was 1.9 in that specific lake. However, increased temperatures inhibited the process of nitrification due to reduced oxygen levels, and this in turn reduced the availability of nitrate required for denitrification (Dudel and Kohl, 1992). During a different study, it was concluded that easily biodegradable and abundant organic matter is the key driver of denitrification. The same study concluded that in aerobic systems, like the settlement lagoon in March 2011, most of the nitrate consumed during denitrification is produced within the sediments by nitrification (Seitzinger, 1988). Nitrification was also noticed in the shallow eutrophic Lake Nuldernauw, in the Netherlands, and tightly coupled with denitrification (Van Lujin et al, 1999). Same mechanisms were observed in the shallow Lake Donghu, in China (Chen et al, 2009).

Dissolved iron and sulphate in the pore waters of the settlement lagoon remained constant down the profiles indicating that no anoxic respiration took place in March (Froelich et al, 1979). However, alterations in the oxic state of iron could have occurred at the redox boundary, which would have resulted in a consumption or release of dissolved P (Christophoridis and Fytianos, 2006). Also, polyphosphates accumulating organisms would have affected the cycling of P at the redox boundary, where they are most likely to break down or start accumulating polyphosphates. Importantly, concentrations of SRP remained constant below the depth at which nitrate was depleted, suggesting that no cycling of P was taking place below 2 centimetres under the SWI in March.

5.3.2 June 2011

5.3.2.1 Water chemistry near the SWI

It was demonstrated in Chapter 4 that June 2011 represented the point of collapse of the algal bloom and the minimum rate of photosynthesis. By this time fresh algae had been being deposited for several weeks on the sediments, and this supplied easily available organic matter to microorganisms, increasing their rate of respiration and depleting therefore oxygen and nitrate from the water column (see Figures 5.3 and 5.10). This was accompanied by increased temperatures. This was reflected in the chemistry of the water just above the SWI, where concentrations of ammonium peaked. This, in turn, indicated that nitrification was less intense in June, compared to March and that ammonium accumulated at the SWI, probably due to low oxygen concentrations (DO March: 97% saturation, DO June: 18% saturation).

In a study carried out on cores from Aarhus Bight, in Denmark, The authors concluded that the addition of fresh organic matter to the sediment cores caused a major increase in heterotrophic microbial activity (Hensen and Blackburn, 1992). Similar conclusions were reached from the results of the shallow eutrophic Lake Müggelsee, in Germany, as it was discussed in Section 4.4.1.1. The authors related the increase in denitrification rates with the supply of rich organic matter and with the increased temperatures of early summer (Dudel and Kohl, 1992). Increasing the temperatures of incubation experiments of sediments from three Chinese lakes also resulted in increased mineralisation rates of organic matter (Wang et al, 2008). The slowing down in rates of nitrification due to lack of oxygen during the summer months was explained by Van Lujin et al (1999), in their study of the shallow eutrophic Lake Nuldernauw, in the Netherlands, and by Chen et al (2009) during their study of the shallow Lake Donghu, in China.

5.3.2.2 Chemistry of the pore water

The depletion of nitrate above the SWI allowed iron reducing bacteria, and sulphate reducing bacteria to mineralise organic matter near the SWI (Jansson 1987). This is reflected, on one hand, by the high rate of consumption of sulphate at shallow depths and, in part, by the increase of dissolved iron in the pore waters. SRP showed a localised peak at the depth where dissolved Fe peaked, at site 1 (see Figures 5.14, 5.18 and 5.26). When iron minerals are dissolved, any P on their surfaces or incorporated into their lattices becomes dissolved immediately (Christophoridis and Fytianos, 2006). The differences between sites 1 and 2, regarding concentrations of dissolved iron, have been observed in previous studies of shallow lakes. Sediments from Lake Wellington, Australia, showed great variability in their reactivity, mainly associated to iron oxides (Monbet et al, 2008). In the study of the settlement lagoon of 2009, concentrations of pore water iron were consistently higher at site 2 that at site 1 (different from sites 1 and 2 in this study), both in March and June 2009.

Concentrations of SRP in the pore waters increased by one order of magnitude since March, and concentrations of ammonium in the pore waters increased by two orders of magnitude in the same period. These results indicated that intense rates of respiration were taking place within at least, the top 8 centimetres of sediments. This should have been fuelled mainly by organic matter that was in place already in March (i.e. bird faeces), because given the rate of sedimentation in the settlement lagoon, only 1 centimetre of sediment would have been deposited since then. Since the source of organic matter was in the sediments in both March and June, but evidence of high levels of respiration only were observed in June, this suggested that the mineralisation of organic matter was restricted by the low temperatures of March (2 to 6°C) and that they were promoted when temperatures increased some time between March and June. This is supported by the results of the sediment incubations and by other studies in eutrophic shallow lakes, discussed above. Also, while the peak in ammonium happened above the SWI, SRP peaked below the SWI. This indicated that the

increase in concentration in SRP in the sediments was related to a different process than the oxidation of freshly deposited algae over the SWI.

5.3.2.3 The solid phase

Following the last paragraph of the previous section, the source of organic matter that maintained the levels of respiration evidenced by the chemistry of the pore water should have been the bird faeces that accumulated in the top 6 centimetres of sediments between the summer of 2010 and the summer of 2011, whose presence was discussed in Section 5.3.1.2. Figure 4.42 shows how by June 2011 the levels of Organic P in the top 6 centimetres of sediments had been depleted to their background levels (10 to 13 moles P / gram dry sample), which as discussed in Section 5.3.1.2 represented the Organic P contained in the refractory matter that sediment microorganisms were unable to mineralise. Concordantly, Aspila fractionation performed on samples of bird faeces collected from the grounds of the WWT wetland centre yielded values of Organic P of 16 moles P / gram dry sample (error: 16%, n=4). This fraction of the SEDEX scheme represents refractory organic matter that resisted the previous extraction of 1M HCl (Ruttenberg et al, 1992).

