Nutrient retention capacity of a constructed wetland in the Cox Creek sub-catchment of the Mt. Bold Reservoir, South Australia

by

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List of abbreviations

Aluminium	Al
Analysis of variance	ANOVA
Calcium	Ca
Carbon dioxide	CO_2
Dissolved inorganic phosphorus	DIP
Dissolved organic phosphorus	DOP
Dry weight	DW
Equilibrium phosphorus concentration	EPC
Filterable reactive phosphorus	FRP
Hydraulic loading rate	HLR
Iron	Fe
Organic matter	OM
Particulate inorganic phosphorus	PIP
Particulate organic phosphorus	POP
Phosphorus accumulation rate	P_{accum}
Phosphorus	P
Sediment accumulation rates	SR_{accum}
Sedimentation rate	SR
Subsurface flow	SSF
Surface flow	SF
Suspended solids	SS
Total nitrogen	TN
Total phosphorus	TP
Water residence time	WRT

Declaration

I declare that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference has been made in the text.

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Nor Azman Kasan

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Abstract

The Cox Creek sub-catchment is located in the Piccadilly Valley, South Australia. It exports disproportionately high loads of nutrients and sediment to the downstream Mount Bold reservoir. The excessive application of inorganic fertilisers to agricultural land in the Cox Creek sub-catchment has enhanced nutrient exports downstream. This has led to eutrophication and algal blooms in Mount Bold Reservoir, an important water supply for the city of Adelaide, which has a population of approximately 1.3 million people. The Cox Creek constructed wetland includes a sedimentation basin and a series of constructed wetland ponds, which were implemented to reduce nutrient loads passing downstream. The objective of this research was to evaluate the capacity of the constructed wetlands to retain nutrients and better understand key processes for nutrient retention such as macrophyte uptake, sediment sorption and sedimentation in the Cox Creek wetland system. How different flow regimes influence these processes was also investigated.

Based on historical inflow and outflow data from 2004 to 2009 for the Cox Creek wetland system, six different flow rate classes were classified and the nutrient loads delivered by each of these flow rate classes were calculated. It was hypothesized that the higher the flow class the shorter the water residence time and so reduced opportunity for nutrient retention through processes such as sedimentation. The very dry flow class (0 to 1 ML day^{-1}) had the longest water residence time (14.8 days) and contributed the lowest total phosphorus (TP) and total nitrogen (TN) loads (TP: 10.2 kg yr^{-1} and TN: 81.0 kg yr^{-1}). In comparison, the high flow class (46 to 300 ML day^{-1}) had the shortest water residence time (0.1 days) and contributed the highest nutrient loads (TP: 433.4 kg yr^{-1} and TN: 1726.2 kg yr^{-1}). The percentage of TP and TN retention (TP: 60 to 69% and TN: 18 to 76%) showed that nutrient loads at the inflow were greater than that of the outflow after the construction of the wetland in 2006. Therefore there was a net retention of nutrients in the Cox Creek wetland system during the study period, suggesting it is effective at reducing nutrient loads passing downstream.

In order to investigate the ability of macrophytes to store nutrients, the seasonal TP and TN storage by *Schoenoplectus validus* and *Phragmites australis* were compared between

Reed Bed and Pond 1 of Cox Creek wetland system. The TP and TN storage were significantly higher in Reed Bed (TP: 22.0 gP m^{-2} and TN: 118.5 gP m^{-2}) than in Pond 1 (TP: 1.0 gP m^{-2} and TN: 10.3 gP m^{-2}). TP storage peaked in spring 2008 for *S. validus* and *P. australis* in Pond 1. This was also the case for *S. validus* in Reed Bed, but TP storage peaked in summer 2009 for *P. australis* in Reed Bed. TN storage peaked in spring 2008 by both species in Reed Bed. This was also the case for *S. validus* in Pond 1, but TN storage peaked in summer 2009 for *P. australis* in Pond 1. Based on the results, it appears that the presence of macrophytes can reduce nutrient loads passing downstream, with the amount of nutrients stored highest during spring and summer. Therefore, the best timing for harvesting for removal of wetland nutrients is after spring, when nutrient storages are expected to be highest, preferably in mid summer season.

The sediment redox potential was higher in Reed Bed than in Pond 1, suggesting macrophytes may have the ability to release oxygen from roots and increase phosphorus (P) adsorption in Reed Bed. Using P adsorption-desorption experiments, the equilibrium P concentration (EPC) was calculated as a measure the P adsorption capacity of sediments in Reed Bed and Pond 1. EPC is used to identify sediment as a source or sink of P. When P concentration of porewater is greater than the EPC, then the sediment will adsorb P and vice versa. The EPC values were lower in Reed Bed than in Pond 1, indicating greater P adsorption capacity of Reed Bed sediment than Pond 1 sediment. Phosphorus fractionation of the sediments showed that of the inorganic forms of P (loosely sorbed-P, Ca/Mg-P and Fe/Al-P) and the Fe-P was consistently higher in Reed Bed than in Pond 1. Under oxidised conditions, the ferric ion complexes adsorb P, reducing the amount of P available for diffusion to the overlying water. Therefore, it appears oxygen release by macrophytes in Reed Bed may promote P storage in sediments, with greater P-binding capacity in Reed Bed than Pond 1.

Sedimentation was determined as the main process that determines the nutrient retention capacity of the Cox Creek wetland system. Based on measured sedimentation rates at the inlet and outlet of Reed Bed and Pond 1 in three different flow events, the average of sedimentation rate across the study was 2.2 kg m^{-2} yr^{-1}. Even though the presence of vegetation has been shown to enhance sedimentation elsewhere, P accumulation rates were greater in Pond 1 (0.4 to 4.6 kg m^{-2} day^{-1}) than in Reed Bed (0.3 to 2.0 kg m^{-2} day^{-1}). This is likely a result of greater inflowing loads of sediment and nutrients in Pond 1 than in Reed Bed. Pond 1 receives water from both sedimentation pond and Reed Bed whereas Reed Bed only receives overflow from the sedimentation basin.

In order to quantify the performance of the Cox Creek wetland system for reducing P exports, a P mass balance was calculated. This study found that 281.6 kg yr^{-1} of P is retained in the wetland. Although there is an unaccounted amount of P in the mass balance (112 kg yr^{-1}), the relative contributions of uptake by macrophytes (36 kg yr^{-1}), sediment P adsorption (43.5 kg yr^{-1}) and sedimentation (90.1 kg yr^{-1}) are believed to be the most important mechanisms in P removal. Consequently, wetland design and operation should aim to promote these processes to maximise P removal. This should include increasing macrophyte diversity, using nutrient-poor sediments as substrate and increasing residence time of water to create favourable conditions for sedimentation in the wetland.

Chapter one

1 General introduction

1.1 Eutrophication

Currently, water pollution is a major problem throughout the world. The main sources of water pollution are: industrial effluents (e.g. chemicals, organics, and thermal wastes), municipal wastes (e.g. sewage, organics and detergents) and agricultural wastes (e.g. animal manures, pesticides, and fertilisers) (Sharpley *et al*. 1994; Ekholm *et al.* 2000). Indiscriminate human activities such as large-scale land clearing, logging and housing development disrupt and alter natural river systems with regards to water quantity and quality as well as natural habitats (Tam and Wong 1996; Rydin 2000; Harris 2001). Pollution degrades the natural capital of the world by causing natural wetland and groundwater contamination, reducing plant and wildlife habitats, and altering aquatic ecosystems.

Many estuaries, rivers, reservoirs and lakes around the world suffer from artificial eutrophication, the nutrient enrichment of surface water caused by human activities (Young *et al.* 1996). Eutrophication is caused by excessive anthropogenic inputs of the nutrients into the water bodies from various sources (e.g. agriculture, housing and industry). Nitrogen (N) and phosphorus (P) are often considered most important because they are generally the most limiting nutrients in aquatic ecosystems (Schindler 1977; Sharpley *et al.* 1994). Eutrophication is a global water quality problem affecting natural waterways. Symptoms of eutrophication include increased algal and aquatic plant biomass, oxygen depletion, pH variability and disruption to the natural food chain (Smith 2003; Smith and Schindler 2009). One of the major impacts of eutrophication is the increased incidence of nuisance algal blooms, which can degrade water quality by depleting dissolved oxygen (anoxia), producing foul odours and affecting taste (Boulton and Suter 1986; Sharpley *et al*. 1994; Boulton 1999;

Jacob 2002). These blooms can restrict the beneficial use of surface water for fisheries, recreational, industrial and drinking purposes and increasing water treatment cost (Sharpley *et al*. 1994; Smith 2003). There are also environmental costs, with increased respiration of microorganisms associated with the build-up of organic material reducing dissolved oxygen in the water. Consequently, fish and other aquatic organisms which depend on the "healthy" ecosystems as a food source and shelter will leave the area or die.

Improved understanding of eutrophication processes is necessary to develop sustainable practices for watersheds and reservoir management. To improve water quality it is important to identify the causes of eutrophication and understand nutrient sinks, sources and transformations. Due to difficulties in controlling the air-water exchange of N and carbon (C), most studies have focused on P as the limiting nutrient for excessive algal growth in freshwater (Sharpley *et al*. 1994; Craft 1997; Nungesser and Chimney 2006). By controlling the P inputs from non-point sources of pollution (e.g. agricultural runoff), the impacts of eutrophication on downstream areas can be reduced. Wetlands are considered 'hot spots' for nutrient cycling and function as nutrient sinks when the input is greater than the output of a particular nutrient. If the level of output exceeds the input, a wetland is considered as a nutrient source. In cases where the level of output and input of nutrient is similar, but in different form, the wetland is considered as a transformer of nutrients (Mitsch and Gosselink 2000).

1.2 Constructed wetland systems as water treatment facilities

Constructed wetland systems can be defined as engineered complexes of substrates (sediment soils), water column, macrophytes and microbial communities that has been developed for water quality improvements (Brix 1994; Hammer 1997; Mitsch and Gosselink 2000; Katsenovich *et al.* 2009). They support a large variety of plants and animal species that are adapted to periodic fluctuating water levels. The soils of these highly productive ecosystems are more or less continuously waterlogged, despite periodic fluctuations in water level (Mitsch and Gosselink 2000). They consist of both biotic (e.g. plants, animals and microorganisms) and abiotic components (e.g. water, soil, sediment and air) (Kadlec and Knight 1996; Reddy *et al.* 1999). There is an increasing demand for constructed wetlands in water pollution management as communities seek to improve water quality and replace habitat that has been lost due to human development.

Research on the use of constructed wetlands for restoration of water pollution began in the 1950's and has increased substantially in the last 20 years largely due to public interest in "green" water treatment technology (Kadlec and Knight 1996; Greenway and Wooley 1999; Kadlec *et al.* 2010; Zhang *et al.* 2010). Constructed wetlands have several advantages over the conventional water treatment methods including: the ability to tolerate variable loading; relatively low construction and maintenance cost; improved habitat for aquatic organisms; increased aesthetic value and recreational opportunities (Bolton and Greenway 1994; Reddy and Gale 1994; IWA 2000). As well as reducing downstream nutrient exports, constructed wetlands provide many ecosystem services, including: facilitating the storage, decomposition and reconstitution of organic matter; reducing pollutants before they enter the receiving water bodies; providing habitats for aquatic life; filtering out pathogenic organisms; and lessening the severity of flood runoff through storage and the natural adsorption of water into the soil (Moore *et al.* 1994; Kadlec and Knight 1996; Brix 1997; Tanner *et al*. 1999; Mitsch and Gosselink 2000).

Constructed wetlands are capable of treating water pollutants at various latitudes and different climatic conditions in various seasons (Kadlec 2009). There is a wide range of interrelated physical, biological and chemical mechanisms within constructed wetland systems that enable water quality improvements. These mechanisms include biochemical conversion, evapotranspiration, volatilization, settling of suspended particulate matter, filtration, chemical precipitation, adsorption and ion exchange of pollutants onto sediments, and direct uptake of nutrients by macrophytes and microorganisms (Reddy *et al.* 1999; Kadlec and Knight 1996). The most effective constructed wetlands are those that can promote all these mechanisms.

The residence time of water in a wetland largely determines effectiveness of wetland system. Longer residence times may create favourable conditions for the settlement of particles, so increasing the effectiveness of the wetland system to retain nutrients (Craft 1997; Wen 2002). Therefore, constructed wetlands are designed to reduce the flow velocity of water, allowing fine suspended sediment particles to settle out from the water column. The calm conditions and shallowness in constructed wetlands encourage the settlement of particles with their associated nutrients, resulting in greater retention of nutrients. Besides sedimentation, design of constructed wetlands should encourage other mechanisms such as sediment adsorption, macrophytes uptake and microbial decomposition, to enhance a good performance for treating agricultural runoff.

The nature and type of chemical constituents in the solute of wetland sediments also play an important role in the retention and conversion of pollutants. As such, the soil organic content, texture, ion-exchange, pH and redox potential are important factors requiring further investigation for the improvement of wetland efficiency. A high capacity of sediment to adsorb phosphorus is a priority for most constructed wetlands, in which sediment serves as an efficient phosphorus trap (Craft and Casey 2000; Søndergaard *et al.* 2001; Börling 2003). Nowadays, constructed wetland systems may make an important contribution to reduce point and non-point sources of pollution including agricultural runoff, industrial effluent and municipal wastewater (Table 1.1). Constructed wetlands have proved to be effective in the control of P losses from agricultural land to water bodies. For example, in the Lower River Murray, South Australia, the average P removal efficiency was 44.2 percent using a pilot-scale constructed wetland (surface area: 5 m^2) for the treatment of agricultural drainage water from dairy farms (Wen 2002).

Table 1.1: Performance of constructed wetland systems for removal of water pollutants

Sources	**Types of wetlands**	**HLR ($L\ d^{-1}m^{-2}$)**	**TN retention (%)**	**NH^4-N retention (%)**	**NO^3-N retention (%)**	**TP retention (%)**	**Country**	**References**
Agricultural								
i) Runoff	SF	340	46	88	99	89	The United States of America	Carleton *et al*. 2001
ii) Swine	SF	230	99	94	NA	94	The United States of America	Cronk 1996
iii) Dairy farm	SSF	70	48	34	NA	37	New Zealand	Tanner *et al*. 1995
Industrial								
i) Cheese dairy	SSF	30	45	30	NA	52	Germany	Kern and Idler 1999
ii) Meat processing	SSF	50	21	NA	NA	27	New Zealand	Oostron and Cooper 1990
Municipal	SF	40	50	29	70	9	Australia	Greenway and Wooley 1999
	SF	10	77	NA	NA	22	Australia	Sakadevan and Bavor 1999
	SSF	120	77	97	NA	44	The United States of America	House *et al*. 1999
	SSF	50	64	59	73	55	China	Li *et al*. 1995

*Note: SSF, Subsurface flow constructed wetlands; SF, Surface flow constructed wetlands; HLR, Hydraulic loading rates; TN, Total nitrogen; NH^4-N, nitrate-N; NO^3-N, nitrite-N; TP, Total phosphorus

1.3 Phosphorus retention mechanisms

Phosphorus (P) present can be classified into two different forms: particulate P and dissolved P. Both particulate P and dissolved P include various forms of organic and inorganic P. For the most part, dissolved P is readily available for biological uptake while particulate P can provide a long-term source of P for aquatic plant growth (Sharpley *et al*. 1994). Particulate P becomes bioavailable through the conversion to dissolved P. These reactions are influenced by the surface area, pH and redox potential of the substrate and temperature (Reddy and D'Angelo 1997).

Mechanisms for P retention within constructed wetlands are primarily by the processes of sedimentation, biological uptake (e.g. macrophytes, phytoplankton) and sediment adsorption (Figure 1.1; modified from Reddy *et al*. 1999). P can either be sequestered by the binding of P in organic matter as a result of incorporation into living biomass or precipitation of insoluble phosphates with magnesium (Mg), ferric iron (Fe), calcium (Ca), aluminum (Al), manganese (Mn) and particulate P adsorption onto clay particles. (Kelderman *et al.* 2007). A large quantity of particulate P can be settled into wetland sediments, if the inflowing runoff contains a high level of suspended solids, due to slow flow velocity (Walbridge and Struthers 1993). In sediments, settled P can be buried in its original forms or involved in various physico-chemical and biological reactions prior to final burial as inert material in sediments (Gonsiorczyk *et al*. 2001; Wen 2002; Baldwin and Williams 2007). However, the movement of benthic animals and wave activity can resuspend settled sediment particles. Therefore, P bound by the settled sediment sediment may also be released into the water column.

The presence of vegetation distributes and decreases the flow velocity of water, which encourages sedimentation of suspended particles (Brueske and Barret 1994; Brix 1997). The roots system provides an excellent support medium for bacteria and for filtration of suspended solids (Wigand *et al*. 1997; Stephen *et al*. 1997; Huang *et al*. 2010). Additionally, macrophytes assimilate P in order to meet their nutritional requirements (Brix 1997; Liu *et al*. 2000). In addition, macrophytes have the ability to influence the redox potential, which is an important determinant of the exchange of P between the sediment and water column (Holtan *et al.* 1988; Sundby *et al.* 1992; Khosmanesh *et al.* 1999). In transferring oxygen to their below ground biomass, macrophytes inadvertently release oxygen into sediment (Jensen and Andersen 1992; Moore *et al*. 1994; Wigand *et al*. 1997; Wen 2002), increasing the sediment redox potential and the P adsorption capacity of the wetland sediments (Carpenter *et al.* 1983; Brix 1997; Reddy and D'Angelo 1997). Oxygenated sediments retain P by fixation to iron (III) (Fe^{3+}) while reduced sediments release P by reduction of iron and subsequent dissolution of $FeOOH\text{-}PO_4$ complexes (Roden and Edmonds 1997). The equilibrium phosphorus concentration (EPC) and P adsorbed by sediment have been used extensively to qualify and predict the retention capacity of wetland sediments (Olsen and Wanatabe 1957; Barrow 1978; Reddy *et al.* 1995; White 2000). EPC can be defined as P concentration in which adsorption by solid phase equals to desorption, thus higher EPC indicates a low P sorption capacity and vice versa.

The P adsorption by wetland sediments provides long-term P retention in constructed wetlands (Walbridge and Struthers 1988; Johnston 1991), where adsorption and desorption are the dominant processes governing the behavior of dissolved P in solutions (Bache and Williams 1971; Phillips *et al.* 1994). As the wetland system "ages", sediments can reach a state of P saturation due to saturation of a finite number of adsorption sites (Richardson 1985; Mann 1990; Kadlec and Bevis 1997). In addition, decomposing organic matter tends to increase the release of P from sediment to water column, owing to the sorption capacity of the sediment. Subsequently, the sediments may become a net source of P to the overlying water column and the wetland may become a net source to downstream ecosystems.

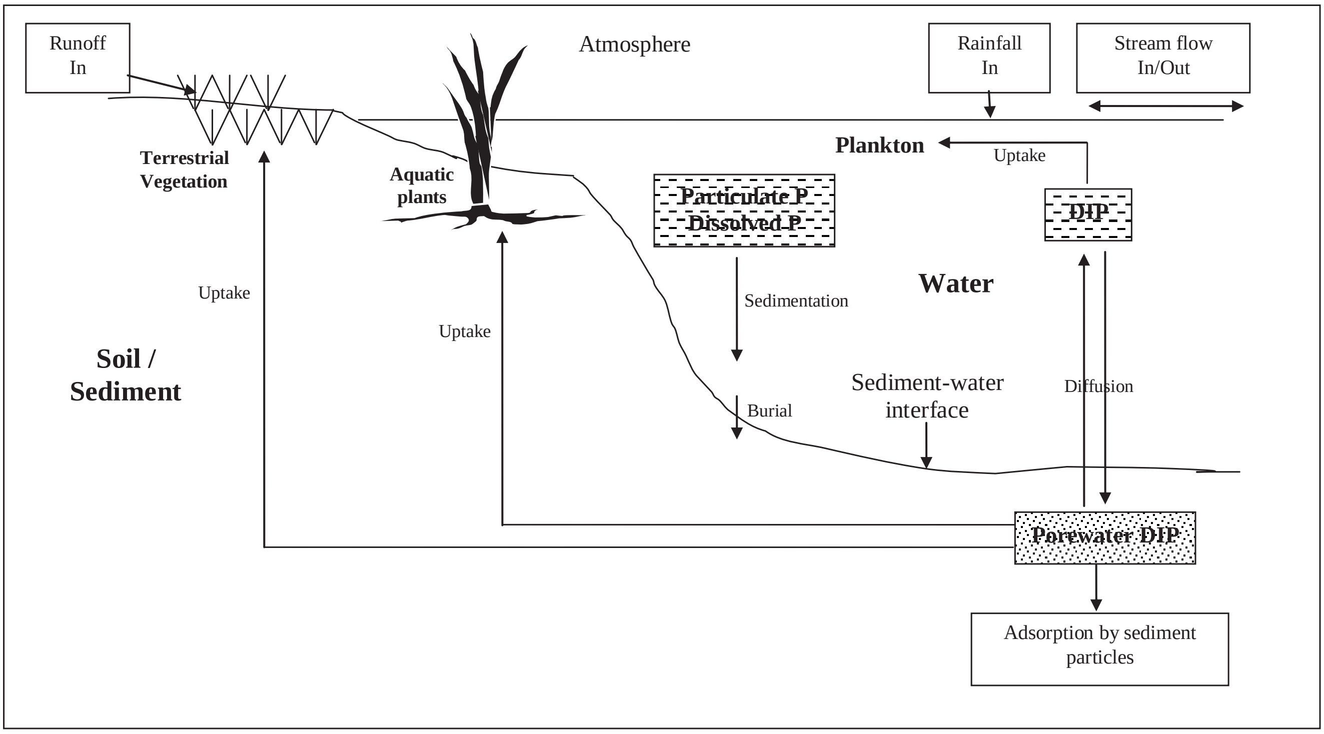

Figure 1.1: Conceptual diagram of phosphorus mass balances in the water column and sediments in the Cox Creek wetland. P, phosphorus; DIP, dissolved inorganic phosphorus. Modified from Reddy *et al*. 1999.

1.4 The project

1.4.1 Sources and management of phosphorus in the Cox Creek sub-catchment

Generally, intensive horticultural farms apply fertilisers in order to increase crop yields. However, high fertiliser application will increase the levels of nutrients mobilised during runoff events. In the Cox Creek sub-catchment, South Australia (SA), the effects of land use practices, mainly from crop production and vineyards, contribute large amounts of sediments and nutrients to the streams (Fisher 2005; Bradley *et al*. 2007). This is a result of historical land use where high rates of fertiliser were applied to intensive agricultural land, resulting in the area having a disproportionately large impact on P supply to downstream water bodies (Weaver and Reed 1998; Ekholm *et al.* 2000). Consequently, management practices aimed at altering P exports were made. This included minimising P availability in the upper area of the Cox Creek sub-catchment by improving land management such as reduction in application rates of fertiliser, planting of buffer strips and improving quality of cover crop (e.g. green manure cropping and mulching between vegetable crops). In addition, a sedimentation basin and constructed wetland system were implemented in 2006 by the SA Water Corporation to reduce nutrient loading from agricultural runoff.

1.4.2 Objectives of the study

The overall objective of this research is to assess the efficiency of the Cox Creek wetland system to retain P inputs from the surrounding agricultural catchment area. In addition, the importance of different retention mechanisms under various flow conditions was explored to gain a better understanding of the functioning of the Cox Creek wetland system. In achieving the project objectives, the following research questions were investigated:

1) How efficient is the functioning of the Cox Creek wetland system? (Chapter three)
2) Do macrophytes influence P retention capacity? (Chapter four)
3) Does sediment P adsorption influence P retention capacity? (Chapter five)
4) Does P sedimentation influence P retention capacity? (Chapter six)

In order to address these questions, four major hypotheses were identified:

1) The Cox Creek wetland system is relatively immature and will have a high affinity for P and so will be efficient at removing P. However, under high flow conditions, the ability of the wetland system will be reduced due to decreased water residence time.

2) Macrophytes will act as a significant storage of P and promote P storage in sediments. Therefore sections of the wetland containing macrophytes will have a greater storage capacity for P than those without.

3) Upstream sediments of the wetlands are exposed to higher P loads and so will be more saturated with P compared to downstream areas. Consequently, the ability of sediments to adsorb P will increase longitudinally through the wetlands. In addition, it is expected that the vegetated pond will have a lower equilibrium phosphorus concentration (EPC) and therefore a higher P retention capacity than the unvegetated pond. This is due to the ability of macrophytes to transfer oxygen to their below ground biomass and inadvertently release of oxygen into sediment. Consequently, those macrophytes may increase the sediment redox potential and the P adsorption capacity of the sediments.

4) Macrophytes will slow the flow velocity of water and so the vegetated pond will have greater sedimentation and P accumulation than the unvegetated pond. In addition, high flow events will transport more particles, will result in a higher sedimentation rates compared to low flow event.

Information developed within the project is used to propose potential improvements to management of the Cox Creek wetland system for better water quality conditions.

Chapter two

2 Study site

2.1 Background

The Cox Creek sub-catchment encompasses an area of approximately 2600 ha (Figure 2.1). The Cox Creek originates from the eastern slopes of Mount Lofty and Mount Bonython and flows through the Piccadilly Valley (Bradley *et al*. 2007). The topography of this sub-catchment is characterised as steep hills in the headwaters. Further downstream the Cox Creek flows through the towns of Bridgewater and Aldgate before joining the Onkaparinga River. The Onkaparinga River then feeds into Mount Bold reservoir, which supplies approximately 40% of the drinking supply of Adelaide, which has a population of approximately 1.3 million people (Tonkin Consulting 2002; Fisher 2005; Bradley *et al*. 2007). The region has warm, dry summers and cool, wet winters (Wen 2002; Kim 2009).

The Cox Creek sub-catchment is a major source of nutrients to the Mount Bold Reservoir, with nutrient concentrations often exceeding levels recommended by the Australian and New Zealand Environment Conservation Council and the EPA Water Quality Policy 2003 (ANZECC 2000; Bradley *et al*. 2007). The impact of these high loads result in poor ecological stream health within the sub-catchment and downstream reaches (Ingleton 2003). Even though Cox Creek sub-catchment comprises only 1.5% of the area of the Onkaparinga River Catchment, it carries disproportionately high loads of nutrients (27% of TP and 34% of TN) and sediment (41% of SS) to the Mount Bold reservoir (Fisher 2005). Flow in Cox Creek is highly variable and ceases during most of summer and autumn. Generally, the majority of nutrients enter Cox Creek during high flow events driven by rainfall (Fisher 2005). In addition, Cox Creek experiences groundwater flow (base flow) throughout the whole year, the majority of which occurs in winter and spring. These high nutrient loadings increase the incidence of algal blooms (e.g. cyanobacteria), which produce toxic compounds and create taste and odour problems in drinking water. Consequently, the efficient control of the nutrient loadings from Cox Creek may lower the risk of outbreaks of algal blooms in the Mount Bold Reservoir.

NOTE:
This figure is included on page 12 of the print copy of the thesis held in the University of Adelaide Library.

Figure 2.1: Location of the upper Cox Creek sub-catchment within the Onkaparinga River catchment (Fisher 2005).

High nutrient loadings in the Cox Creek sub-catchment result from historical rather than current land practices (Ingleton 2003; Bradley *et al*. 2007). The area has long been recognised for vegetable production and horticulture, which utilise inorganic fertilisers to increase vegetable production (Fisher 2005). However, more recently land practices have changed due to increase demand for residential properties, which has decreased the amount of land being used purely for vegetable production and horticulture. However, this change in land use is unlikely to result immediate reductions of nutrient loads, since much of the nitrogen and phosphorus applied as fertilisers may remain in the soil or groundwater for several years (Fisher 2005; Bradley *et al*. 2007). The proportion of land use activities throughout the sub-catchment are currently intensive broad scale grazing (38%), vegetable production (4%), vineyards (7%), urban areas (24%) and protected areas (10%). Less than 20% of the area exists as native vegetation (Ingleton 2003; Fisher 2005; Bradley *et al*. 2007).

Due to the disporportionate impact of the Cox Creek sub-catchment of nutrient loads to Mount Bold Resevoir, the South Australian Water Corporation (SA Water) constructed a wetland system (Figure 2.2) within the Cox Creek sub-catchment. The design of the wetland system, along with broad scale rehabilitation of riparian areas, were aimed at reducing nutrient exports from the sub-catchment and reducing nutrient concentration and the frequency of algal blooms in the downstream Mount Bold reservoir. An additional aim was to improve river health in the Cox Creek sub-catchment. These works were completed in August 2006.

Figure 2.2: Location of the Cox Creek wetland system within the Cox Creek sub-catchment and path of flow ····· from Piccadilly valley to Mount Bold.

2.2 Phosphorus transport into the Cox Creek sub-catchment

Phosphorus is transported as dissolved and particulate forms and reaches watercourses through surface runoff, erosion and leaching of groundwater (Sharpley *et al*. 1994; Kadlec and Knight 1996). Phosphorus forms are transported by stream flows through the upstream area and exported to the downstream water bodies, with phosphorus cycling occurring as phosphorus is passed downstream, as described by the nutrient spiraling concept (Newbold *et al.* 1983; Stream Solute Workshop 1990). The main pathway of transport of phosphorus in the Cox Creek sub-catchment appears to be transportation of sediment and soils, as shown in Figure 2.3. Phosphorus transported to Cox Creek is mainly from non-point sources associated with agricultural runoff (fertiliser application), irrigation water, manure and breakdown of primary producers/plants (Chittleborough 1983; Fisher 2005). Phosphorus attaches to soil particles through adsorption, forming iron-phosphorus complexes in either the overlying oxic sediments or the oxic part of the water column (Moore and Reddy 1994; Webster *et al*. 2001). Since phosphorus is commonly associated with soil particles, it enters waterways following erosion of catchment soils or riverbanks, a process which is accelerated by vegetation clearing from adjacent land (Craft and Richardson 1993; Behrendt and Opitz 2000).

Most of the particulate and dissolved phosphorus is introduced into the Cox Creek during high flow periods, particularly during rain events (Fisher 2005). The annual load of phosphorus is highly variable and largely reflects changes in stream discharge. Flows in autumn (April-May) always contribute greater nutrient loads than in the spring (October-November) due to the greater amount of rainfall.

Figure 2.3: Conceptual diagram of phosphorus sources and transport within the Cox creek wetland. Modified from Fisher (2005).

2.3 Cox Creek wetland system

Cox Creek wetland system originated from a series of intensive investigations in the late 1980’s and early 1990’s between Department of Primary Industries and Resources of South Australia (PIRSA) and The Commonwealth Scientific and Industrial Research Organisation (CSIRO). Even though improved land management practices had been implemented, subsequent monitoring and analysis conducted by SA Water, the Environmental Protection Agency and the Onkaparinga Catchment Water Management Board had shown that water quality was still poor. In 2004/2005, Australian Water Environment (AWE) conducted a feasibility study for nutrient reduction in the Cox Creek sub-catchment. They suggested that the use of a sedimentation basin and a series of wetland ponds could reduce pollutant loads and intercept nutrients in the stream flow. In August 2006, the construction of the Cox Creek wetland system, consisting of two complex engineered systems was completed: Brookes Bridge sedimentation basin and Woodhouse Wetland.

2.3.1 Brookes Bridge sedimentation basin

A sedimentation basin was constructed at the upstream of Brookes Bridge on Swamp Road (34°58’23.25”S, 138°44’8.16”E) (Figure 2.4 and Figure 2.6), which is approximately 1.5 km south of Summertown (Figure 2.2). This offline sedimentation basin was designed to capture sediment loads originating from erosion in the upper Cox Creek area. Since there was a strong relationship between suspended sediment loads and nutrient concentration (Stubbs *et al.* 2004; Stutter *et al.* 2009; Ghosh and Gopal 2010), the sedimentation basin was designed to capture fine sediment particles and associated nutrients. The design of the sedimentation basin allows for the regulation of water flows at three flow scenarios, following the Hydraulic Modelling study using the HEC-RAS model (Fisher 2005). In late summer flow, the sedimentation basin was expected to receive 0.2 ML day^{-1} of water flow. This low flow represents a stream flow generated by groundwater (base-flow). In winter flow, there was an increase in water level and the sedimentation basin was expected to receive 9 ML day^{-1} of water flow from both groundwater and surface runoff. When the sedimentation basin was subjected to 1 in 100 Annual Exceedence Probability (AEP) flow, the sedimentation basin was expected to receive 864 ML day^{-1} of water flow which represents very infrequent and extremely high flow events. The construction of concrete weir from the offline sedimentation basin allows water to bypass the sedimentation basin during high flood levels (Figure 2.7) (Fisher 2005). The water depth in the sedimentation basin can reach up to 2.5 m at its full capacity.

2.3.2 Woodhouse Wetland

A series of in-stream wetland ponds was constructed downstream of Brookes Bridge (34°59’2.62”S, 138°44’12.74”E) (Figure 2.5), which is approximately 1 km east of Piccadilly (Figure 2.2). The location was selected in order to reduce nutrient input associated with runoff from the upper area of the Cox Creek sub-catchment. The purpose of the wetlands was to reduce flow rates and act as “biological filter”. The wetland was designed to increase the residence time of water by reducing the volume of water flowing into the wetland, allowing fine suspended sediment particles to settle out of the water column. As for the flow regulation in the Brooke Bridge sedimentation basin, water flow through this wetland is also highly regulated. Following three flow scenarios using the HEC-RAS model, the wetlands are expected to receive 0.32 ML day^{-1} of water flow in late summer flow. The wetlands are expected to receive 25 ML day^{-1} and 1495 ML day^{-1} of water flow during winter flow and 1 in 100 AEP flow, respectively. Similar to Brookes Bridge sedimentation basin, the construction of a concrete weir within Woodhouse Wetland allows water to bypass the wetland during high flood levels (Figure 2.7) (Fisher 2005). Flow paths, surface areas and vegetation types of the wetlands were designed to maximise nutrient uptake from the water column.

2.3.2.1 Sedimentation pond

The sedimentation pond is the first pond of the Woodhouse wetlands (Figure 2.5). The sedimentation pond was designed to increase retention of suspended sediments and associated nutrients accumulated in the pond. The area of this pond is 3445 m^2 and the volume of water can reach up to 3.7 ML at its full capacity. The water flows to Pond 1 and Reed Bed at the outflow by natural gravity.

2.3.2.2 Reed Bed

Reed Bed pond was placed parallel to Pond 1 (Figure 2.5 and Figure 2.8). The aquatic plants found in Reed Bed are *Phragmites australis*, *Schoenoplectus validus*, *Typha domingensis*, *Eleocharis acuta*, *Juncus pallidus* and *Juncus sarophorus*. The dominant plant species in Reed Bed are *P. australis* and *S. validus*. Reed Bed pond was constructed in order to increase uptake of nutrients by plants to be stored in the plant biomass. Reed Bed recieves water from the outflow of sedimentation pond during high flow events (intermittent flow). The area of this pond is 1070 m^2 and the volume of water can reach up to 0.3 ML at its full capacity. Water from Reed Bed flows to Pond 1 at the outflow.

2.3.2.3 Pond 1

Pond 1 functions as a second sedimentation pond and therefore no vegetation was planted (Figure 2.5 and Figure 2.9). However, some native aquatic and terrestrial plant species occur around the margins of Pond 1. Some native colonising aquatic plant species found in Pond 1 are Common Reed *Phragmites australis* and Bulrush *Typha domingensis.* Apart from that, seedlings of Red Gum *Eucalyptus camaldulensis* often germinate on mass as a result of drawdown after flooding in the wetland. Pond 1 receives water from both the sedimentation pond and Reed Bed and therefore most of the remaining suspended solids were expected to be settled in this pond. In addition, the presence of most native vegetation is expected to increase nutrient uptake by the plant species. The area of this pond is 705 m^2 and the volume of water can reach up to 1.1 ML at its full capacity. Water from Pond 1 flows to Pond 2 at the outflow.

2.3.2.4 Pond 2 and Pond 3

The two remaining treatment ponds were located downstream of Pond 1: Pond 2 and Pond 3 (Figure 2.5). The area of Pond 2 is 2430 m^2 and the volume of water can reach up to 2.5 ML at its full capacity. Pond 3 is the last pond in the Cox Creek treatment system with the area of 930 m^2 and the capacity to hold water up to 1.2 ML. It is expected that these ponds would provide more area for the retention of the remaining pollutants from the upstream water bodies. The suspended solids and associated nutrients would be removed and accumulated in these ponds before leaving the whole wetland system.

NOTE:
This figure is included on page 20 of the print copy of the thesis held in the University of Adelaide Library.

Figure 2.4: Aerial photo of Brookes Bridge sedimentation basin, located upstream of the bridge on Swamp Road. Note that arrows represent flows of water through the sedimentation basin from the upper Cox Creek sub-catchment.

NOTE:
This figure is included on page 21
of the print copy of the thesis held in
the University of Adelaide Library.

Figure 2.5: Aerial photo of Woodhouse wetland. Note that arrows represent flows of water through the wetland system from the downstream of the Brookes Bridge sedimentation basin.

Figure 2.6: Photo of the offline Brookes Bridge sedimentation basin. Note that arrow represent the inflow of water through the sedimentation basin from the upper Cox Creek sub-catchment.

Figure 2.7: Photo of construction of concrete weir from the offline Brookes Bridge sedimentation basin. Note that similar construction of a concrete weir within Woodhouse Wetland allows water to bypass the wetland during high flood levels.

Figure 2.8: Photo of Reed Bed within Woodhouse Wetland. Note that Reed Bed only recieves intermittent flow from the outflow of sedimentation pond during high flow events and was placed parallel to Pond 1.

Figure 2.9: Photo of Pond 1 within Woodhouse Wetland. Note that Pond 1 receives water from both the outflows of sedimentation pond and Reed Bed.