The mineralisation or the accumulated bird faeces was carried out primarily by iron reducing bacteria and sulphate reducing bacteria, whereas oxygen and nitrate reducing bacteria mineralised the fresh organic matter deposited during the collapse of the algal bloom, on the SWI. In June 2011, sulphate reduction occurred at a shallower depth than iron reduction. Since the quality of the organic matter (deduced from the organic P fraction) seemed to have been relatively constant between the SWI and 6 centimetres below it, the occurrence of sulphate reduction above iron reduction should have been driven by the availability of the respective electron acceptors (sulphate and ferric iron, respectively) at different depths.

This could have resulted due to the high porosities of the top sediments, which ranged from 0.99 at the SWI to 0.90, 4 centimetres below it, to a constant porosity of 0.82 below those depths (see Figure 5.1). Figures 5.49 to 5.53 show the integrated masses of the different species of P (in moles P) at different depths, for the whole of the area of the settlement lagoon. These were calculated by multiplying the results from the SEDEX fractionation by the mass of sediments at different depths, which depended on the sediment densities and on the porosities. It can be observed that due to the high porosities between 0 and 4 centimetres below the SWI, the total masses of every species of P was minimal at those depths, even when the normalised units (moles P / gram dry sample) showed maxima at those depths. Since iron reducing microorganisms need the presence of solid ferric iron, their effects in the pore water only became relevant 4 centimetres below the SWI, where the amount of solid matter increased.

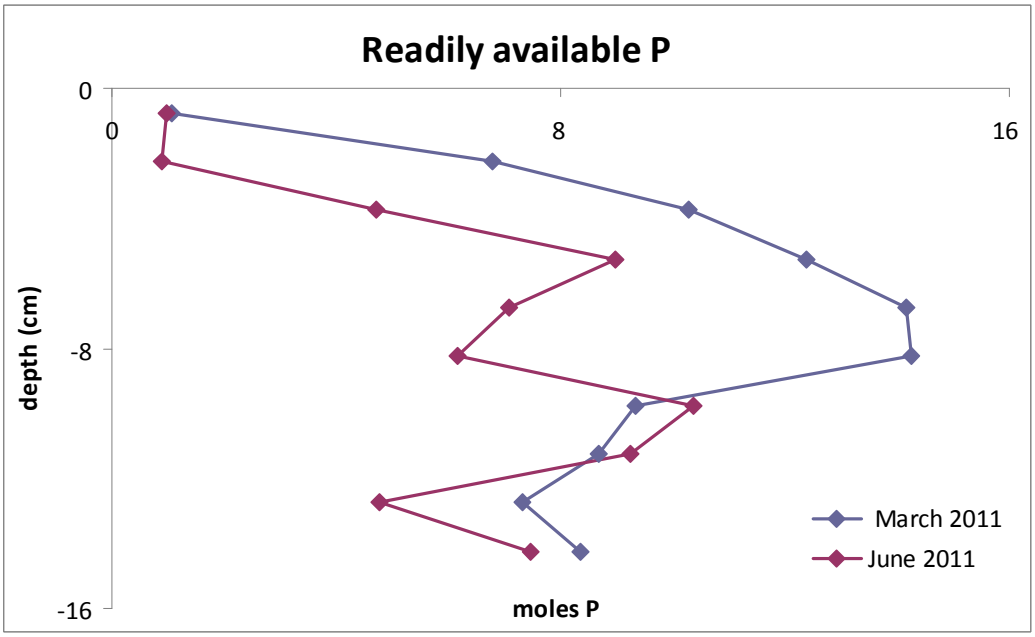


Figure 5-49: Masses of readily available P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2011.

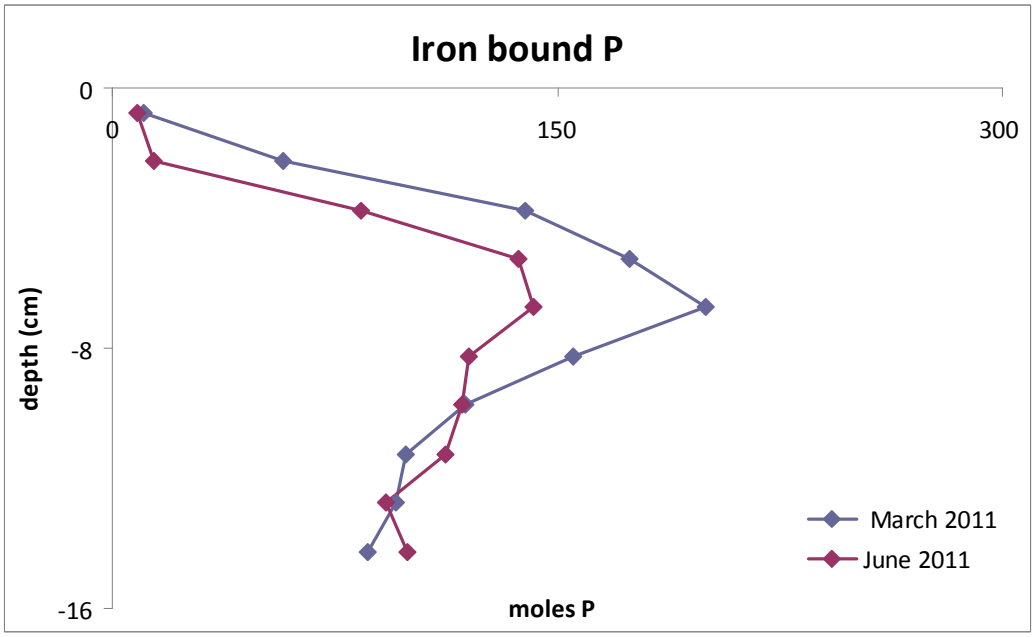


Figure 5-50: Masses of iron bound P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2011.