Chapter three

3 The influence of discharge on the effectiveness of the Cox Creek wetland system at reducing nutrient loads for different flow classes

3.1 Introduction

Australian rivers have the most temporal hydrological variability in the world (Boulton and Suter 1986). A number of Australian studies have shown that Australia experiences many storm events which can transport large amounts of sediments and nutrients over short time intervals (Cullen and O'Loughlin 1982; Browning 2003; Linden *et al.* 2004; Hart *et al.* 2006). The majority of the total sediment and nutrient loadings enter streams and storages (e.g. lakes or reservoirs) during these storm events. These extreme events can lead to algal bloom formation in lakes and reservoirs for years after the events. Therefore, the construction of wetland at the upper area of a catchment could reduce nutrient export by slowing down the flow and providing an area for nutrient retention.

Phosphorus (P) is the key nutrient that limits primary productions in many freshwater wetlands (Mitsch and Gosselink 2000; Mitsch *et al.* 2000). Phosphorus occurs naturally in both organic and inorganic forms and as dissolved and particulate forms (Phillips *et al.* 1994; Reddy *et al.* 1999; Kelderman *et al.* 2007). Dissolved organic phosphorus and particulate forms of organic and inorganic phosphorus are generally not biologically available until transformed into soluble inorganic forms (Mitsch and Gosselink 2000). Dissolved phosphorus consists of mostly inorganic phosphorus (mainly orthophosphate) and some organic phosphorus (Wen 2002; Wen and Recknagel 2006). On the other hand, particulate phosphorus encompasses all solid phase forms, including phosphorus sorbed on soil particle surfaces and organic matter transported during runoff. Particulate phosphorus contributes the major proportion (75-90%) of phosphorus transported from agricultural land (Sharpley *et al*. 1994).

Agricultural runoff may also contain high concentration of nitrogen resulting from the application of fertilisers and manures. The dominant forms of nitrogen in wetland systems include organic and inorganic nitrogen; ammonia (NH_3), ammonium ion (NH_4^+), nitrate (NO_3^-), nitrite (NO_2) and nitrogen gases (N_2) (Patrick and Tusneem 1972; Boon and Sorrel 1991; Wetzel 1993; Bernot and Dodds 2005; Hernandez and Mitsch 2007). The biological transformation of organic nitrogen to inorganic nitrogen occurs during organic matter degradation, or mineralisation (Mitch and Gosselink 1993). Nitrate and ammonium are bioavailable forms of mineralised nitrogen in wetlands Ammonium ions can be converted back to organic matter by assimilation by aquatic organisms or converted to oxidized nitrogen (NOx) and can be bound onto negatively charged soil particles (Patrick and Tusneem 1972; Mitch and Gosselink 1993; Wetzel 1993).

The implementation of the sedimentation basin and wetland system in the Cox Creek catchment was based on “A feasibility study on nutrient load reductions for the Upper Cox Creek” (Fisher 2005). This study used hydraulic modelling and found that both systems were hydraulically feasible, with the modelled velocities low enough for nutrient settling during low flows and preventing scouring of settled sediment during high flow events. The justifications for the site selection of the sedimentation basin and wetland systems were described in section 2.3. This study aims to assess the performance of the Cox Creek wetland system in reducing sediment and nutrient loads from the Cox Creek to downstream water bodies. To do this, the effectiveness of the Brookes Bridge sedimentation basin and Woodhouse wetlands as engineered constructed wetland in the Cox Creek sub-catchment was assessed. The influence of discharge on the ability of the Cox Creek wetland system to retain nutrients and sediments was also assessed.

3.2 Methods

3.2.1 Rainfall measurement

Daily rainfall from January 2004 to December 2009 was obtained from the Australian Bureau of Meteorology. This data was collected at the rainfall station at Piccadilly (Woodhouse).

3.2.2 Composite sampling and water analysis

Composite water samples were collected over the hydrograph with an accumulated flow triggered auto-sampler from upstream Brookes Bridge sedimentation basin (Figure 2.4) and downstream of Woodhouse wetlands (Figure 2.5). This equipment automatically captures a constant volume of water (e.g. 500 mL) in a predetermined volume of flow (e.g. 10 ML) that passes the sampling point. The flow rate is measured on a continuous basis and recorded by a data logger. The chemical analysis of collected water samples was performed at the Australian Water Quality Centre (AWQC) according to the National Drinking Water Guidelines standards, under the framework of a Quality Management System (WDS - NATA AS / NZS ISO 9001/2000). Analytical data was sourced from Mr. Frank Enzmann (SA Water) including suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx). This study used data from 2004 to 2009 upstream of sedimentation basin. However, downstream of the wetlands only data from 2007 to 2009 were available. For this period it was possible to assess the retention capacity of the wetland by comparing differences between upstream and downstream sites. The inclusion of data from upstream from 2004 to 2009 offered an opportunity to compare of nutrient availability prior to the construction of the wetland.

3.2.3 Flow rate classification

The measured daily flow rates at both Brookes Bridge sedimentation basin and Woodhouse wetlands were divided into six different classes: (1) 0 to 1 ML day^{-1}, (2) 2 to 5 ML day^{-1}, (3) 6 to 15 ML day^{-1}, (4) 16 to 30 ML day^{-1}, (5) 31 to 45 ML day^{-1} and (6) 46 to 300 ML day^{-1} for each year. These flow classes were then used to calculate number of days, flow volume, water residence time and loads of SS and nutrient for each corresponding flow class in each year. The flow rates were classified to evaluate the changes in water quality in each year under similar flow conditions.

3.2.4 Water residence time

The water residence time was calculated for each flow class for both sedimentation basin and wetlands in order to analyse relationships between the water residence time and nutrient retention. The water residence time (WRT) was calculated using the following equation:

WRT (days): V / Q **(Equation 3-1)**

where V is the water volume of whole wetland (L) and Q is the flow rate (L day^{-1}).

3.2.5 Suspended solids and nutrient loading

The loads of suspended solids and nutrient at the inflows and outflows of sedimentation basin and wetlands for each flow class in each year were calculated as follow:

Loads (g day^{-1}) = C x Q **(Equation 3-2)**

where C is the concentration of the nutrient species or suspended solids (g L^{-1}).

3.2.6 Suspended solids and nutrients budget

The difference between loads upstream of the sedimentation basin and downstream of the wetland was considered to be the amount retained or lost from the Cox Creek sub-catchment. The percentage of SS and nutrients retained in the Cox Creek wetland system were calculated based on the total loadings and discharges following this equation:

$$\text{Retention (\%)} = (\sum C_i Q_i - C_o Q_o / \sum C_i Q_i) \times 100 \quad \textbf{(Equation 3-3)}$$

where C_i and C_o are the concentration of the nutrient species or suspended solids at the inflow and outflow (g L^{-1}), Q_i and Q_o are the flow rate at the inflow and outflow (L day^{-1}).

3.2.7 Statistical analysis

All data were tested for homogeneity (O'Brien, Brown-Forsythe, Levene and Bartlett tests) and normality (Shapiro-Wilk test). However, the variances of these data were unequal or non-normally distributed. Differences between annual loadings of SS and nutrients were compared in each flow class and each year using a non-parametric ANOVA (Wilcoxon Mann-Whitney test followed by Kruskal-Wallis test). Relationships between SS and nutrient loads with the flow were analysed by regression analysis. Differences of SS and nutrient concentrations between inflow and outflow and each year were compared using a non-parametric ANOVA (Wilcoxon Mann-Whitney test followed by Kruskal-Wallis test). Differences of SS and nutrients budget between inflow and outflow were compared between 2007 and 2009 using a non-parametric ANOVA (Wilcoxon Mann-Whitney test followed by Kruskal-Wallis test). When significant differences were found using a non-parametric ANOVA, Tukey-Kramer HSD was applied to determine which years were significantly different from one another. Statistically significant differences were accepted with α of 0.05. All statistical analysis was performed using JMP-IN (Version 4.0.3, S.A.S Institute Inc. Cary, USA).

3.3 Results

3.3.1 Rainfall data

The total amount of rainfall from January 2004 until December 2009 for the Cox Creek sub-catchment was 6353.8 mm, with an average monthly rainfall of 88.2 mm. The majority of annual rainfall occurred between May and October (Figure 3.1).

NOTE:
This figure is included on page 29 of the print copy of the thesis held in the University of Adelaide Library.

Figure 3.1: Rainfall for the Cox Creek sub-catchment from the year 2004 until 2009. Note that the meteorological data was collected at the Piccadilly (Woodhouse) rainfall station in the Mount Lofty Ranges watershed (source: www.bom.gov.au)**.**

3.3.2 Flow patterns of the Cox Creek wetland system

For both upstream of Brookes Bridge sedimentation basin and downstream of Woodhouse wetlands, flow was highly variable with the highest rates between May and October (Figure 3.2). The hydrograph shows the peak flows mostly occurred in July following the peak rainfalls (Figure 3.1). The flow rates then quickly receded between December and May coinciding with lower rainfall during these periods (Figure 3.1).

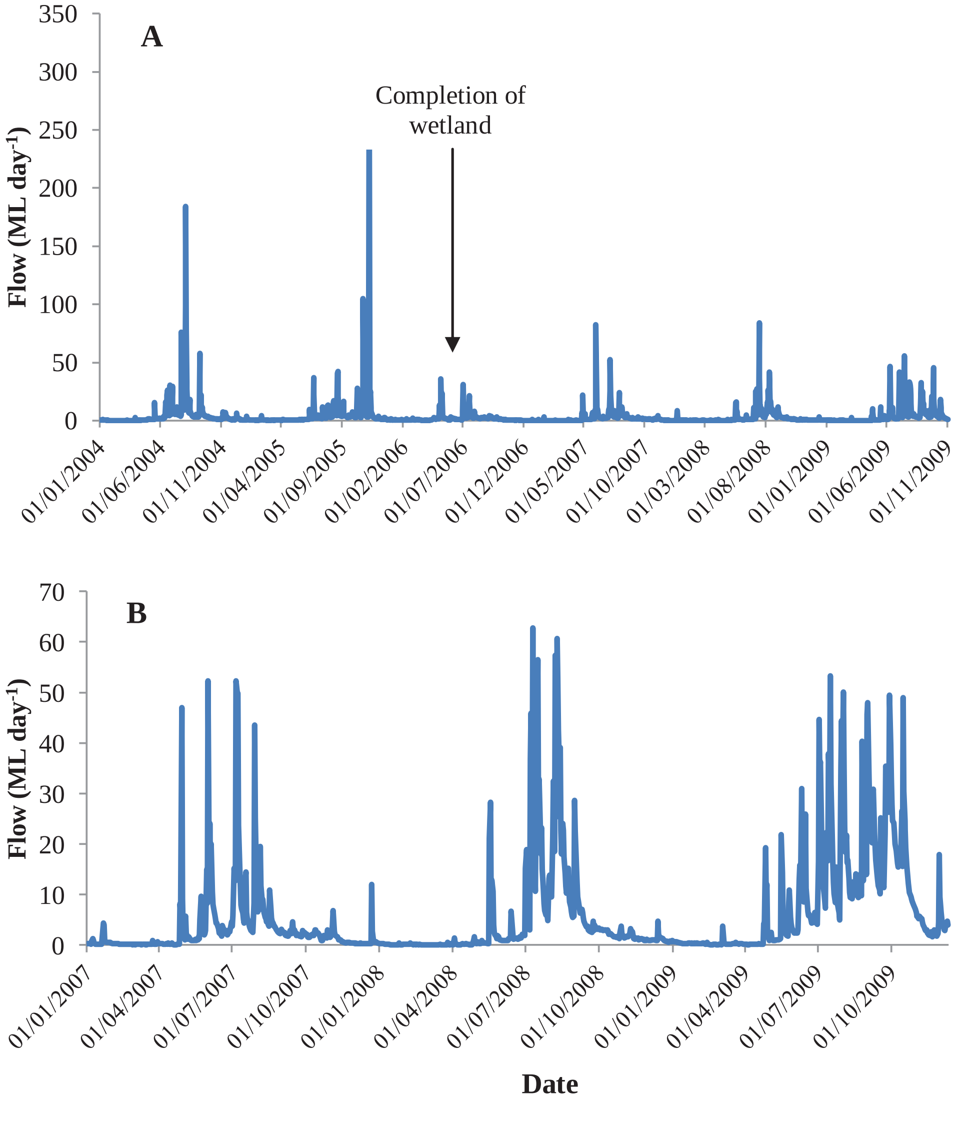

Figure 3.2: Daily flow rate (ML day^{-1}) recorded at the upstream of Brookes Bridge sedimentation basin (A) and downstream of Woodhouse wetland (B). Note that the composite sampling station was installed for continuous monitoring of water quality from the upper Cox Creek sub-catchment.

3.3.3 Frequency of flow rate classes

In each year, the greatest number of days occured in the 0 to 1 ML day^{-1} flow class, ranging between 157 and 236 days per year (Figure 3.3). Flows in the range of 2 to 5 ML day^{-1} and 6 to 15 ML day^{-1} occured 81 to 149 and 12 to 52 days per year, respectively. The flow classes 16 to 30 ML day^{-1} and 31 to 45 ML day^{-1} were less well represented and flow days ranged between 3 and 14 days and 1 and 5 days per year, respectively. The lowest number of days was recorded within the 46 to 300 ML day^{-1} flow class which was ranged between 0 and 6 days per year.

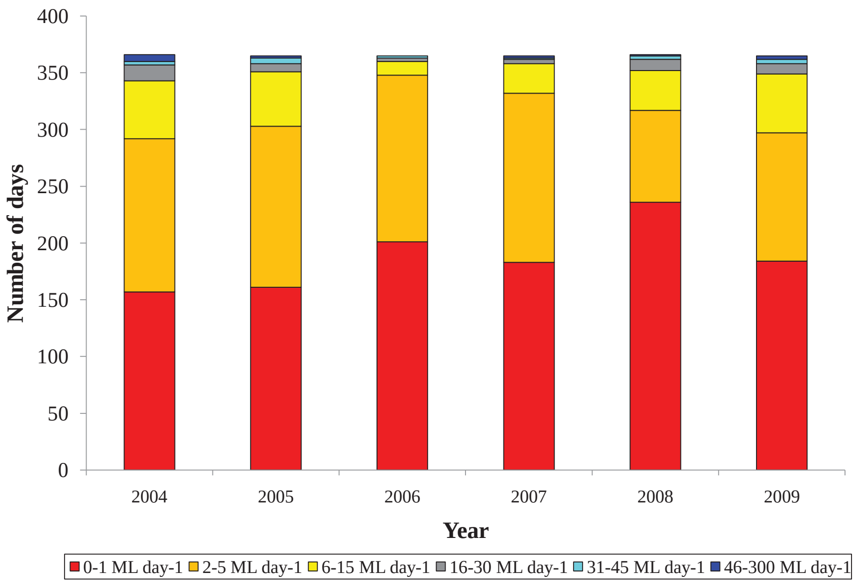

Figure 3.3: Total number of days within each flow rate classes (ML day^{-1}) for the Cox Creek wetland system.

3.3.4 Flow volume of each flow rate class

The highest flow volume was classified within 46 to 300 ML day^{-1} flow class, ranging between years from 134.7 to 558.9 ML/yr (Figure 3.4), with an averaged of 122 ML. In the 6 to 15 ML day^{-1}, 2 to 5 ML day^{-1} and 16 to 30 ML day^{-1} flow classes, there were reductions in the flow volume ranging between years from 91.4 to 433.2 ML/yr, 69.7 to 328.3 ML/yr and 61.5 to 308.8 ML/yr, respectively. The remaining 0 to 1 ML day^{-1} and 31 to 45 ML day^{-1} flow classes showed lower amounts of flow volume ranging between years from 36.6 to 86.4 ML/yr and 44.7 to 203.1 ML/yr, respectively.

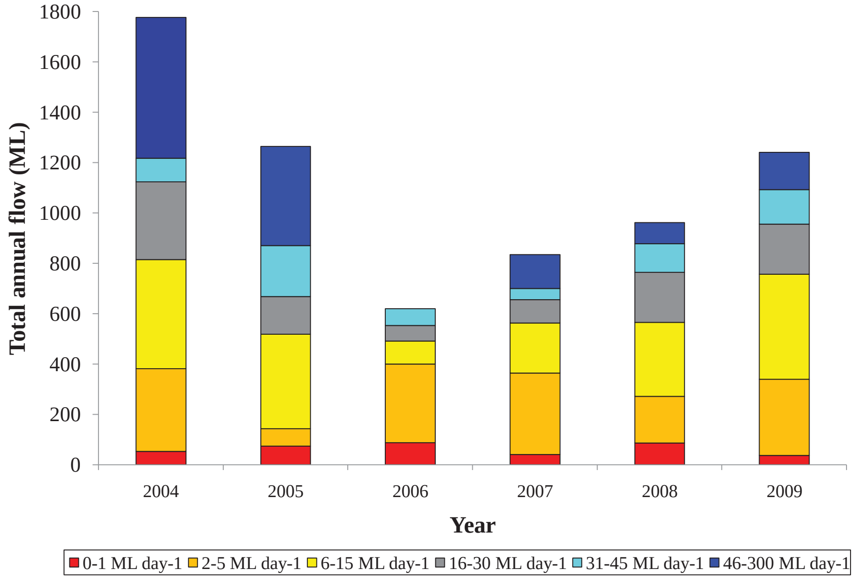

Figure 3.4: Total annual flow (ML/yr) within the flow rate classes (ML day^{-1}) for the Cox Creek wetland system.

3.3.5 Water residence time of each flow rate class

As expected, the longest water residence time of an average of 10 days was for the flow class of 0 to 1 ML day^{-1} (Table 3.1). This is then followed by the 2 to 5 ML day^{-1} (2.5 days), 6 to 15 ML day^{-1} (0.4 days), 16 to 30 ML day^{-1} (0.2 days) and 31 to 45 ML day^{-1} (0.1 days) flow classes. The shortest water residence time was for the 46 to 300 ML day^{-1} flow class (0.03 days).

Table 3.1: Calculated water residence time within six different flow classes.

Parameters	**Year**	**Flow classes (ML day^{-1})**					
		0–1	**2-5**	**6-15**	**16-30**	**31-45**	**46-300**
	2004	14.3	2.0	0.6	0.2	0.2	0.1
	2005	9.4	8.7	0.5	0.2	0.1	0
WRT (day)	2006	3.7	0.7	0.2	0.1	0.1	0
	2007	10.4	1.0	0.3	0.1	0.1	0
	2008	7.1	1.1	0.3	0.1	0.1	0
	2009	14.8	1.3	0.4	0.2	0.1	0.1
Average		9.9	2.5	0.4	0.2	0.1	0.03

3.3.6 Loadings of suspended solids and nutrients of each flow rate class

The inflowing loads of SS ranged between 19.1 and 387.4 tonnes and was lowest in 2006. There was a significant reduction in the annual SS loads from 2004 to 2009 (Table 3.2 and Table 3.5; $p = 0.0422$) except a 93 percent increase from 2006 to 2007 as SS loads were particularly low in 2006. The highest load of SS was for the 46 to 300 ML day^{-1} flow class (Table 3.2 and Table 3.5; $p < 0.0001$). However no SS loads were recorded within this flow class in 2006, as no flow occurred in this flow class. The lowest load of SS was generally recorded in the 0 to 1 ML day^{-1} flow class ranging from 1.0 to 6.4 tonnes. The outflowing loads of SS was highest within the 46 to 300 ML day^{-1} in 2007 and was lowest in 2009 within the 0 to 1 ML day^{-1} flow class (Table 3.3 and Table 3.5; $p = 0.0253$). A positively linear regression of the loadings of SS and nutrients with daily flow demonstrates that higher flow volumes are able to transport higher loads of these pollutants (Table 3.4).