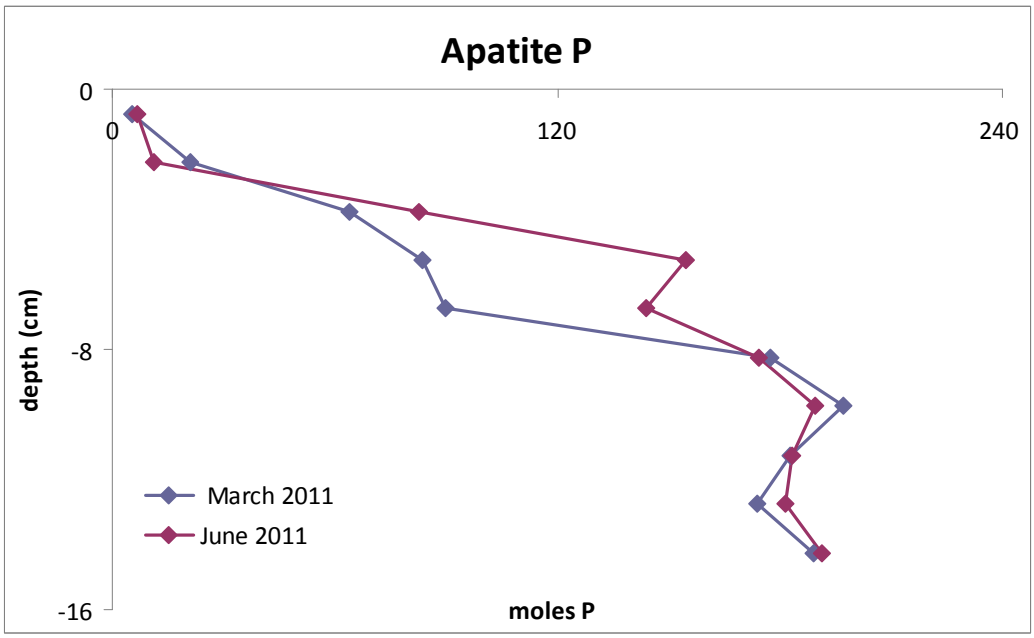


Figure 5-51: Masses of apatite P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2011.

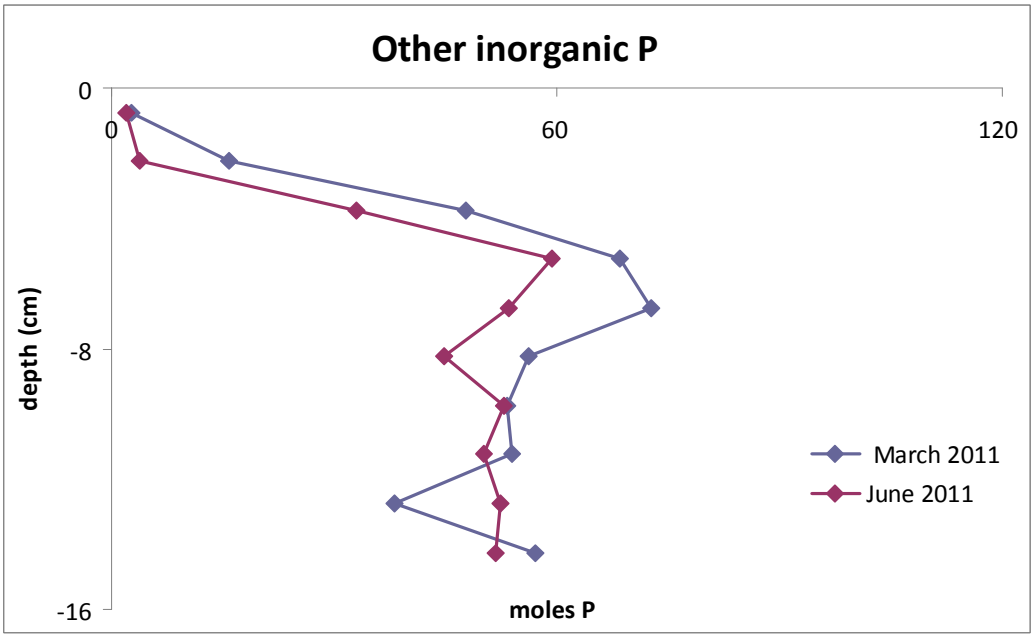


Figure 5-52: Masses of other inorganic P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2011.

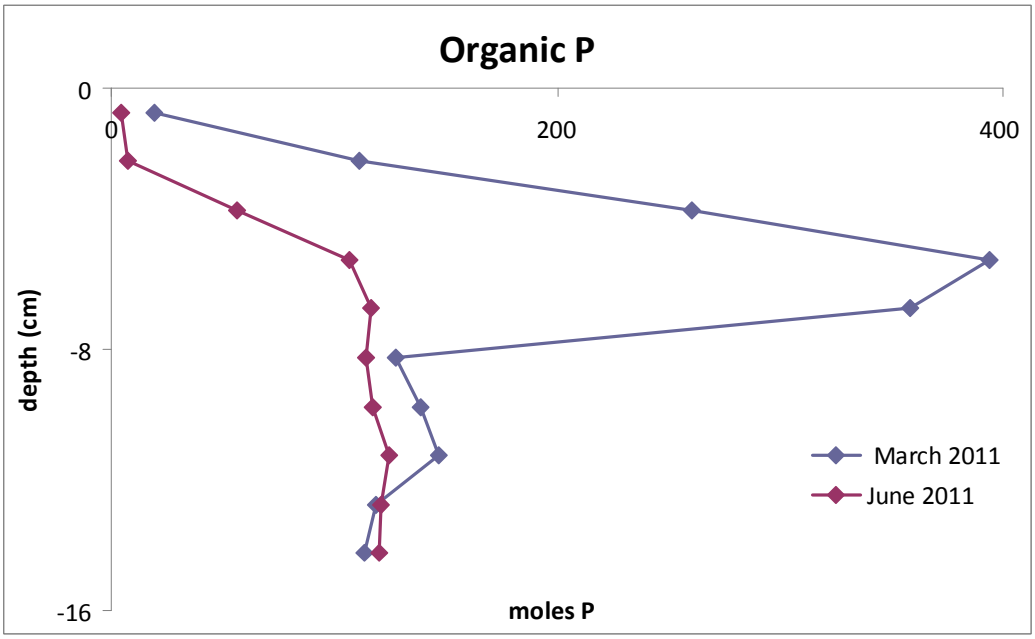


Figure 5-53: Masses of organic P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2011.

The integrated massed of P with depth also showed a clear shrinking in the pool of Iron Bound P, which was not apparent in the graphs expressed in the normalised units. The highest reduction in the masses of Iron Bound P occurred at depths where dissolved iron seemed to have peaked in the pore waters (i.e. somewhere below 5 centimetres below the SWI). The dissolution of iron minerals and their incorporated P within anoxic sediments contradicts the classical theories of Mortimer (1941) and Einsele (1936), which stated that the dissolution was governed by the redox potential of the water. Further studies, however, concluded that the dissolution of iron minerals and its attached P can be caused solely by microorganisms, through the activity of different reducing enzymes (Munch et al, 1978). For example, iron reducing bacteria utilise ferric iron as their terminal electron acceptor, which becomes reduced and it dissolves as Fe_2^+ (Froelich et al, 1979). Other studies, on the other hand, coincide with the classic theory of Mortimer (1941) and Einsele (1936). Lakes Volvi and Koronia, in Greece, exhibited P release under reducing conditions (Christophoridis and Fytianos, 2006). P release in Lake Koronia was very sensitive to small changes in the redox potential of its sediments. The authors attributed this sensitivity to the saturation of P in relation to iron (Christophoridis and Fytianos, 2006). The same study found that P release from Lakes Volvi and Koronia also responded to elevated pH in the pore waters. This mechanism has been described repeatedly in the literature, and it is related to the substitution of PO_4^{3-} ions by OH^- on the surfaces of iron minerals (Søndergaard et al, 2003, Boström 1988b).

The normalised graphs of Apatite P for March and June 2011 showed that this calcium P mineral was precipitated between those two dates, between the SWI and 7 centimetres below it. Solubility calculations (Parkhurst and Appelo 2013) indicated that given the concentrations of P, Ca, pH and Temperature, apatite could have been precipitated in March. This explained the existence of apatite (approx 10 µ mole P/gram dry sed) in the sediments in March in the top 7 centimetres of sediments. However, in only 3 months (between March and June), concentrations of apatite doubled to approximately 20 µ mole P/gram dry sediments.

The sudden increase in the concentrations of Apatite P between March and June 2011 could have been caused by different mechanisms occurring simultaneously, contributing in different degrees to the precipitation of authigenic apatite:

1. An increase in temperature between spring and summer, given that temperature affects the rates of precipitation of apatite (Parkhurst and Appelo 2013).
2. The large quantities of SRP released from the mineralisation of organic matter and the dissolution of ferric iron could have favoured the precipitation of apatite at higher rates between March and June, given that in both March and June, Ca was in saturation with respect of P (Parkhurst and Appelo 2013).
3. Higher temperatures promoted the activity of poly-P accumulating organisms, and it has been suggested that Poly-P accelerates the growth of apatite (Diaz et al 2008, and Goldhamer et al 2010).

Simultaneous uptake and release of P by different P fractions in the sediments have been reported in the literature. Uptake of P by the apatite fraction occurred simultaneously with the release from the organic and iron bound P at the shallow eutrophic Loch Leven (Spears et al 2007). During the study of four shallow Swedish lakes, it was concluded that in all of them apatite was precipitated when other fractions released P (Boström et al 1988b). More generally, Patterson et al (1988) concluded that apatite is the only real authigenic P mineral, and that due to diagenetic processes, organic P is, to a large extent, transformed into apatite P. In the oceans, similar processes have also been reported but at a much longer time scale (years) (Ruttenberg and Berner, 1993, Noffke et al 2012), due to the usual low levels of organic matter within the sediments.

Pore water pH is assumed to be the main limiting factor in the precipitation of apatite (Boström et al 1988b). Only at pHs higher than 8, precipitation of apatite occurs at rates that can be observed. (Ryding 1985). The precipitation of apatite can also be reversed if the pH in the pore water decreased during the biological mineralisation of organic matter (Søndergaard et al 2003), although such decreases rarely occur in conditions normally found in the sediments of lakes

(Ryding et al 1985). Pore water pH at the settlement lagoon was found to be above 8, therefore apatite could be considered stable within those sediments. This is significant because it meant that the sediments of the settlement lagoon were in fact capturing P permanently. The long term stability of apatite in sediments of shallow lakes have been reported by Boström and Pettersson 1982 and Boström 1984, by Nurnberg 1987, and by Marsden 1989 among others.

The mediation of polyphosphates in the precipitation of apatite has been studied in the oceans. Schulz and Schulz (2005) suggested that polyphosphates accumulated by sulphur bacteria were involved in the formation of apatite, locking this way P within the sediments. Goldhammer et al (2010) observed, using radiotracers experiments, that the largest conversion of phosphate into apatite was carried out by sulphur bacteria too. Diaz et al (2008) related the appearance of apatite granules in the ocean floor with their nucleation around individual polyphosphates granules.

5.3.3 Mass balances and the controls for the release of P from sediments

The masses of the different species of P for the whole area of the settlement lagoon, shown in Figures 5.49 to 5.53, were integrated between 0 and 14 centimetres below the SWI, for March and June 2011. These results are presented in Table 5.1.

Table 5.1 indicated that the release of P during summer of 2011 resulted primarily from 1) the mineralisation of organic matter, and 2) the dissolution of iron minerals. The precipitation of apatite only resulted in the capture of approximately 10% of the released P, although apatite represented 35% of the buried mass of P in June. Evidence of the mineralisation of organic matter was present primarily in the pore water chemistry, as discussed in Section 5.3.2. The dissolution of ferric iron and its attached P occurred well below the redox boundary, suggesting that it was triggered by enzymatic activity of iron reducing

bacteria, instead of solely by changes in redox conditions, as it was also discussed in Section 5.3.2.3.