The trends for inflowing loads of TP were similar to that for SS. Inflowing TP loads ranged between 106.4 and 1244.9 kg and were lowest in 2006 compared to the other five years (Table 3.2 and Table 3.5; $p < 0.0001$). The highest loads of TP were in the 46 to 300 ML day^{-1} flow class, which ranged from 33.5 to 433.4 kg, while the lowest loads of TP were generally in the 0 to 1 ML day^{-1} flow class, which ranged from 10.2 to 42.5 kg (Table 3.5; $p < 0.0001$). The inflowing loads of FRP was highest in 2005 and was lowest in 2006 (Table 3.2 and Table 3.5; $p < 0.0001$). Similarly to the loads of TP, the highest load of FRP was in the 46 to 300 ML day^{-1} flow class, which ranged between 5.9 and 106.9 kg, while the lowest load of FRP was generally recorded in the 0 to 1 ML day^{-1} flow class ranging from 1.8 to 13.9 kg. The outflowing loads of TP and FRP were significantly higher within 46 to 300 ML flow class compared to other flow classes (Table 3.3 and Table 3.5; $p < 0.0001$ for TP, $p = 0.0062$ for FRP).

The patterns for the inflowing loads of TN was lowest in 2006 across the six years study periods (Table 3.2 and Table 3.5; $p < 0.0001$). The highest load of TN was in the 6 to 15 ML day^{-1} flow class which ranged between 488.5 and 1908.3 kg. The lowest load of TN was in the 0 to 1 ML day^{-1} flow class, which ranged between 81. 0 to 178.4 kg, corresponding with the lowest total load of SS. The inflowing load of TKN was highly varied between flow classes, with the lowest load of TKN was in the 0 to 1 ML day^{-1} flow class (Table 3.2 and Table 3.5; p = 0.0025). Similarly to the loads of TKN, the inflowing load of NOx was also varied between flow classes, with the lowest load of NOx was generally recorded in the 0 to 1 ML day^{-1} flow class, ranging from 26.2 to 230.4 kg. Most of the outflowing loads of TN, TKN and NOx showed similar trends as for that inflowing loads of TN, TKN and NOx in which the highest loading was in 2007 within the 46 to 300 ML day^{-1} (Table 3.3 and Table 3.5; $p < 0.0001$ for TN, $p < 0.0001$ for TKN, $p = 0.0308$ for NOx).

Table 3.2: Calculated inflowing loads of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) within six different flow classes from the year 2004 until 2009. Inflowing loads were calculated from measurements of discharge and concentrations measured upstream of the Brookes Bridge sedimentation basin.

Parameters	**Year**	**Flow classes (ML day^{-1})**						**TOTAL**
		0–1	**2-5**	**6-15**	**16-30**	**31-45**	**46-300**	
	2004	3.2	42.7	56.8	86.8	26.3	171.6	387.4
	2005	2.9	30.1	42.9	23.9	56.1	210.3	366.2
SS (tonnes)	2006	1.5	6.2	4.5	4.4	2.5	0.0	19.1
	2007	7.2	30.7	46.6	13.7	21.7	158.7	278.6
	2008	6.4	4.8	22.9	31.1	26.6	15.1	106.9
	2009	1.0	9.5	23.8	10.6	7.3	5.2	57.4
	2004	23.8	179.5	255.9	277.8	74.5	433.4	1244.9
	2005	23.1	164.7	145.6	85.4	132.1	305.7	856.6
TP (kg)	2006	20.2	33.3	19.6	17.4	15.9	0.0	106.4
	2007	33.8	96.1	125.6	63.7	32.5	200.4	552.1
	2008	42.5	35.2	119.5	99.7	48.0	95.5	440.4
	2009	10.2	64.3	142.7	57.9	51.3	33.5	359.9
	2004	2.3	15.9	4.1	112.8	51.7	18.0	204.8
	2005	9.8	47.6	52.6	27.3	48.2	106.9	292.4
FRP (kg)	2006	7.8	17.7	9.2	6.5	7.5	0.0	48.7
	2007	6.9	24.5	25.7	12.8	7.0	31.6	108.5
	2008	13.9	12.1	37.0	27.3	14.7	27.5	132.5
	2009	1.8	11.4	25.2	10.2	9.1	5.9	63.6
	2004	154.9	1339.5	1908.3	1489.8	362.8	1726.2	6981.5
	2005	178.4	1689.9	1527.9	597.7	712.0	1172.3	5878.2
TN (kg)	2006	162.9	1005.7	488.5	344.5	403.6	0.0	2405.2
	2007	138.9	1114.6	949.0	515.0	273.9	894.4	3885.8
	2008	354.4	649.9	1316.3	1117.4	404.2	392.1	4234.3
	2009	81.0	987.1	1411.4	672.2	434.5	504.2	4090.4

Table 3.2: Calculated inflowing loads of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) within six different flow classes from the year 2004 until 2009. Inflowing loads were calculated from measurements of discharge and concentrations measured upstream of the Brookes Bridge sedimentation basin (continued).

Parameters	**Year**	**Flow classes (ML day^{-1})**						**TOTAL**
		0–1	**2-5**	**6-15**	**16-30**	**31-45**	**46-300**	
	2004	33.7	292.3	498.3	468.0	135.4	754.1	2181.8
	2005	41.9	312.3	393.5	183.8	255.5	571.1	1758.1
TKN (kg)	2006	55.2	139.9	53.5	47.4	38.1	0.0	334.1
	2007	81.2	301.6	185.2	291.4	98.1	252.6	1210.1
	2008	124.0	163.4	341.9	275.0	139.2	191	1234.5
	2009	54.9	339.1	655.7	302.2	253.4	334.7	1940.0
	2004	121.3	1047.3	1409.8	1021.8	227.4	972.1	4799.6
	2005	136.4	1402.6	890.8	435.2	584.8	670.3	4120.1
NOx (kg)	2006	105.7	865.6	435.0	297.4	367.2	0.0	2070.9
	2007	113.6	256.9	463.9	523.7	575.8	741.8	2675.7
	2008	230.4	486.5	941.1	842.1	265.1	234.6	2999.8
	2009	26.2	419.2	655.7	470.1	209.1	369.5	2149.8

Table 3.3: Calculated outflowing loads of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) within six different flow classes from the year 2007 until 2009. Outflowing loads were calculated from measurements of discharge and concentrations measured downstream of the Woodhouse wetland.

Parameters	**Year**	**Flow classes (ML day^{-1})**						**TOTAL**
		0–1	**2-5**	**6-15**	**16-30**	**31-45**	**46-300**	
	2007	1.9	13.2	15.4	12.1	8.7	51.9	103.2
SS (tonnes)	2008	3.2	4.8	10.6	11.9	17.2	13.6	61.3
	2009	0.1	0.5	2.0	0.6	0.3	0.4	3.9
	2007	16.7	35.7	26.1	44.9	25.5	74.2	223.1
TP (kg)	2008	11.2	8.5	42.2	25.9	21.5	63.4	172.7
	2009	6.2	20.1	37.3	24.8	11.3	12.2	111.9
	2007	1.2	1.4	3.2	1.8	2.1	2.4	12.1
FRP (kg)	2008	1.6	3.1	1.8	2.4	4.1	3.4	16.4
	2009	0.9	2.0	3.1	3.1	1.2	2.5	12.8
	2007	72.6	889.6	870.3	469.2	231.4	671.2	3204.3
TN (kg)	2008	183.5	201.6	504.0	151.2	203.7	166.8	1410.8
	2009	62.0	121.6	114.8	318.3	118.6	252.6	987.9
	2007	72.8	299.3	177.3	282.3	87.9	198.1	1117.7
TKN (kg)	2008	94.9	22.3	77.0	90.6	63.7	83.4	431.9
	2009	23.7	106.2	136.8	93.1	67.2	74.0	501.0
	2007	62.5	229.5	413.6	440.2	519.4	421.4	2086.6
NOx (kg)	2008	163.6	224.4	253.2	129.5	54.3	153.9	978.9
	2009	12.9	57.4	102.6	78.9	34.7	200.4	486.9

Table 3.4: Relationships between loadings of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) on daily flow

Parameters	**Relationship**	**Daily flow**	
		Inflow	**Outflow**
SS (tonnes)	r^2	0.611	0.965
	Relationship	Positive linear	Positive linear
TP (kg)	r^2	0.792	0.981
	Relationship	Positive linear	Positive linear
FRP (kg)	r^2	0.914	0.902
	Relationship	Positive linear	Positive linear
TN (kg)	r^2	0.850	0.762
	Relationship	Positive linear	Positive linear
TKN (kg)	r^2	0.817	0.869
	Relationship	Positive linear	Positive linear
NOx (kg)	r^2	0.756	0.402
	Relationship	Positive linear	Positive linear

Table 3.5: Results of non-parametric ANOVA (Wilkoxon/Kruskal-Wallis test) on the loadings of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) between flow rates classes and years. Significant effects were determined when *p* value is less than 0.05.

Parameters	**Flow rate classes**		**Years**	
	Inflow	**Outflow**	**2004-2009**	**2007-2009**
SS (tonnes)	<0.0001	<0.0001	0.0422	0.0253
TP (kg)	0.0000	<0.0001	0.0002	<0.0001
FRP (kg)	<0.0001	<0.0001	0.0070	0.0062
TN (kg)	0.0001	<0.0001	0.0003	<0.0001
TKN (kg)	0.0000	<0.0001	0.0025	<0.0001
NOx (kg)	<0.0001	<0.0001	0.0001	0.0308

*Note: P<0.001, extremely significant difference; P<0.01, moderately significant difference; P<0.05, significant difference

Table 3.6: Percentage of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) retention within six different flow classes of the Cox Creek wetland system.

Parameters	**Year**	**Percentage of retention in each flow classes (%)**					
		0–1 (ML day^{-1})	**2-5 (ML day^{-1})**	**6-15 (ML day^{-1})**	**16-30 (ML day^{-1})**	**31-45 (ML day^{-1})**	**46-300 (ML day^{-1})**
SS (tonnes)	2007	74	57	67	12	60	67
	2008	50	0	54	62	35	10
	2009	90	95	92	94	96	92
TP (kg)	2007	51	63	79	30	22	63
	2008	74	76	65	74	55	34
	2009	39	69	74	57	78	64
FRP (kg)	2007	83	94	88	86	70	92
	2008	88	74	95	91	72	88
	2009	50	82	88	70	87	58
TN (kg)	2007	48	20	8	9	16	25
	2008	48	69	62	86	50	57
	2009	23	88	92	53	73	50
TKN (kg)	2007	10	1	4	3	10	22
	2008	23	86	77	67	54	56
	2009	57	69	79	69	73	78
NOx (kg)	2007	45	11	11	16	10	43
	2008	29	54	73	85	80	34
	2009	51	86	84	83	83	46

3.3.7 Relationship between flow, suspended solids and nutrient concentrations

Suspended solids and nutrient concentrations were generally higher between June and July, coinciding with peak flow rates (Figure 3.5, Figure 3.6, Figure 3.7, Figure 3.8, Figure 3.9 and Figure 3.10). In all cases, the concentrations of SS and nutrient have poor correlation with daily flow rates (Table 3.7), resulting in no clear trend across the six years examined.

Within the upstream of Brookes Bridge sedimentation basin, the concentration of SS varied between years (Figure 3.5 A). The concentration of SS was highest in 2007 compared to the other five years (Figure 3.5 A). The concentration of SS decreased initially after the completion of the sedimentation basin in mid June 2006, with the concentration measured in 2009 being the lowest compared to the remaining years (Figure 3.5 A). A lower concentration of SS was found at the downstream of Woodhouse wetland compared to upstream of Brookes Bridge sedimentation basin, corresponding with lower flow rates (Figure 3.5 B). Significant differences were found in the concentration of SS between upstream and downstream of the wetlands (Table 3.8).

The concentration of TP at the upstream of Brookes Bridge sedimentation basin was highly variable, with highest concentrations between April and July (Figure 3.6 A). There was a generally lower in concentration of TP in October to March, coinciding with lower flow during this period. The concentration of TP was greater in 2004 than in the other five years (Figure 3.6 A). In the downstream of Woodhouse wetland, the concentration of TP was lower than in the upstream of Brookes Bridge sedimentation basin (Figure 3.6 B and Table 3.8). Trends in FRP concentrations in the upstream of Brookes Bridge sedimentation basin were similar to that of TP. The FRP concentrations were higher in April and July and were lower in October to March (Figure 3.7 A). The highest concentration of FRP was in 2008 than in the other five years (Figure 3.7 A). Statistically, significant differences were found in the concentration of FRP between upstream and downstream of the wetlands (Table 3.8).

The concentration of TN at the upstream of Brookes Bridge sedimentation basin was highest after the peak flows (Figure 3.8 A). The concentrations of TN recorded in April to July 2007 and 2008 were significantly greater than those detected in the other four years

(Figure 3.8 A). The concentration of TN at the downstream of Woodhouse wetland was lower than that in the upstream of Brookes Bridge sedimentation basin, with the concentration measured in 2008 being the lowest than that observed at any other years (Figure 3.8 B). The concentration of NOx was significantly higher in June and July in each year following the peak flow during these periods (Figure 3.9 A and Table 3.8). In the downstream of the Woodhouse wetland, the concentrations of NOx were lower than that observed in the Brookes Bridge sedimentation basin, corresponding with lower flow rates (Figure 3.9 B and Table 3.8).

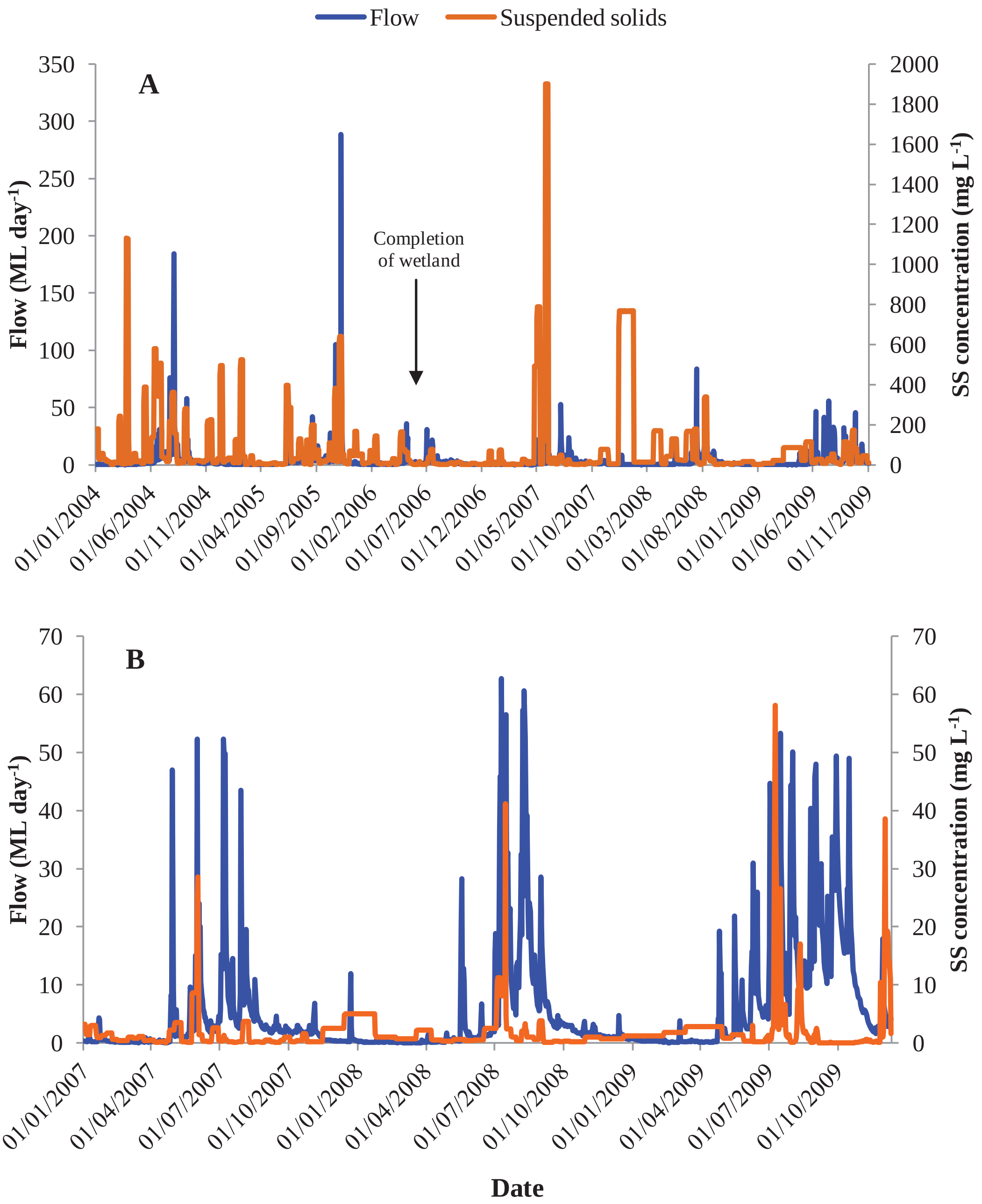

Figure 3.5: Suspended solids concentration (mg L^{-1}) and flow variabilities (ML day^{-1}) recorded at the upstream of Brookes Bridge sedimentation basin (A) and downstream of Woodhouse wetland (B).