	Readily avalilable P (moles P)	Iron-P (moles P)	Apatite P (moles P)	Other Inorganic P (moles P)	Organic P (moles P)
March	90	1100	1200	500	1800
June	60	900	1300	500	900
Mass Balance	-30	-200	100	0	-900

Table 5-1: Mass balances of the different species of P in sediments between March and June 2011

Although the sediments released approximately 1000 moles of P from the top 14 cm of sediment between March and June, the mass of P in the pore waters only increased by approximately 100 moles of P between the same period and in the same depth interval. Therefore, approximately 900 moles P should have been released into the water column of the settlement lagoon between March and June 2011, which represents an average of 10 moles P per day between March and June.

The measured rates of release of P, using benthic chambers (see Chapter 4) were approximately 0 in March 2011, and 13 moles day^{-1} in June. Therefore, in order to release 900 moles of P into the water column, the sediments should have released P at higher rates that 13 moles day-1 some time between March and June 2011, and the rates of release measured in June 2011 were probably the tail of a larger peak that occurred during the previous weeks. This does not agree entirely with the hypothesis that temperature controlled the rates of mineralisation of organic matter and the subsequent release of SRP discussed in Section 5.3.2, given that temperatures kept increasing between March and June (Bablake Weather Station, west Midlands).

Although the release of P from sediments seemed to have been triggered by the increased temperatures, it slowed down before temperatures started to decrease in autumn. A counteracting control could have limited the release of P from sediments. This was likely to have been the availability of labile organic matter in the sediments. It was demonstrated in Table 4.1 that the main contributor to the release of P in sediments was the organic matter; and it was argued in Section 5.3.2.3 that by June 2011 the relatively labile organic P had been consumed and only the more refractory organic P remained in the sediments. The exhaustion of the main source of P in the sediments by June caused the decrease in the rates of release through the SWI.

The limiting effect of the availability of labile organic matter has been recorded in the literature. Respiration rates in the sediments of the shallow eutrophic Lake Nuldemauw, in the Netherlands, increased with temperature but they were also governed by the availability of labile organic matter (Van Luijn et al, 1999). Seitzinger (1988) concluded that the availability of easily biodegradable organic matter was the key controller of respiration in sediments.

5.3.4 The sediments of the settlement lagoon in 2012, compared to 2011

The masses of P in different forms in the sediments during March and June 2012 are presented in Figures 5.54 to 5.58. These were integrated using the normalised values obtained from the SEDEX protocol (in µ mole P / gram dry sediment), the measured porosities down the profiles, the densities of the sediments and the surface area of the settlement lagoon. The masses of different species of P between the SWI and 14 centimetres below were integrated for the surface area of the settlement lagoon, for March and June 2012. See Table 5.2.

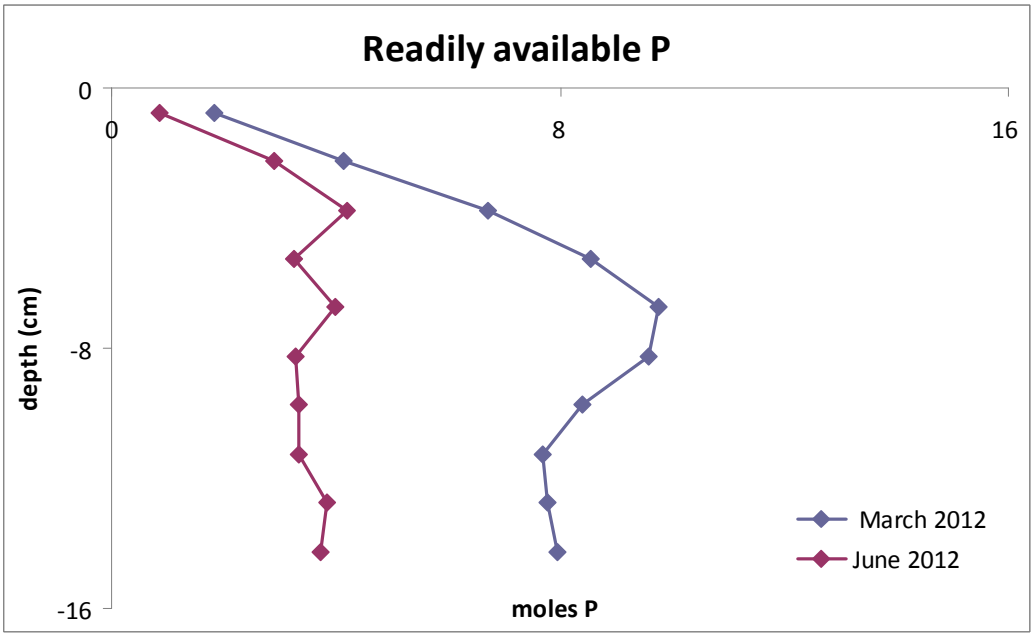


Figure 5-54: Masses of readily available P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2012.

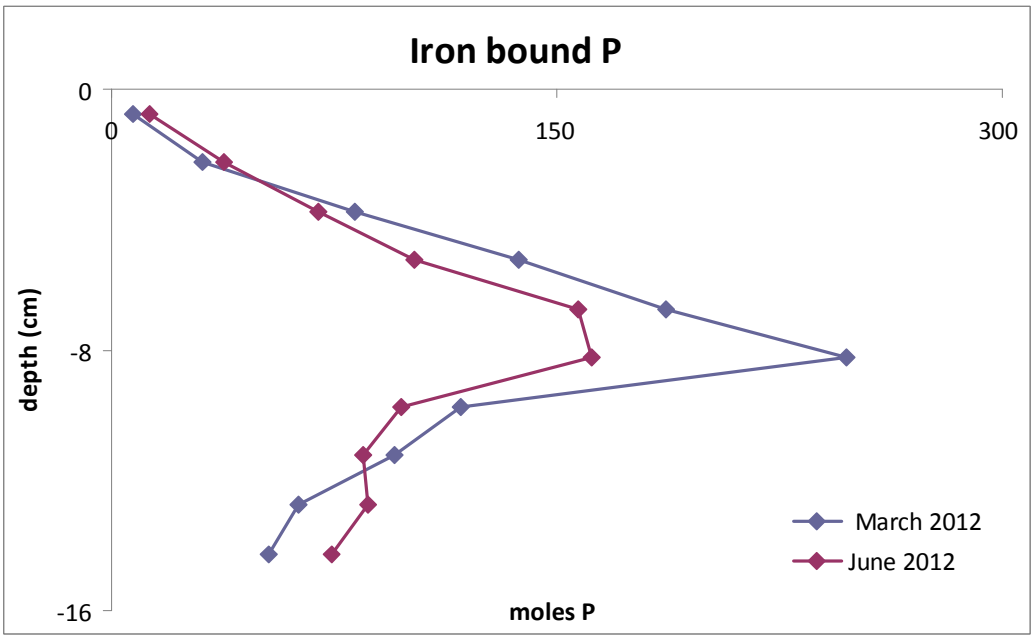


Figure 5-55: Masses of iron bound P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2012.

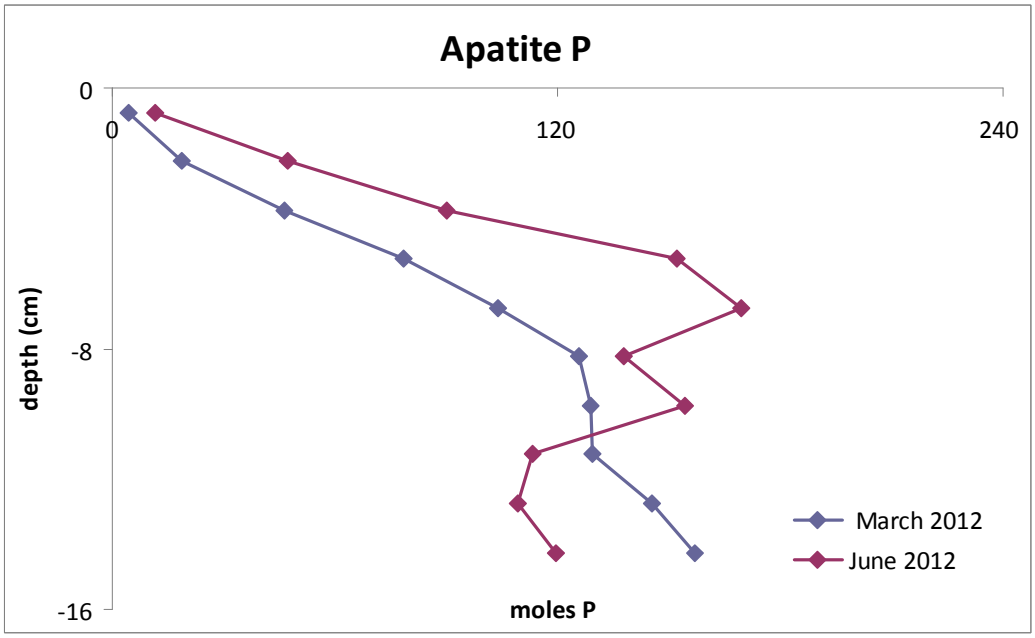


Figure 5-56: Masses of apatite P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2012.

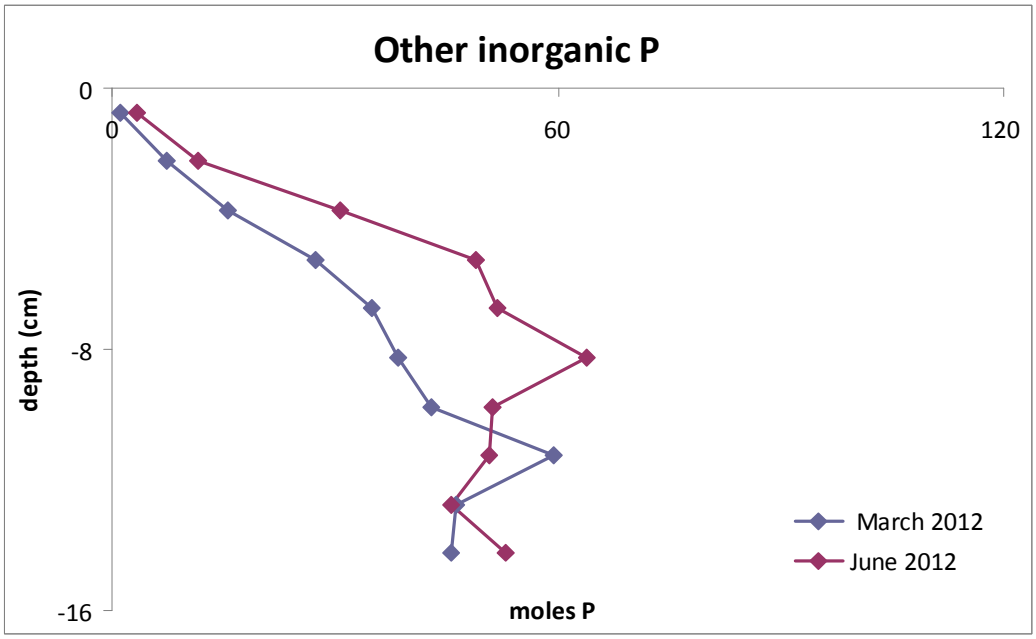


Figure 5-57: Masses of other inorganic P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2012.