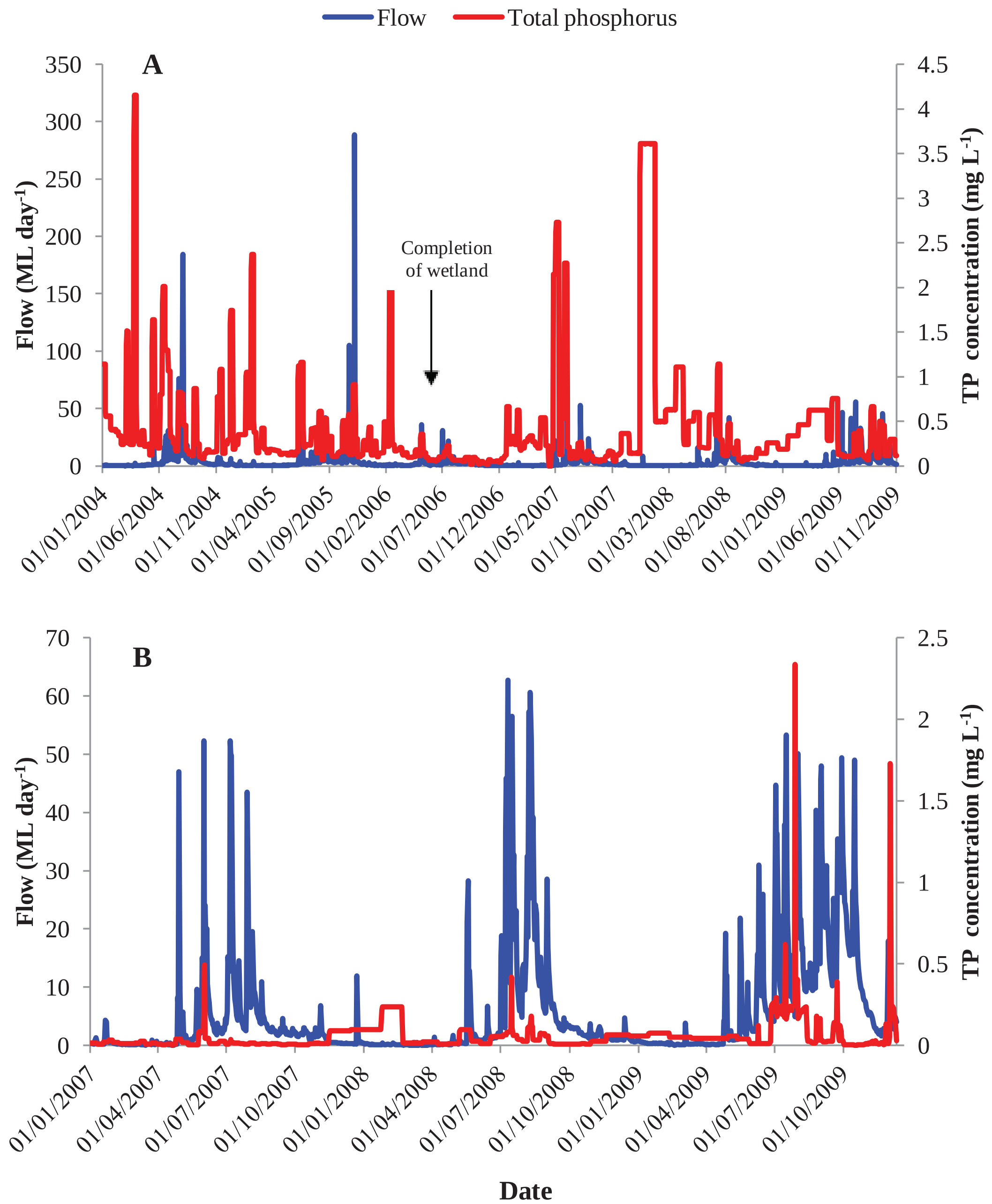

Figure 3.6: Total phosphorus concentration (mg L^{-1}) and flow variabilities (ML day^{-1}) recorded at the upstream of Brookes Bridge sedimentation basin (A) and downstream of Woodhouse wetland (B).

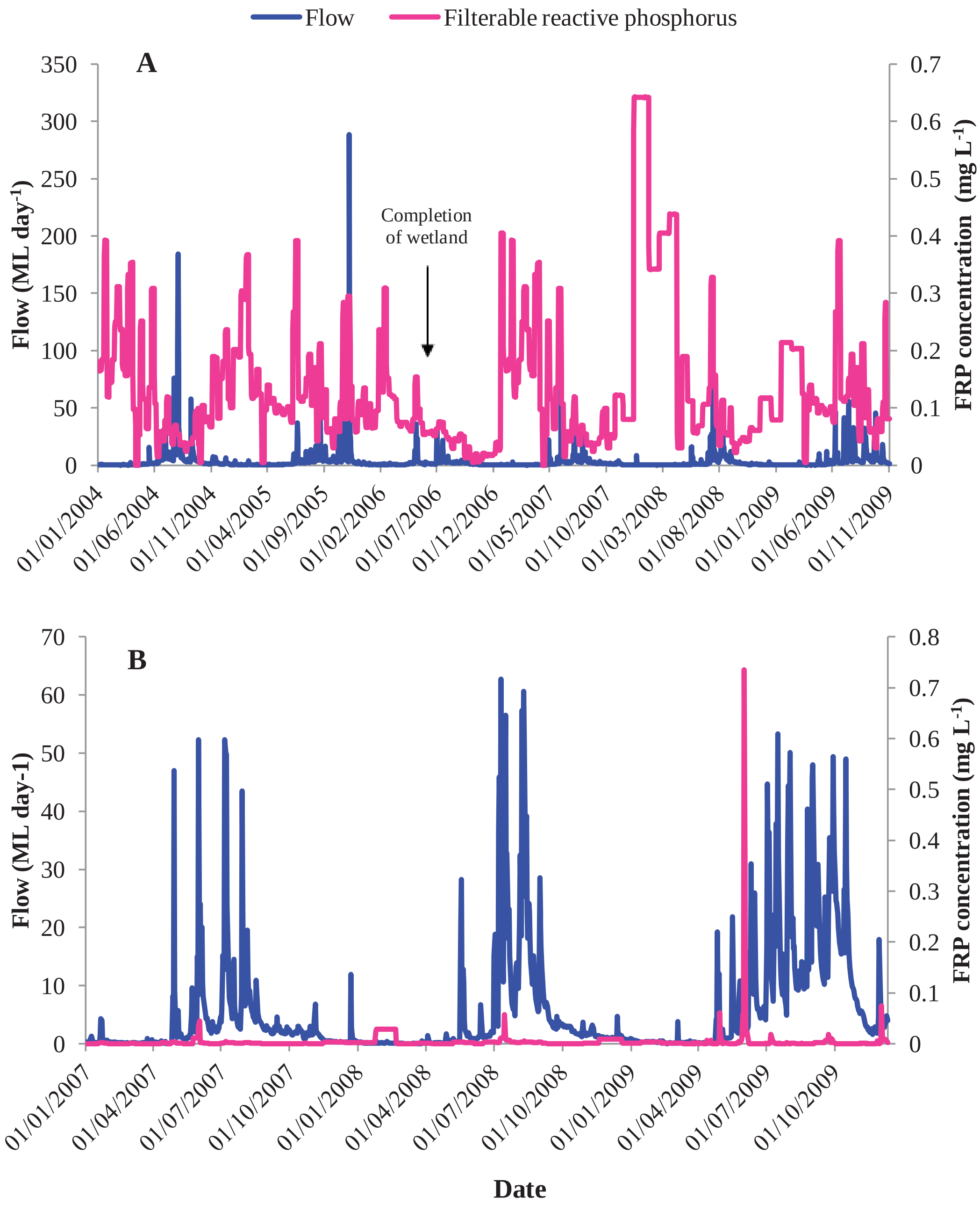

Figure 3.7: Filterable reactive phosphorus concentration (mg L^{-1}) and flow variabilities (ML day^{-1}) recorded at the upstream of Brookes Bridge sedimentation basin (A) and downstream of Woodhouse wetland (B).

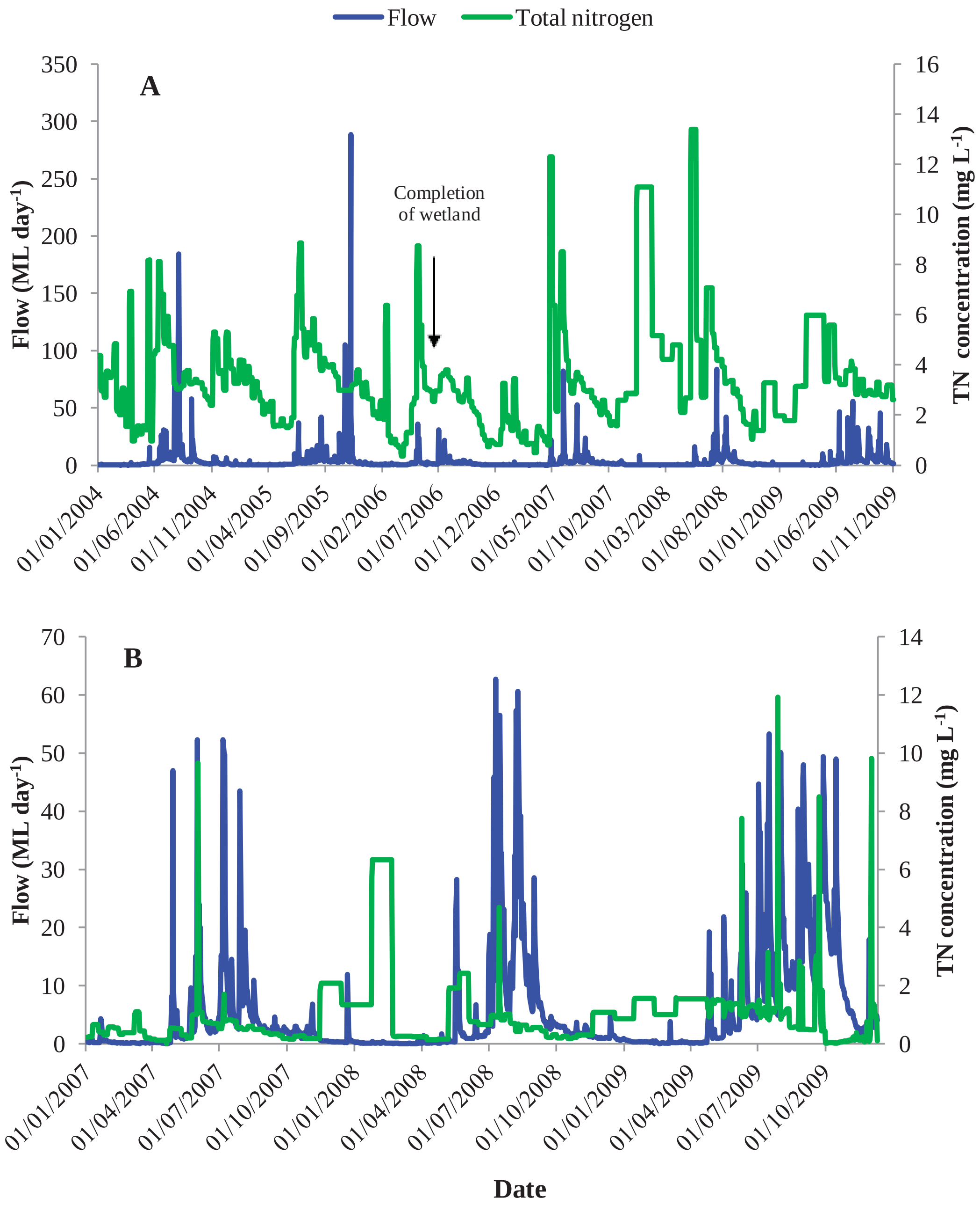

Figure 3.8: Total nitrogen concentration (mg L^{-1}) and flow variabilities (ML day^{-1}) recorded at the upstream of Brookes Bridge sedimentation basin (A) and downstream of Woodhouse wetland (B).

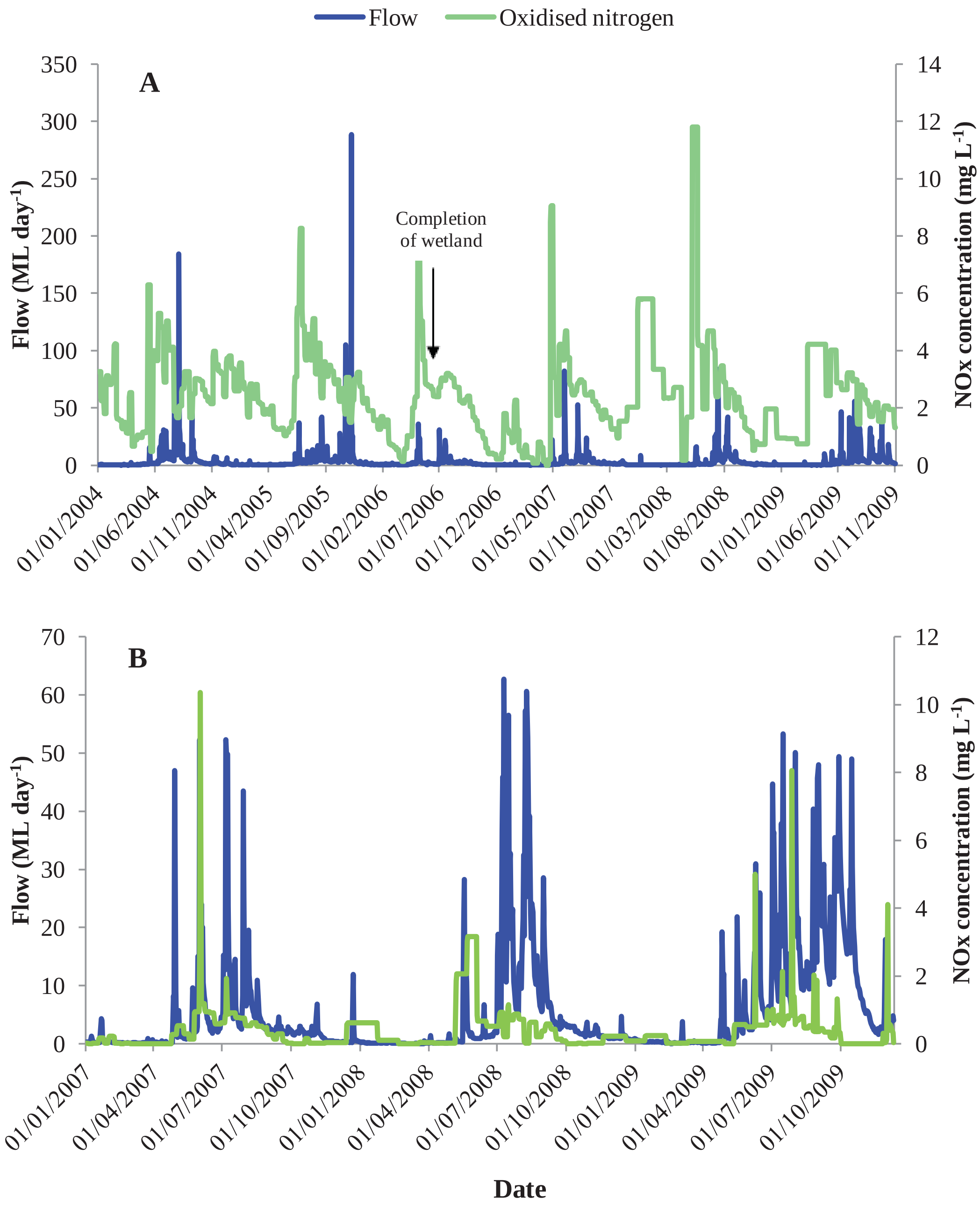

Figure 3.9: Oxidised nitrogen concentration (mg L^{-1}) and flow variabilities (ML day^{-1}) recorded at the upstream of Brookes Bridge sedimentation basin (A) and downstream of Woodhouse wetland (B).

Table 3.7: Relationships between concentrations of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN) and oxidised nitrogen (NOx) on daily flow.

Parameters	**Relationship**	**Daily flow**
SS (mg L^{-1})	r^2	0.025
	Relationship	-
TP (mg L^{-1})	r^2	0.411
	Relationship	-
FRP (mg L^{-1})	r^2	0.070
	Relationship	-
TN (mg L^{-1})	r^2	0.006
	Relationship	-
NOx (mg L^{-1})	r^2	0.006
	Relationship	-

Table 3.8: Results of non-parametric ANOVA (Wilkoxon/Kruskal-Wallis test) on the concentrations of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN) and oxidised nitrogen (NOx) between sites (inflow-outflow) and years. Significant effects were determined when *p* value is less than 0.05.

Parameters	**Inflow vs. outflow**	**Years**
SS (mg L^{-1})	<0.001	<0.001
TP (mg L^{-1})	<0.001	<0.001
FRP (mg L^{-1})	<0.001	<0.001
TN (mg L^{-1})	<0.001	<0.001
NOx (mg L^{-1})	<0.001	<0.001

*Note: $p < 0.001$, extremely significant difference; $p < 0.01$, moderately significant difference; $p < 0.05$, significant difference.

3.3.8 Suspended solids and nutrients budget

From the year 2007 to 2009, inflowing loads of SS ranged between 57.4 and 278.6 tonnes and were significantly higher than outflowing loads, which ranged between 3.9 and 103.2 tonnes (Table 3.9; Table 3.10 and Table 3.11). This suggests that the wetland was effective at reducing SS loads from the Cox Creek.

Similar findings were observed for all other nutrient species retained in the Cox Creek wetland system (Table 3.9). The inflowing loads of TP were significantly higher than outflowing loads in which TP retained in the wetland ranged between 248.8 and 329.0 kg (Table 3.9; Table 3.10 and Table 3.11). The FRP budgets showed that up to 88 percent of inflowing loads were retained within the wetland (Table 3.9). This suggests that the wetland was also effective at reducing dissolved phosphorus loads from the Cox Creek.

The inflowing loads of TN ranged between 3885.8 and 4090.4 kg and were significantly higher than outflowing loads, which ranged between 681.5 and 3102.5 kg (Table 3.9 and Table 3.10 p = 0.015). The inflowing loads of TN showed no significant differences (p >0.05) between 2007 to 2008 and 2008 to 2009 (Table 3.11). The inflowing loads of TN retained in the wetland were 18, 67 and 76 percent in 2007, 2008 and 2009, respectively. Trends in TKN and NOx budget were similar to that of TN. The inflowing loads of TKN and NOx budgets showed that up to 74 and 77 percent of inflowing loads were retained within the wetland. Also, statistical analysis revealed that there was significant different between sites (Table 3.10; p = 0.001 for TKN and p = 0.013 for NOx). This suggests that the wetland was effective at reducing nitrogen loads and its dissolved forms from the Cox Creek.

Table 3.9: Annual suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) budget for the inflow and outflow of the Cox Creek wetland from 2007 to 2009. Note that inflow site was recorded at the Brookes Bridge sedimentation basin and outflow site was recorded at the Woodhouse Wetland.

Parameters	**Year**	**Inflow**	**Outflow**	**Net retention**	**Percentage of retention (%)**
SS (tonnes)	2007	278.6	103.2	175.4	63
	2008	106.9	61.3	45.6	43
	2009	57.4	3.9	53.5	93
TP (kg)	2007	552.1	223.1	329.0	60
	2008	440.4	172.7	267.7	61
	2009	359.9	111.9	248.0	69
FRP (kg)	2007	105.6	12.1	93.5	88
	2008	127.2	16.4	110.8	87
	2009	79.9	12.8	60.3	84
TN (kg)	2007	3885.8	3204.3	681.5	18
	2008	4234.3	1410.8	2823.5	67
	2009	4090.4	987.9	3102.5	76
TKN (kg)	2007	1210.1	1117.7	92.4	8
	2008	1234.5	431.9	802.6	65
	2009	1940.6	501.0	1439.6	74
NOx	2007	2675.7	2086.6	589.1	22
	2008	2999.8	978.9	2020.9	67
	2009	2149.8	486.9	1662.9	77

Table 3.10: Results of non-parametric ANOVA (Wilkoxon/Kruskal-Wallis test) on the loadings of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) between sites (inflow-outflow) and years.