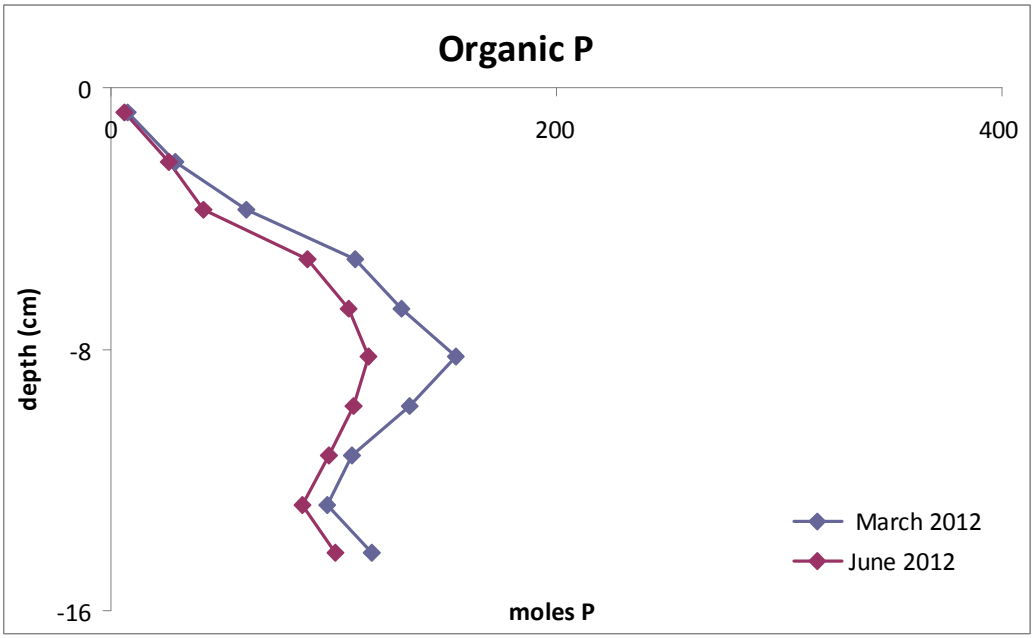


Figure 5-58: Masses of organic P across the whole area of the settlement lagoon, between the SWI and 14 centimetres below it, for March and June 2012.

	Readily avalilable P (moles P)	Iron-P (moles P)	Apatite P (moles P)	Other Inorganic P (moles P)	Organic P (moles P)
March	70	1000	900	300	900
June	30	900	1100	400	800
Mass Balance	-40	-100	200	100	-100

Table 5-2: Mass balances of the different species of P in sediments between March and June 2012

5.3.4.1 Organic P

The mass balances of all species of P between March and June 2012 were similar to those between March and June 2011, except for that of Organic P. The discrepancies in the mass balances of organic P were the result of less organic P being present in March 2012 (900 moles) compared to March 2011 (1800 moles).

This could have been the result of changes in the nature of the supplied particulate matter into the settlement lagoon between 2011 and 2012, compared to the previous year. Between 2011 and 2012 intense maintenance work was carried out in some of the ponds of the wetland centre upstream of the settlement lagoon, which could have altered the composition of the suspended sediments that flowed into the settlement lagoon, in particular the total mass of organic matter exported from them.

Another possible explanation for the lower values of organic P in March 2012 compared to March 2011 could have derived from the fact that mineralisation of organic matter in 2012 started earlier than in 2011, and that the two instances were not entirely comparable. This was suggested by the concentrations of pore water ammonium in March 2012, which were two orders of magnitude higher than in March 2011. Also, pore water SRP in March 2012 showed higher levels than in 2011. However, results form nitrate, dissolved iron or sulphate were inconclusive regarding this argument. A definitive trigger for an earlier mineralisation of organic matter in March 2012, such as increased temperatures, could not be identified conclusively.

A final cause for a depletion of organic P in the sediments in March 2012, compared to 2011 could have been the occurrence of more frequent resuspension events during 2011-2012 than in the previous year. The mechanisms are related to the exposure of anoxic organic rich sediments, to oxygenated waters during the resuspension events (Sordergaard et al 1992). See Section 3.4.3.5.

5.3.4.2 Apatite P

The mass of apatite P did not vary much between March and June 2011, and the same period in 2012. However, while the precipitation of apatite in 2011 represented only 10% of the released P, in 2012 it equalled the masses of P released from iron-P and organic P. This was a reflection of the small amounts of released P in 2012 compared to 2011, rather than an increased rate of apatite formation.

6 Summary

In general, the South Finger wetland has performed poorly in improving the quality of the water leaving the visitor centre. The primary reason for this failure has been suggested to be the short retention time of the water in its passage through the wetland. The bibliography suggests that the residence time should be increased between 6 to 12 times.

The construction of the South Finger wetland did not appear to have reduced considerably the levels of P in the water leaving the Visitor Centre of the WWT site at Slimbridge. The management of WWT recognised this failure and commissioned a series of monitoring and research projects, in order to understand why their systems were failing. The different studies identified the source of the problem as being the settlement lagoon of the treatment wetland, and most likely the sediments of the lagoon, although this last finding was inconclusive.

In chapter 4 it was demonstrated that the sediments of the settlement lagoon do release P in summer, although that is only a minor part of the problem of excess P in summer. The main source of high levels of P during the summer month is not the settlement lagoon but the ponds of the visitor centre of the WWT site.

It was also demonstrated in chapter 4 that microbial degradation of freshly deposited organic matter started in spring and it occurred just above the SWI. This caused a decrease of DO levels and the release of SRP just above the SWI. The sediments and planktonic organisms rapidly took up the released SRP. SRP and DOP were released from the sediments in summer, indicating the breakdown of organic matter within the sediments. Bad weather during the evening of the 6th June caused the resuspension of sediments. This showed that the cycling of P in the settlement lagoon can be very variable.