Parameters	**Inflow vs. outflow**	**Years (2007 to 2009)**
SS	0.039	0.020
TP	0.026	0.017
FRP	<0.001	0.001
TN	0.015	0.032
TKN	0.001	<0.001
NOx	0.013	<0.001

*Note: p <0.001, extremely significant difference; p <0.01, moderately significant difference; p <0.05, significant difference.

Table 3.11: Result of post-hoc comparison (Tukey-Kramer HSD) on the loadings of suspended solids (SS), total phosphorus (TP), filterable reactive phosphorus (FRP), total nitrogen (TN), total Kjeldahl nitrogen (TKN) and oxidised nitrogen (NOx) between years.

Year-Year	SS	TP	FRP	TN	TKN	NOx
2007-2008	##	#	###	NS	NS	NS
2007-2009	#	##	#	#	##	#
2008-2009	##	##	##	NS	NS	NS

*Note: ###, extremely significant difference (p <0.001); ##, moderately significant difference (p <0.01); #, significant difference (p <0.05); NS, not significant (p >0.05).

3.4 Discussion

The duration and intensity of rainfall events in the Cox Creek sub-catchment had an effect on the total loading of nutrients and flows travelling downstream. Since the majority of rainfall events occurs in May to October, stream flow increased with the corresponding catchment runoff (Figure 3.1). Indeed, nutrient loads have been shown to be predominantly driven by the stream flow in a catchment (Linden *et al*. 2004). Catchment runoff and stream flows are highly associated with interannual climate variability in Australia, associated with the El Nino-Southern Oscillation (ENSO) (Simpson *et al*. 1993; Linden *et al*. 2004; Nicholls and Kariko 1993). The interannual variation in the Cox Creek rainfall intensity drives the interannual variation in the overall loads of pollutants.

Differences in the interannual variability of daily flow were observed within Brookes Bridge sedimentation basin and Woodhouse Wetland of the Cox Creek wetland system. A decrease in both the annual load and average concentration of SS, TP, FRP, TN, TKN and NOx were found in Brookes Bridge sedimentation basin and Woodhouse Wetland. The improvement in water quality was demonstrated by a significant reduction in the annual loads of SS, TP, FRP, TN, TKN and NOx across the study period (Table 3.9). The annual load of SS and nutrients decreased with time, with changes were observed from 2007 to 2009 when all the years were compared (Table 3.11). Of the nutrients species measured, the annual load of FRP was found to decrease most significantly across the sampling period (Table 3.9 and Table 3.10). Thus it is necessary to investigate the changes in both concentration magnitude and annual load when determining the changes in water quality.

Constructed wetlands are capable of treating water pollutants at various latitudes and different climatic conditions (Némery *et al.* 2005; Nungesser and Chimney 2006; Rücker and Schrautzer 2009; Kadlec 2009; Neal *et al.* 2010). The relationship between suspended solids loads and flow in the Cox Creek sub-catchment shows that the impacts of rainfall had driven the flow events which could export suspended solids and nutrients into water bodies (Table 3.4). This might be due to that the majority of nutrient loads are driven by stream flow and therefore a majority of the nutrients enter the wetland system during high flow events. The nutrient loadings are the product of the nutrient concentration and the volume of water passing through a wetland. Therefore, transport mechanisms during flow events determine nutrient import in wetland systems.

Both phosphorus and nitrogen can reach watercourses through surface runoff, subsurface flow and groundwater inputs (Sharpley *et al*. 1994; Kadlec and Knight 1996). In drainage water, Wen (2002) found that 26% and 22% of the TP was FRP in the River Murray and Reedy Creek Lagoon, Australia, respectively. In addition Harris (2001) found that FRP represents about 10-30% of the TP in Australian rivers. In the Cox Creek the ratios of FRP:TP are much higher (more than 70%) than recorded in the River Murray (26%) (Wen 2002). This difference is most likely due to high levels of historical application of inorganic P fertilisers in the Cox Creek sub-catchment. Following rainfall, large amounts of soil P can be released as dissolved inorganic P, as rainfall leaches P from the soil.

Even though there are also strong relationships between daily flow and loads of nitrogen as TN, TKN and NOx (Table 3.4), the process of transporting nitrogen is different from phosphorus as it undergoes the complexities of the nitrogen cycle (Linden *et al*. 2004). Biological nitrogen fixation is the process in which nitrogen gas in the atmosphere is reduced to ammonia nitrogen by autotrophic and heterotrophic bacteria, blue-green algae and higher plants (Armstrong and Armstrong 1991; Kadlec 2009). The most likely source of inorganic nitrogen at the Cox Creek sub-catchment is a consequence from the past fertiliser application across the catchment (Ingleton 2003; Fisher 2005). Fisher 2005 found that a large portion of the nitrogen source was attributed from historic land activities which caused elevated levels of oxidised nitrogen in the shallow groundwater table. Improvements in present land management practices such as uses of buffer strips between farmland and drainage lines can be expected to result in a reduction of the nutrient and sediment load reaching into the wetland systems. Sediments and associated nutrients may be physically trapped, while nutrients may also be removed by biological uptake and storage (Stubbs *et al.* 2004; Fisher *et al.* 2008).

This study also demonstrated that there was a significant reduction in the annual loads of SS and nutrients after the completion of the Cox Creek wetland systems in 2006

(Table 3.6 and Table 3.9). It is believed that supply of SS and nutrient would mainly be from the erosion of stream banks and soil loss from the upstream area of the catchment (Fisher 2005). Nutrient loads of the Cox Creek sub-catchment (0.0410-0.4790 kg P $ha^{-1}yr^{-1}$) were higher compared to the Myponga catchment (0.0099-0.2160 kg P $ha^{-1}yr^{-1}$; Linden *et al*. 2004) but was lower compared to a study by Fisher 2005, who found 15 kg P ha^{-1} yr^{-1} at this site over the period from 1995 to 2002. Thus a reduction in the nutrient loads of more than 90% was found, indicating that the Cox Creek wetland system played a major role in decreasing high nutrient loads exports from the Cox Creek sub-catchment. In Ireland and in England, P export by surface runoff in intensively agricultural area ranged between 0.4 and 3.0 kg P ha^{-1} yr^{-1} (Jordan and Smith 1985; Haygarth and Javis 1995). This can be partly explained by relatively low soil nutrient availability of Australian soils and the high levels of fertilisers application in the Cox Creek sub-catchment (Ingleton 2003; Fisher 2005; Bradley *et al*. 2007).

In most cases water residence time is a key determinant for nutrient retention in a wetland system **(**Behrendt and Opitz 2000; Tao *et al.* 2006). Comparing within six different flow classes, the Cox Creek wetland systems exhibited the longest residence time of water (average of 10 days) within 0 to 1 ML day^{-1} flow class with generally lower SS and nutrient loads (Table 3.1). Longer water residence time of water in a wetland may create a favourable condition for the settlement of large soil particles, resulting in more retention of nutrients (Craft 1997; Wen 2002). On the other hand, the shortest residence time of water fell within 46 to 300 ML day^{-1} (less than 1 day) which corresponds to the highest nutrient loadings (Table 3.2) and flow rates (Figure 3.4). While there was considerably high flow within 46 to 300 ML day^{-1} flow class, the percentage of nutrient retention showed that the Cox Creek wetland system was still able to remove nutrients at high flow (Table 3.6). This is due to the ability of the Cox Creek wetland system to retain water and acts as a sink for nutrients during high flow periods even though there is increasing turbulent flows.

Overall, the percentage of nutrient retention in the Cox Creek wetland system fell within the range of other constructed wetland receiving agricultural runoff (Table 1.1 in chapter one). The net P retention of the Cox Creek wetland system ranged between 248 and

329 kg yr^{-1}, which is well above the net P retention of 202 kg yr^{-1} in the North American Wetland Treatment System (Knight *et al.* 1993). The annual averaged of SS and nutrient budget were used to determine the performance of the Cox Creek wetland system as a successful engineered wetland to retain the sediment and nutrient loads being delivered to downstream reservoir, Mount Bold.

Chapter four

4 Nutrient storage capacity of macrophytes in the Cox Creek wetland system

4.1 Introduction

In constructed wetlands, macrophytes play a vital role in reducing the impacts of eutrophication by reducing nutrient loads passing downstream (Dowling and Stephen 1995; Greenway and Wooley 1999; Browning 2003; Greenway 2003; Thullen *et al.* 2008). For example, the presence of macrophytes improved phosphorus (P) removal by 50% - 70% in a constructed wetland in the Lower River Murray, South Australia (Wen 2002). Three main types of macrophytes are used in constructed wetlands; emergent, submerged and free-floating plants (Greenway 2003; Sainty and Jacobs 1994). Emergent plants such as reeds (*Phragmites sp.*), cattails (*Typha sp.*), sedges (*Carex sp.*), bulrushes (*Scirpus sp.* and *Schoenoplectus sp.*); submerged plants such as water weed (*Elodea sp*.); and free-floating plants such as duckweeds (*Lemna sp.*), water hyacinths (*Eichhornia crassipes*) and water lettuce (*Pistia stratiotes*) are common species used in constructed wetlands (Guntensbergen *et al.* 1989; Moss *et al*. 1986; Brix 1997; Pitt *et al*. 1997). In subartic regions, species such as buckbeans (*Meyanthes trifolia*) and pendant grass (*Arctophila fulva*) have proved to be useful for metal and nutrient uptake (Pirjo *et al*. 2007; Greenway and Wooley 2001). Macrophytes may reduce the nutrient loads in constructed wetland through physical, chemical and biological processes (Brix 1997; Balls *et al*. 1989; Kadlec 1997).

Physical effects of macrophytes on nutrient dynamics include promoting sedimentation and reducing resuspension of sediment particles (Brix 1997; Dowling and Stephen 1995). Dense plant stands of macrophytes such as reeds and bulrushes can reduce water velocity and reduce wind-generated turbulence at the sediment-water interface, resulting in greater deposition of organic and inorganic nutrients (Rogers *et al.* 1991; Brueske and Barret 1994; Fennesy *et al.* 1994; Gleason and Euliss Jr. 1998). Furthermore, macrophytes in constructed wetland provide a surface area for photosynthetic and microbial heterotrophic organisms to grow. Inorganic nutrients may be assimilated by these communities, thus reducing the amount and composition of nutrients passing downstream (Scinto and Reddy 2003; Gachter and Meyer 1993).

There are also indirect biogeochemical pathways by which macrophytes contribute to P retention in constructed wetlands. Macrophytes have the ability to influence the redox potential, which is an important determinant of the exchange of P between the sediment and water column (Sundby *et al.* 1992; Khosmanesh *et al.* 1999; Holtan *et al.* 1988). This is based upon the formation of $FeOOH\text{-}PO_4$ complexes within the sediment. Under oxic conditions PO_4^{3-} will adsorb to Fe^{3+} but will desorb under anoxic conditions. During iron reduction, iron-reducing bacteria use Fe^{3+} oxides and oxyhydroxides as the terminal electron acceptors for anaerobic respiration (Roden and Edmonds 1997). These bacteria catalyse the reduction of solid ferric minerals (Fe^{3+}) to form dissolved ferrous iron (Fe^{2+}). Therefore, any phosphate ions associated with the solid mineral's surface will be released (Lovley *et al.* 1991; Roden and Edmonds 1997). In transferring oxygen to their below ground biomass, macrophytes inadvertently release of oxygen into sediment, increasing the sediment redox potential and the P adsorption capacity of the sediments (Wen 2002; Moore *et al*. 1994; Jensen and Andersen 1992; Wigand *et al*. 1997). Konnerup *et al.* (2010) stated that convective gas flow allows macrophytes to transfer gases more efficiently than simple diffusion. Consequently, those species that utilise convective flow may increase the P adsorption capacity to a greater extent than those that rely on diffusion alone (Aldridge and Ganf, 2003).

Direct uptake of nutrients by macrophytes to meet their nutritional requirements is considered to be one of the important mechanisms for nutrient retention in constructed wetlands (Brix 1997; Liu *et al*. 2000; Qiu *et al*. 2002). Nutrients are taken up by the roots and shoots of the plants and nutrients can be stored in the plant biomass (Qiu *et al.* 2002). Plants in nutrient-rich habitats may accumulate more nutrients than plants occurring in nutrient-poor habitats, referred to as luxury uptake of nutrients (Stephen *et al*. 1997; Guntensbergen *et al.* 1989; Kadlec 1989). There is still debate whether macrophytes enhance the performance of constructed wetlands, with some considering macrophytes as transient nutrient storages which take up nutrients during the growing season, but release them during senescence or death of old plant parts (Rogers *et al.* 1991; Qiu *et al.* 2002; Reddy *et al*. 1999) as reflected by Figure 1.1 (chapter one). Swindell *et al*. (1990) found that a lack of seasonal fluctuations in P removal rates indicates that bacterial and algal uptake of nutrients are the primary mechanisms in nutrient removal in wetland systems. This has been dismissed by Richardson *et al*. (1999) who claim that although the initial removal of dissolved inorganic phosphorus from the water column under natural loading levels is largely due to microbial consumption, and later nutrient uptake by macrophytes and soil adsorption are the dominant P removal mechanisms.

This research aimed to determine the nutrient storage capacity of macrophytes in the Cox Creek wetland system and to investigate the influence of macrophytes on sediment redox potential. The following hypothesis was tested: macrophytes act as a significant storage for nutrients and provide suitable redox potential conditions in sediments for P adsorption. Therefore wetlands containing macrophytes will have a greater nutrient storage capacity than wetlands not containing macrophytes. To test this hypothesis, seasonal nutrient storage and sediment redox potential surveys were conducted in vegetated and unvegetated ponds.

4.2 Methods

4.2.1 Macrophyte survey

A macrophyte biomass survey was conducted during spring 2008 (20 October 2008 to 24 October 2008), summer 2009 (12 January 2009 to 16 January 2009), autumn 2009 (18 May 2009 to 21 May 2009) and winter 2009 (06 July 2009 to 09 July 2009) in Reed Bed and Pond 1 of the Cox Creek wetland system (Figure 2.5, chapter two). Reed Bed and Pond 1 were divided into five equal longitudinal cells, with a randomly selected transect chosen in each cell (Figure 4.1 and Figure 4.2). In each transect, 1 m^2 quadrats containing 25 cells (20 cm x 20 cm) were constructed at each end and in the middle of the transect line. Species present within each cell were identified and abundance was recorded following standard procedures 10400 A (APHA 2005; Sainty and Jacobs 1994). The proportion of cells occupied by the plants was used as a measurement of percent cover. As common reed (*Phragmites australis*) and river clubrush (*Schoenoplectus validus*) were the dominant species in the Cox Creek wetland system, these two species were chosen to be monitored.

One randomly selected cell from each transect containing plant material was harvested. The plant material was divided into the above ground (e.g. leaves, stems, flowers) and below ground (e.g. roots, rhizomes) biomass after periphyton, loose detritus and sediments were carefully washed from the plant material under running tap water. For determination of plant dry weight, plant material was dried in an oven at 80^{o}C for 48 hours or until a constant weight was achieved following standard procedures 10400 D (APHA 1998). The total plant biomass (DW_{total}) in each cell was calculated as follows:

$$DW_{total} = DW_{above} + DW_{below} \qquad \textbf{(Equation 4-1)}$$

where DW_{above} is the above ground plant dry weight in a cell (g) and DW_{below} is the below ground plant dry weight in a cell (g).

The total aerial plant biomass (B_{total}, g m^{-2}) in each quadrat was calculated as follows:

$$B_{total} = (DW_{average} / A) \times P_{proportion} \qquad \textbf{(Equation 4-2)}$$

where $DW_{average}$ is the average of total plant dry weight in a cell (g), A is the area of each cell (m^2) and $P_{proportion}$ is the proportion of cells containing plants.

To determine the total nutrient content of plant material, total phosphorus (TP) and total nitrogen (TN) contents of plant material were analysed. TP content was measured by the persulphate digestion method using the ascorbic acid reduction method (Murphy and Riley 1962). TN content was determined by high temperature combustion in an atmosphere of oxygen using a LECO CNS-2000 (Matejovic 1997). The nutrient storage by macrophytes in each transect was calculated for each species following this equation:

$$S_{P/N} = C_{P/N} * B_{total} \qquad \textbf{(Equation 4-3)}$$

where $S_{P/N}$ is the total phosphorus or total nitrogen storage of the plant biomass (g P/N m^{-2}) and $C_{P/N}$ is the total phosphorus or total nitrogen content of plant material (g P/N g^{-1} DW).

To investigate the influence of macrophytes on sediment redox potential, prior to harvesting measurements of redox potential were made within the same cells where plant was harvested (Figure 4.1 and Figure 4.2). Measurements were made at 2 cm below the sediment surface using an oxidation-reduction potential (ORP) electrode (HANNA HI 8424 coupled with EUTECH EC-FC-79602-05B).

4.2.2 Statistical analysis

All data were tested for homogeneity (O'Brien, Brown-Forsythe, Levene and Bartlett tests) and normality (Shapiro-Wilk test). Differences in above ground, below ground, total plant biomass, nutrient contents and nutrient storages were investigated by three-way analysis of variance with plant species, pond and season as the fixed effects. When significant differences were found using three-way ANOVA, Tukey-Kramer HSD was been applied to determine which seasons were significantly different from one another. Differences of sediment redox potential were compared through two-way analysis of variance with pond and season as the fixed effects. Statistically significant differences were determined when *p*-values of less than 0.05 were recorded. All statistical analyses were performed using JMP-IN (Version 4.0.3, S.A.S Institute Inc., Cary, USA). Variability between quadrats is reported as standard errors.

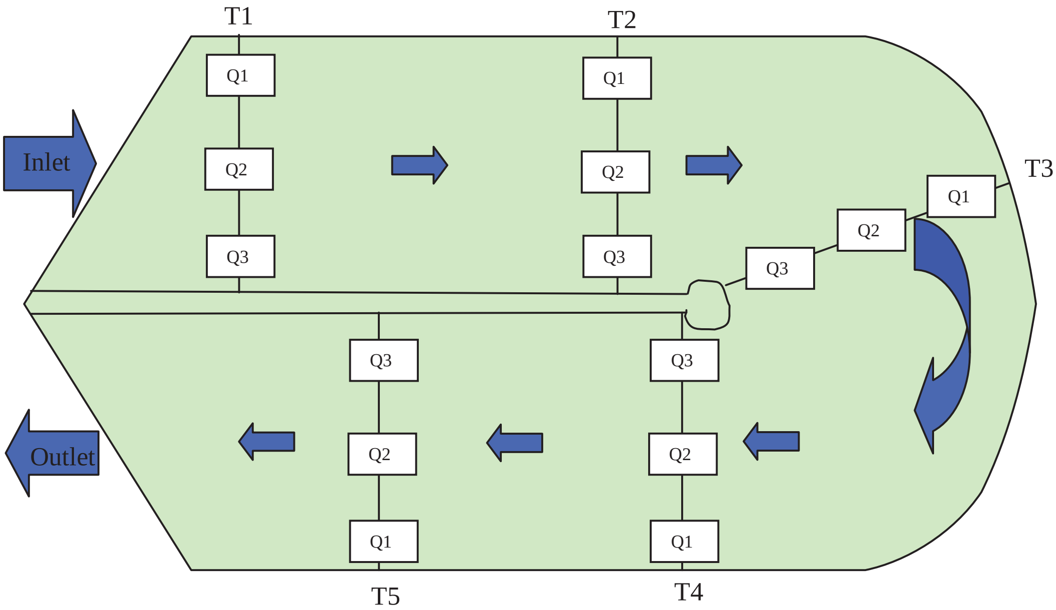

Figure 4.1: Macrophytes sampling strategy for Reed Bed of the Cox Creek wetland. Arrow denotes flow direction of water. T1, transect 1; T2, transect 2; T3, transect 3; T4, transect 4; T5, transect 5; Q1, quadrat 1; Q2, quadrat 2; Q3, quadrat 3.