The processes that take place within the sediments of the settlement lagoon, and that result in the release of P in summer, were studied in detail in chapter 5. These can be summarised as:

Spring

- The rapid mineralisation of falling algae above the SWI was accompanied by a peak of SRP and a small drop in the levels of DO at those depths. Nitrate peaked at the same depths, but ammonium did not, suggesting that nitrification was taking place simultaneously, making use of the released ammonium and the abundant DO generated by the algal bloom.
- Respiration within the sediments occurred by denitrification (probably coupled with the nitrification happening above) and only in the top 2 centimetres of sediments. There was not evidence of iron reduction and sulphate reduction respiration taking place in the sediments in March 2011. The biological activity within the sediments was limited by the low temperatures encountered in March.
- Organic P, Apatite P and iron bound P are important reservoirs of P in the sediments at this time.
- Organic P accumulated in the sediments as two different fractions, 1) a refractory organic material that had not been mineralised and that constituted a background level of organic P, and 2) a more labile organic P that accumulated on the top 6 centimetres of sediments, that represented the still not mineralised labile organic P (by March 2011), that settled during the previous year. This organic matter is derived from the bird faeces and uneaten bird feed, in opposition to the freshly produced algae that is mineralised over the SWI.

Summer

- Intense levels of respiration above the SWI derived in large peaks of ammonium at those depths. Biological activity was promoted by the increased temperatures and by the constant deposition of fresh algae.
- Given the low levels of DO, nitrification was unlikely to happen at this time. This and the low levels of DO, caused nitrate to be exhausted above the SWI.
- Anoxic respiration, such as iron reduction and sulphate reduction occurred at shallow depths within the sediments. Concordantly, levels of ammonium and SRP in the pore waters increased 2 and 1 orders of magnitude, respectively, since March.
- Therefore, while oxic respiration and denitrification were the process by which the fresh falling algae was mineralised, iron and sulphate reduction were the processes that mineralised the organic matter within the sediments.
- The source of organic matter in the sediments was the labile fraction of the deposited bird faeces and bird feed deposited during the previous year, which was completely consumed between March and June 2011.
- The pool of iron bound P also shrank between March and June 2011, due to the high levels of iron reducing respiration was taking place.
- The pool of apatite P increased between March and June 2011, consuming SRP from the pore waters. This storage of P, together with organic P and iron bound P remained the largest reservoirs of P, even after some of them shrank in size.
- The rate of release of SRP through the SWI measured in June 2011 was too low compared with the mass of P that was lost from the solid phase between March and June. This suggested that the peak of the mineralisation of organic matter (and of the release through the SWI) happened earlier than June. This in turn suggested that a slowing down mechanism counteracted the increase of temperatures between March and June. This counteracting factor was proposed to be the exhaustion of the labile organic matter within the sediments by June.

7 Conclusions

In chapter 4, it was concluded that the settlement lagoon of the South Finger wetland experiences algal blooms in early spring and a release of P from the sediments in the early summer. This corresponds closely with many other studies of shallow lakes in temperate climates and it has been studied repeatedly. However, the behaviour of the settlement lagoon of the South Finger wetland, as discussed in chapter 5, differs in that large amounts of P are also released from organic matter that accumulates through the winter and that is mineralised rapidly as soon as the water temperature increases. This discrepancy may be characteristic of stabilisation ponds, where the settling of Particulate P is encouraged. Nutrient cycling in stabilisation ponds has remained understudy lately, although their use has increased to control non-point pollution (Peng et al, 2007). The research presented in this work contributes therefore to the study of nutrient cycling in stabilisation ponds, and it suggests that the subject needs further investigation since it was demonstrated that they do not behave like natural shallow lakes.

Many researchers have concluded that treatment wetlands are ineffective in retaining P in the long term, and that they become saturated shortly after commission (e.g. Braskerud, 2002). The main form of retention of P in treatment wetlands has been found to be the use of settlement ponds to capture particulate P, although they usually become affected by algal blooms and release of P from sediments in summer (Braskerud et al, 2005). The cycling of P in the settlement pond of the South Finger wetland, as discussed in chapter 5, also has important implications for the management of treatment wetlands utilising these kinds of lagoons. Given that an important fraction of P that is released from the sediments in summer is contained in the particulate matter that accumulates during the year, in theory this could be dug out from the ponds yearly, before temperatures increase. This ability to control the source of P that is released by the sediments contrasts with the practically uncontrollable algal blooms that end up in releasing P when they collapse and sink. Concordantly, settlement ponds should be

designed in a way that facilitates their annual dredging, and that topic should be investigated further too.

The deployment of simultaneous experiments on site, and the measurement of different species of P in a time series allowed the reconstruction of the cycling of P in the settlement lagoon. This approach allowed the estimation of the mass of P released during the resuspension event that happened during the June sampling. Work presented in Gerhardt et al (2010), or in Koshi-Vähälä and Hartikainen (2001) demonstrated that resuspension events can either release dissolved P into the water or sequester P from the water. The results presented in this study contribute to that debate, but they also suggest that the design of settlement lagoons should consider the important aspect of resuspension.

DOP has remained understudied in the past (McMahon and Read, 2013), and its incorporation into the research presented in this work demonstrated that this species of P is a very important player in settlement lagoons with high loads of organic matter. This study also discusses some of the relationships between living organisms, decomposing organisms and different species of P, which is another subject of recent research (Reitzel et al, 2007). The importance of DOP in the cycling of P becomes significant for the optimisation of water treatment plants (Saito et al, 2004, Saito et al, 2008, and Jie et al 2007), and the results presented in this study contributes to that research. For example, it is significant that the flux of DOP through the SWI was shut off during the early spring sampling. The implications of this observation for the performance of water treatment plant could be studied further.

The relationships between nutrient levels and the appearance of algal blooms is still being studied and debated due to its significance of water quality and water management (Smith et al, 2003) and also because some those relationships are still not fully understood. (Hagerby et al, 2006). For example, the collapse of the algal bloom by June reported in chapter 4 happened when the concentrations of reactive P and ammonia were maximum. These inconsistencies in the relationships between nutrient levels and primary productivity could also be investigated further.

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