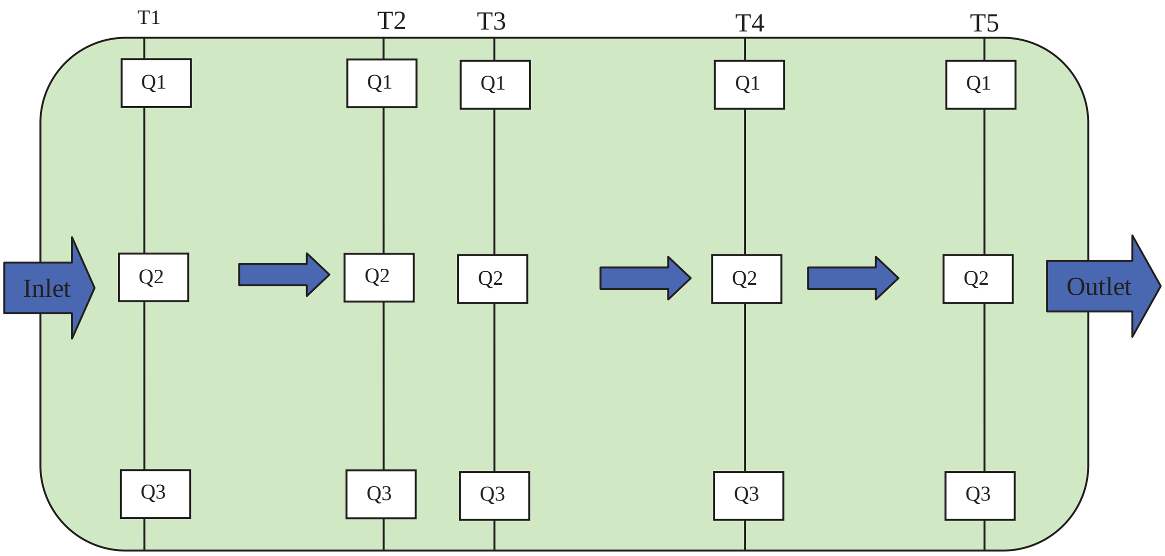

Figure 4.2: Macrophytes sampling strategy for Pond 1 of the Cox Creek wetland. Arrow denotes flow direction of water. T1, transect 1; T2, transect 2; T3, transect 3; T4, transect 4; T5, transect 5; Q1, quadrat 1; Q2, quadrat 2; Q3, quadrat 3.

4.3 Results

4.3.1 Plant biomass in Reed Bed and Pond 1 of the Cox Creek wetland

4.3.1.1 Above ground biomass

Schoenoplectus validus and *Phragmites australis* showed greater above ground biomass in Reed Bed than in Pond 1 (Table 4.1 and Table 4.2; p < 0.0001 for wetland). However, this effect was dependent upon interactions with species and season (Table 4.2). Above ground biomass of *S. validus* was generally greater than that of *P australis* in both the Reed Bed and Pond 1, although there was no apparent difference in winter 2009 in Pond 1. In both Reed Bed and Pond 1 above ground biomass of *S. validus* peaked in spring 2008, followed by a small decline to summer 2009 and more rapid decline to winter 2009 (Table 4.3). Similarly, *P. australis* had a maximum above ground biomass in spring 2008 in Reed Bed, but minimum biomass was observed in autumn 2009. This was also the case in Pond 1, although biomass peaked in both spring 2008 and summer 2009 (Table 4.1).

4.3.1.2 Below ground biomass

As for above ground biomass, the below ground biomass was greater in Reed Bed than in Pond 1 (Table 4.1 and Table 4.2; p < 0.0001 for wetland). However, this effect was dependent upon interactions with species and season (Table 4.2). Above ground biomass of *S. validus* was generally greater than that of *P. australis* in both the Reed Bed and Pond 1, although there was no apparent difference in winter 2009 in Pond 1. In both Reed Bed and Pond 1 below ground biomass of *S. validus* peaked in spring 2008, followed by a small decline to summer 2009 and more rapid decline to winter 2009 (Table 4.3). However, minimum *P. australis* below ground biomass was observed in autumn 2009 and it peaked in spring 2008 in the Reed Bed in summer 2009 in Pond 1 (Table 4.1).

4.3.1.3 Total plant biomass

Due to higher above ground and below ground biomass in Reed Bed than in Pond 1, total plant biomass of *S. validus* and *P. australis* was greater in Reed Bed than in Pond 1 (Table 4.1 and Table 4.2; p = <0.0001 for wetland). However, the effect was dependent upon interactions with species and season (Table 4.2). Total biomass of *S. validus* was generally greater than that of *P. australis* (Table 4.1). In both ponds, *S. validus* had a maximum total plant biomass in spring 2008 and a minimum in winter 2009 (Table 4.1). Unlike the maximum total plant biomass of *P. australis* in Reed Bed (spring 2008), the maximum total plant biomass was recorded in summer 2009 in Pond 1 (Table 4.1 and Table 4.3). Minimum total plant biomass of *S. validus* occurred in winter 2009, while *P. australis* occurred in autumn 2009 for both Reed Bed and Pond 1 (Table 4.1).

Table 4.1: Above ground (Above), below ground (Below) and total plant biomass (Total) of *Schoenoplectus validus* and *Phragmites australis* in Reed Bed and Pond 1 of the Cox Creek wetland system in spring 2008 (Spr 08), summer 2009 (Sum 09), autumn 2009 (Aut 09) and winter 2009 (Win 09). Mean ± standard error, n=15.

		Reed bed			**Pond 1**		
Species	**Season**	**Above ($g\ m^{-2}$)**	**Below ($g\ m^{-2}$)**	**Total ($g\ m^{-2}$)**	**Above ($g\ m^{-2}$)**	**Below ($g\ m^{-2}$)**	**Total ($g\ m^{-2}$)**
S. validus	Spr 08	404 ± 40.2	1036 ± 64.9	1441 ± 93.0	81 ± 5.5	204 ± 10.9	286 ± 82.9
	Sum 09	346 ± 49.6	915 ± 19.4	1261 ± 180.3	68 ± 4.0	192 ± 13.5	261 ± 79.2
	Aut 09	102 ± 18.3	218 ± 90.2	320 ± 30.6	20 ± 9.5	44 ± 4.1	64 ± 7.6
	Win 09	61 ± 7.5	134 ± 25.5	195 ± 27.7	13 ± 6.8	36 ± 8.3	49 ± 5.2
P. australis	Spr 08	128 ± 9.6	264 ± 11.2	393 ± 33.0	12 ± 0.2	50 ± 2.8	63 ± 6.9
	Sum 09	122 ± 14.9	247 ± 17.1	369 ± 46.9	12 ± 1.9	75 ± 18.9	88 ± 15.7
	Aut 09	23 ± 8.5	55 ± 5.9	79 ± 8.3	3 ± 0.1	14 ± 2.9	17 ± 3.6
	Win 09	41 ± 5.7	86 ± 8.6	128 ± 15.8	7 ± 2.8	23 ± 9	30 ± 0.2

Table 4.2: *P*-values obtained for the effects of plant species, wetland pond and season (and interaction) on above ground, below ground and total plant biomass. Interaction effects between these parameters denoted with *. Significant difference are recorded when *p*-value less than 0.05.

Effect	Above ground biomass	Below ground biomass	Total plant biomass
Species	0.0260	<0.0001	<0.0001
Wetland	<0.0001	<0.0001	0.0194
Season	<0.0001	<0.0001	0.0403
Species * wetland	0.0242	<0.0001	<0.0001
Species * season	<0.0001	<0.0001	<0.0001
Wetland * season	<0.0001	<0.0001	0.0028
Species * wetland * season	<0.0001	<0.0001	<0.0001

Table 4.3: Result of post-hoc comparison (Tukey-Kramer HSD) on above ground, below ground and total plant biomass between seasons.

Season-Season	Above ground biomass	Below ground biomass	Total plant biomass
Spr 08-Sum 09	#	NS	NS
Spr 08-Aut 09	##	NS	NS
Spr 08-Win 09	###	###	##
Sum 09-Aut 09	##	NS	NS
Sum 09-Win 09	#	#	#
Aut 09-Win 09	#	##	#

*Note: ###, extremely significant difference (p <0.001); ##, moderately significant difference (p <0.01); #, significant difference (p <0.05); NS, not significant (p >0.05).

4.3.2 Plant nutrient contents

4.3.2.1 Above ground nutrient contents

TP contents of above ground biomass of *S. validus* and *P. australis* were higher in Reed Bed than in Pond 1 (Figure 4.3 A, $p = 0.0027$ for wetland). However, the effect was dependent upon interactions with species and season (Table 4.4). In Reed Bed, above ground TP contents of *S. validus* were greater than that of *P. australis* in all seasons except winter 2009. However, in Pond 1 above ground TP contents were higher for *P. australis* than *S. validus* in summer 2009, but the reverse was true for winter 2009 (Table 4.5). TP contents of *S. validus* ranged between 1.7 ± 1.0 and 4.0 ± 0.2 mg P g^{-1} and was highest during spring 2008 in Reed Bed (Figure 4.3 A and Table 4.4; $p < 0.0001$ for season). Unlike *S. validus*, *P. australis* had highest TP contents in winter 2009 in the Reed Bed (2.6 ± 0.4 mg P g^{-1}) and was lowest in autumn 2009 in Pond 1 (Figure 4.3 A and Table 4.5).

TN contents of above ground biomass of both *S. validus* and *P. australis* were higher in Reed Bed than in Pond 1 (Figure 4.3 B and Table 4.4; $p < 0.0001$ for wetland), but the effect was dependent upon interactions with species and season (Table 4.4). TN contents of above ground biomass of both *S. validus* and *P. australis* varied seasonally (Figure 4.3 B and Table 4.4; $p = 0.0236$ for season): highest TN contents during spring 2008 in Reed Bed and during spring 2008 to summer 2009 in Pond 1 (Figure 4.3 B and Table 4.5).

4.3.2.2 Below ground nutrient contents

TP contents in below ground biomass of both *S. validus* and *P. australis* were higher in Reed Bed than in Pond 1 (Figure 4.4 A and Table 4.4, $p = 0.0003$ for wetland). However, the effect was dependent upon interactions with species and season (Table 4.4). In Reed Bed, TP contents in below ground biomass of both *S. validus* and *P. australis* were highest in autumn 2009 and were lowest in winter 2009 (Figure 4.4 A and Table 4.5). In Pond 1, TP contents in below ground biomass of both plants were highest in spring 2008 (Figure 4.4 A and Table 4.5).

TN contents in below ground biomass of both *S. validus* and *P. australis* were higher in Reed Bed than in Pond 1 (Figure 4.4 B and Table 4.4, $p < 0.0001$ for wetland). However, this effect was dependent upon the interaction with species and season (Table 4.4). TN contents in below ground biomass of both *S. validus* and *P. australis* varied considerably between seasons with highest TN contents of *S. validus* in summer 2009, but highest TN contents of *P. australis* in autumn 2009 in Reed Bed and spring 2008 in Pond 1 (Figure 4.4 B and Table 4.5). In Pond 1, the lowest TN contents of *S. validus* were in winter 2009, while *P. australis* were in autumn 2009 (Figure 4.4 B and Table 4.5).

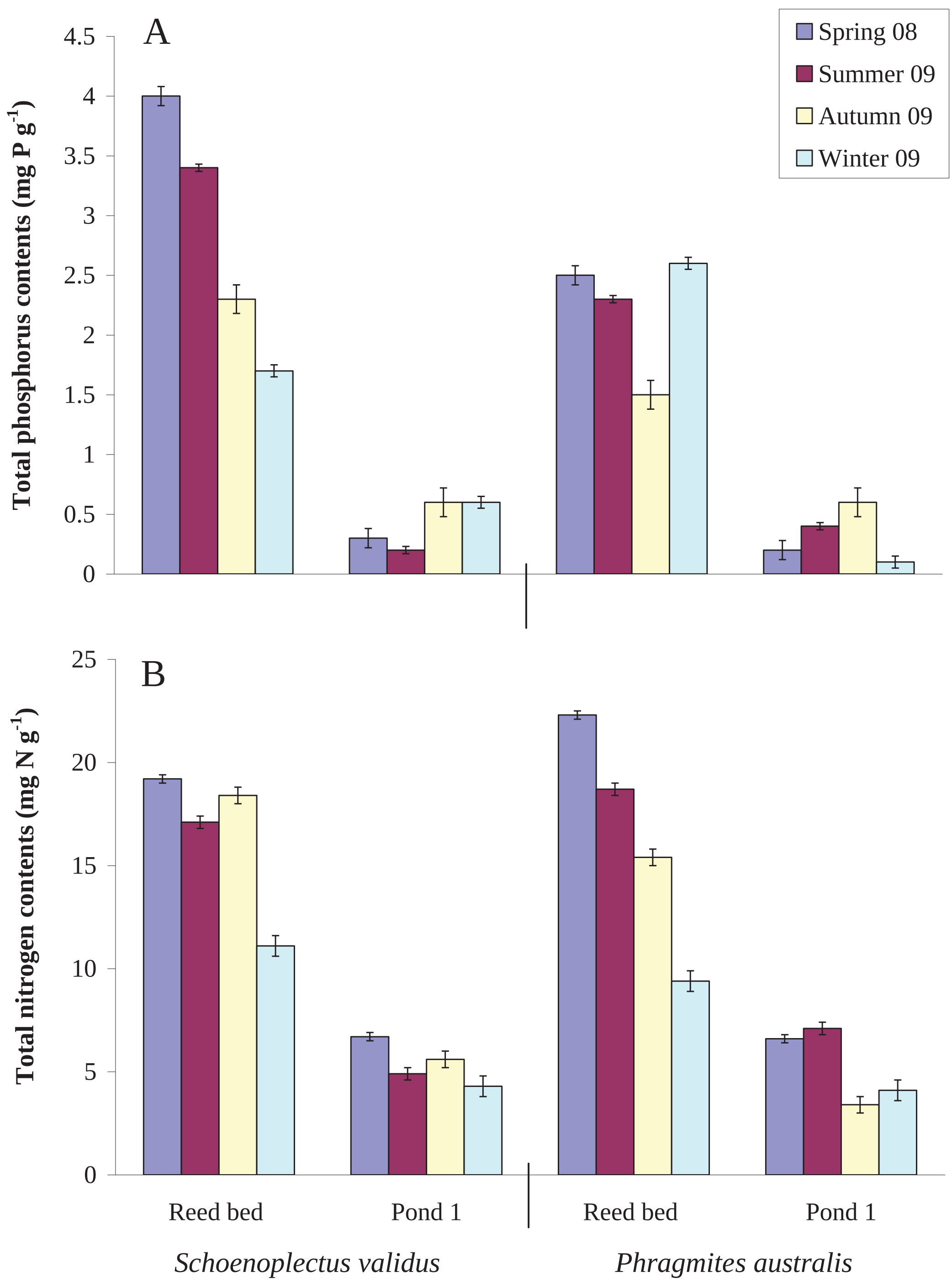

Figure 4.3: Mean total phosphorus (A) and total nitrogen (B) contents in above ground biomass of *Schoenoplectus validus* and *Phragmites australis* for Reed Bed and Pond 1 of the Cox Creek wetland. Error bars represent standard errors.

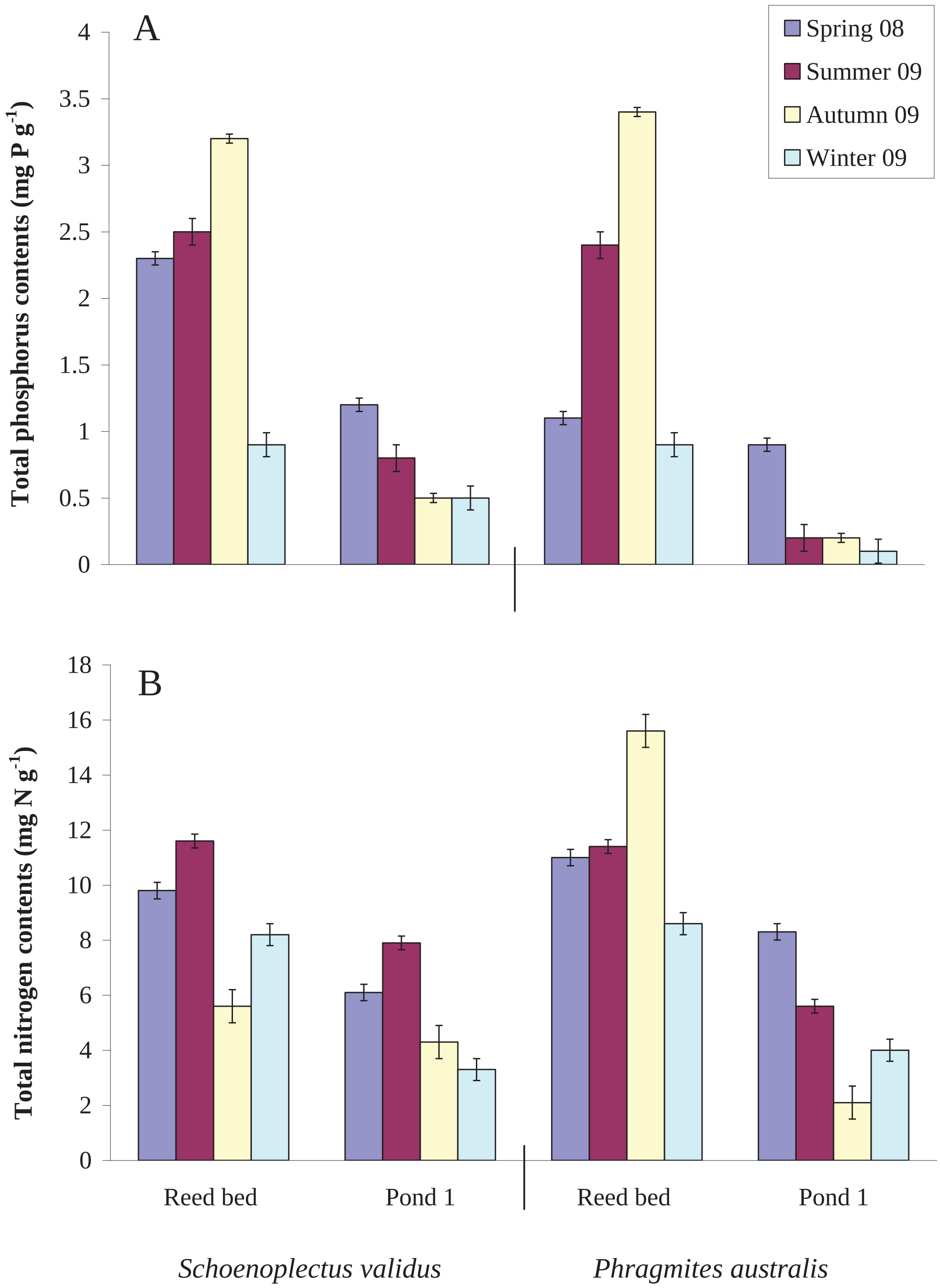

Figure 4.4: Mean total phosphorus (A) and total nitrogen (B) contents in below ground biomass of *Schoenoplectus validus* and *Phragmites australis* for Reed Bed and Pond 1 of the Cox Creek wetland. Error bars represent standard errors.

Table 4.4: *P*-values obtained for the effects of plant species, wetland pond and season (and interaction) on above ground and below ground nutrient contents. Interaction effects between these parameters denoted with *. Significant difference are recorded when *p*-value less than 0.05.

Effect	**Phosphorus contents**		**Nitrogen contents**	
	Above ground	**Below ground**	**Above ground**	**Below ground**
Species	0.0361	0.0158	0.0184	0.0047
Wetland	0.0027	0.0003	<0.0001	<0.0001
Season	<0.0001	<0.0001	0.0236	<0.0001
Species * wetland	<0.0001	<0.0001	<0.0001	0.0024
Species * season	<0.0001	<0.0001	0.3115	<0.0001
Wetland * season	0.0231	0.0054	<0.0001	<0.0001
Species * wetland * season	<0.0001	<0.0001	<0.0001	<0.0001

Table 4.5: Result of post-hoc comparison (Tukey-Kramer HSD) on above ground and below ground nutrient contents between seasons.

Effect	**Phosphorus contents**		**Nitrogen contents**	
	Above ground	**Below ground**	**Above ground**	**Below ground**
Spr 08-Sum 09	##	#	###	###
Spr 08-Aut 09	#	###	##	###
Spr 08-Win 09	##	#	##	#
Sum 09-Aut 09	NS	NS	NS	NS
Sum 09-Win 09	#	NS	#	NS
Aut 09-Win 09	NS	#	NS	NS

*Note: ###, extremely significant difference (*p* <0.001); ##, moderately significant difference (*p* <0.01); #, significant difference (*p* <0.05); NS, not significant (*p* >0.05).

4.3.3 Plant nutrient storage

4.3.3.1 Phosphorus storage

Phosphorus storage of both *S. validus* and *P. australis* were higher in Reed Bed than in Pond 1 (Table 4.6 and Table 4.7, $p = 0.0029$ for wetland) due to the high plant biomass and P contents observed in Reed Bed (see also Table 4.1 and Figure 4.3). However, the effect was dependent upon interactions with species and season (Table 4.7). P storage by *S. validus* was greater than that of *P australis* with the P storage by both species decreasing from spring 2008 to winter 2009 in Pond 1 and for *S. validus* in the Reed Bed. However, in Reed Bed P storage by *P. australis* peaked in summer 2009 and fell rapidly to a minimum in autumn 2009 (Table 4.6, Table 4.7 and Table 4.8).

4.3.3.2 Nitrogen storage

Similar patterns of N storage were observed as for P storage with the higher N storage in the Reed Bed than in Pond 1 (Table 4.6 and Table 4.7, $p = 0.0109$ for wetland), but this effect was dependent upon interactions with species and season (Table 4.7). N storage by *S. validus* was greater than that of *P. australis*, with the N storage by both species decreasing from spring 2008 to winter 2009 in Reed Bed and for *S. validus* in the Pond 1. However, in the Pond 1 N storage by *P. australis* peaked in summer 2009 and fell rapidly to a minimum in autumn 2009 (Table 4.6, Table 4.7 and Table 4.8).

Table 4.6: Mean nutrient storage (gP m^{-2} and gN m^{-2}) of *Schoenoplectus validus* and *Phragmites australis* for Reed Bed and Pond 1 of the Cox Creek wetland system. Spr 08, spring 2008; Sum 09, summer 2009, Aut 09, autumn 2009; Win 09, winter 2009. Mean ± standard error, n=15.

Species	Nutrient storage	Reed bed				Pond 1			
		Spr 08	Sum 09	Aut 09	Win 09	Spr 08	Sum 09	Aut 09	Win 09
S. validus	P storage (gP m^{-2})	9.1± 2.5	7.2 ± 1.3	1.1 ± 0.2	0.6 ± 0.07	0.4 ± 0.01	0.3 ± 0.002	0.07 ± 0.001	0.05 ± 0.001
P. australis	P storage (gP m^{-2})	1.4 ± 0.3	1.7 ± 0.5	0.4 ± 0.05	0.5 ± 0.02	0.07 ± 0.004	0.05 ± 0.003	0.01 ± 0.003	0.006 ± 0.001
S. validus	N storage (gN m^{-2})	41.8 ± 10.3	36.2 ± 6.1	7.7 ± 1.9	3.8 ± 0.4	3.7 ± 1.3	3.3 ± 0.9	0.6 ± 0.009	0.4 ± 0.04
P. australis	N storage (gN m^{-2})	13.1 ± 3.0	11.1 ± 3.3	2.5 ± 0.8	2.3 ± 0.3	0.9 ± 0.2	1.1 ± 0.004	0.09 ± 0.008	0.2 ± 0.04

Table 4.7: *P*-values obtained for the effects of plant species, wetland pond and season (and interaction) on above ground and below ground nutrient storages. Interaction effects between these parameters denoted with *. Significant difference are recorded when *p*-value less than 0.05.

Effect	Phosphorus storages	Nitrogen storages
Species	0.0195	0.0318
Wetland	0.0029	0.0109
Season	<0.0001	<0.0001
Species * wetland	0.0371	<0.0001
Species * season	<0.0001	0.0053
Wetland * season	<0.0001	<0.0001
Species * wetland * season	<0.0001	<0.0001

Table 4.8: Result of post-hoc comparison (Tukey-Kramer HSD) on above ground and below ground nutrient storages between seasons.

Effect	**Phosphorus storages**	**Nitrogen storages**
Spr 08-Sum 09	##	#
Spr 08-Aut 09	#	#
Spr 08-Win 09	##	#
Sum 09-Aut 09	###	###
Sum 09-Win 09	##	#
Aut 09-Win 09	NS	NS

*Note: ###, extremely significant difference (p <0.001); ##, moderately significant difference (p <0.01); #, significant difference (p <0.05); NS, not significant (p >0.05).

4.3.4 The influence of macrophytes to sediment redox potential

The sediment redox potential was significantly higher in Reed Bed than in Pond 1 (Figure 4.5, p = 0.0038 for wetland). In Reed Bed, the sediment redox potential indicated relatively oxidised conditions and was highest during winter 2009 and lowest during summer 2009 (Figure 4.5 and Table 4.9; p = 0.0152 for season). In contrast, sediment redox potential in Pond 1 which had less macrophytes biomass, indicated less oxidised conditions. In Pond 1 sediment redox potential was highest during autumn 2009 (+20 ± 7.5 mV) and was lower in winter 2009 (8 ± 1.3 mV), spring 2008 (-12 ± 3.8 mV) and summer 2009 (-22 ± 10.5 mV). Consequently, these response sediment redox potential to wetland was dependent upon the interaction with season (Table 4.9; p = 0.0119).

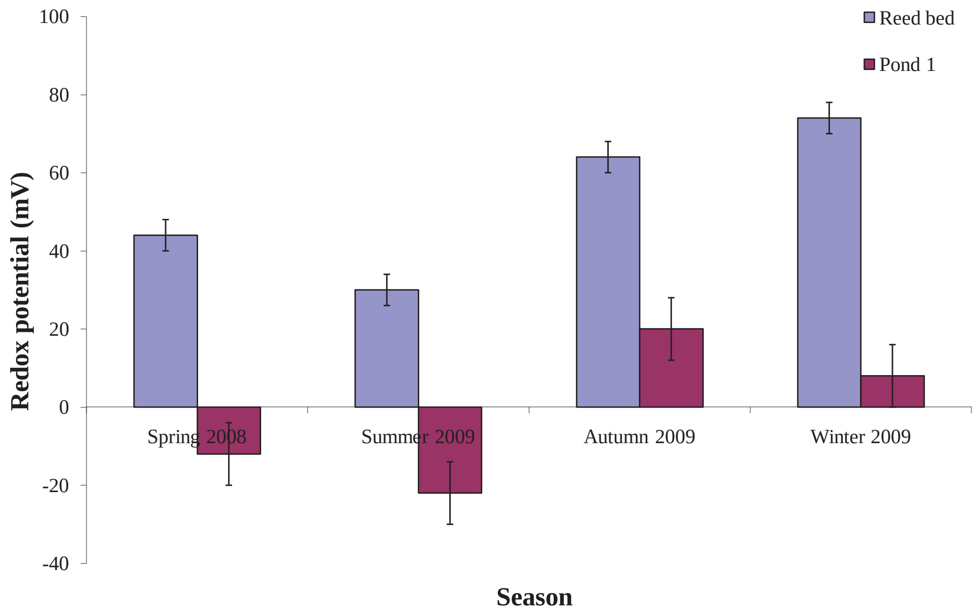

Figure 4.5: Comparison of sediment redox potential between Reed Bed and Pond 1 of the Cox Creek wetland system. Error bars represent standard errors.

Table 4.9: *P*-values obtained for the effects of wetland pond and season (and interaction) on sediment redox potential. Interaction effects between these parameters denoted with *. Significant difference are recorded when *p*-value less than 0.05.

Effect	**Redox potential**
Wetland	0.0038
Season	0.0152
Wetland * season	0.0119

4.4 Discussion

Constructed wetlands with dense vegetation are considered an effective ecotechnology for removing phosphorus and nitrogen (Brix *et al*. 1994; Granėli 1999; Wen 2002; Arias and Brix 2005). They are used throughout the world for controlling various sources of pollution such as domestic sewage, abattoir wastewater, landfill leachate, contaminated groundwater, animal wastes and extensive agricultural activities (Reddy and Gale 1994). The catchment pollution of Cox Creek primarily originates from agricultural land-use, including market gardens and vegetable production. Past and current application of fertiliser has been identified as the major source of the observed loads of nutrients (Fisher 2005; Bradley *et al*. 2007). As a result, a series of constructed wetlands (Figure 2.4 in chapter two), including a reed bed pond, were implemented to reduce the amount of nutrients being delivered to the downstream reservoir, Mount Bold.

Macrophytes may remove pollutants by their direct uptake of nutrient for their growth and function as nutrient storages (Karjalainen 2001; Wen 2002; Kim 2009). Nutrient storage by macrophytes in the Cox Creek wetland system was much lower than reported in the study by Reddy and DeBusk (1987). Reddy and DeBusk (1987) reported nutrient storage of 140 – 1560 g N m^{-2} and 14 – 375 g P m^{-2} for a wetland containing *Typha*, *Schoenoplectus*, *Scirpus* and *Phragmites*. This is compared to 0.09 ± 0.008 – 41.8 ± 10.3 g N m^{-2} and 0.006 ± 0.001 – 9.1 ± 2.5 g P m^{-2} for this study, which might be due to lower plant biomass. Nutrient storage for the two species (*Schoenoplectus* and *Phragmites*) that were observed in the Cox Creek wetland system have been used successfully in a constructed wetland in Queensland, Australia (Greenway and Woolley 2001; Greenway 2002). These two species proved to be useful in terms of the ability to store phosphorus and nitrogen. Many studies have demonstrated that *P. australis* remove both nutrients and heavy metals such as lead, copper, zinc, nickel and cadmium (Breen 1990; Vymazal *et al*. 1999; IWA 2000; Greenway 2002; Iamchaturapar *et al*. 2007; Thullen *et al*. 2008).

The nutrient retention in wetland system increases as the plant biomass and density increase (Boyd, 1970; Tanner, 1996, Brix 1997; Greenway and Woolley, 1999). Hence, greater plant biomass and density will result in a greater nutrient uptake by plants. The present study is limited only to two dominant species (*P. australis* and *S. validus*) which are commonly used in constructed wetlands and no conclusions can be drawn regarding the contribution of the whole macrophyte community. Therefore, the potential of macrophytes community to remove nutrients contributed little to biomass production due to other macrophytes species were not recorded. In this study, the seasonal dynamics of above ground and below ground biomass of two dominant species present in the system were observed. Total plant biomass ranged between 0.08 and 1.44 kg m^{-2} for Reed Bed, and 0.02 and 0.29 kg m^{-2} for Pond 1, respectively. In comparison, Jespersen *et al.* (1998) investigated reed growth in nutrient-rich sewage sludges and found a maximum above ground biomass of 2-3 kg m^{-2}, whereas Adcock and Ganf (1994) have recorded a lower above ground biomass of 0.8 kg m^{-2} in natural and constructed wetland system in Australia. Total plant biomass for *S. validus* was also slighly lower than found in a previous study by Tanner (1996) in sub-surface wetlands where mean plant biomass was in the range of 1.8 kg m^{-2}. The biomass production in form of dry weight measured of the reed bed indicated that the primary productivity of the Reed Bed was relatively high, which also correspond with the nutrient concentrations and storage.

The plant nutrient content in both ponds was generally highest in the growing season (spring and summer) than in the non-growing season (autumn and winter) (Figure 4.3 and Figure 4.4). Nutrient content for above and below ground plant components were within the range recorded for the same species growing in treatment wetland in Australia (total nutrient contents = 1.8 – 4.0 mg P g^{-1} and 9.8 – 20.3 mg N g^{-1}) (Wen 2002; Kim 2009). From the present study, below ground biomass was found to be higher than above ground biomass (Table 4.1). However, more than 50% of nutrients were found to be stored in above ground portions of the plants than in below ground portions (Figure 4.3 and Figure 4.4). Therefore nutrient removal in constructed wetland has a positive impact in which the amount of nutrient storage can be removed if the above ground biomass is harvested. In the annual life cycles of 2008 to 2009, the above ground nutrient concentration was significantly higher during spring 2008 and summer 2009 maybe due to flowering and new plant growth increasing the above ground nutrient contents (Breen 1990). During autumn 2009 and winter 2009, the plants entered the phase of decreasing above ground nutrient concentration that might be due to plant decomposition and the process of translocations of nutrient to the below ground plant components when plant senesce (Davis and van der Valk 1978; Suzuki et al. 1989). In the following growing period these nutrients may be remobilised upwards for growth of the young shoots (e.g. stems and leaves) (Davis 1991).

Besides direct assimilation of nutrient by macrophytes, rooted macrophytes can increase the sediment redox potential by pumping oxygen into the sediment (Carpenter *et al.* 1983; Stephen *et al*. 1997; Tanner *et al*. 1999). The present study shows that sediment redox potential was higher in Reed Bed than Pond 1 (Figure 4.5), suggesting that both or one species may have the ability to release oxygen from roots. Species possessing an internal convective flow-through ventilation system have higher internal oxygen concentrations in the rhizomes and roots than species relying exclusively on the diffusive transfer of oxygen (Armstrong and Armstrong 1991; White and Ganf 1998; Sorrell and Tanner 2000). Freshwater macrophytes including *Schoenoplectus validus*, *Baumea articulata*, *Phragmites australis*, *Eleocharis sphaceolata* and *Cyperus involucratus* have been shown to cause internal pressurisation and convective flow of oxygen (Brix *et al.* 1992). Therefore the present study indicated that Reed Bed containing greater plant biomass of *S. validus* and *P. australis* than Pond 1 could better oxidise the sediment, increasing the capacity for sediment phosphorus adsorption processes.

The maintenance of vegetation is considered to be one of many management tools in ensuring successful operation of a constructed wetland. The change in nutrient contents in the above ground plant material was of particular interest if harvesting of the standing crop were to be implemented. As for the Cox Creek wetland, most of the nutrient storage within plant species peaked during spring to summer seasons, corresponding with the highest total plant biomass and nutrient contents. Therefore, it appears that the best timing for harvesting the standing crop is after spring, when nutrient concentrations are expected to be highest, preferably in mid summer season to ensure maximum amount of nutrient concentrations would be harvested. Regular harvesting of *S. validus* and *P. australis* in Reed Bed could potentially avoid recycling of nutrients into the wetland system during winter season when the plants senesce (Bald 2001; Greenway and Woolley 2001; Greenway 2002; Browning

2003). Harvesting before winter season will be the most effective in removing nutrients from the wetland and will remove plant matter which may fall into the water and rot over winter if allowed to die back (Browning 2003).

In conclusion, nutrient storage by macrophytes was highest in Reed Bed than in Pond 1 as a result of higher total plant biomass and nutrient contents of two dominant species, *S. validus* and *P. australis*. Using the dry weight and nutrient data from the survey which was conducted in 2009, the annual P storage of 36 kg P yr^{-1} can be removed if the standing crop biomass is harvested (Figure 7.1 in chapter seven). This is an estimation from this study where the P uptake rate of 0.05 kg m^{-2} yr^{-1} was calculated, assuming an annual constant growth of the macrophytes community.

Chapter five

5 Phosphorus sorption and nutrient storage in sediment of the Cox Creek wetland system

5.1 Introduction

Phosphorus has been recognised as the primary limiting nutrient of algal growth in many freshwater aquatic ecosystems (Baldwin *et al*. 2000; Maberly *et al.* 2003; Kadlec 2006). Following the extensive replacement of native vegetation by agricultural crops and application of fertilisers, nutrient inputs from the land to inland water bodies have increased, leading to eutrophication of many freshwater systems (Horne and Goldman 1994; Sharpley and Tunney 2000; Viney *et al*. 2000). Many studies demonstrate that P input has caused eutrophication in freshwater around the world (e.g. Elser and Foster 1998; Walling *et al.* 2003; Wang *et al.* 2009). Indeed, the risk of eutrophication has become a major concern throughout Europe, North America and Australia due to increased nutrient levels, particularly phosphorus (Department for Water Resources 2000; Smith 2003; Bruland and Richardson 2006).

Phosphorus enters water bodies as dissolved P or bound with suspended mineral or organic particles eroded during flow events from agricultural land through surface runoff (Sharpley *et al.* 1994; Smith *et al.* 1996). Once in receiving water bodies, the process of adsorption and desorption of P at the water column and sediment interface plays an important role in regulating P concentrations. This process involves weak atomic and molecular interactions or stronger ionic-type bonds (Nair *et al*. 1984; Berkheiser *et al*. 1980; Webster *et al*. 2001). Wen (2002) found that the sorption of P is important to the overall function of constructed wetlands at the Lower River Murray, South Australia, Australia.

Given the high ability of wetland sediments to retain P is likely to be an important process resulting in the retention of P in the Cox Creek wetland.

It was hypothesised that the movement of organic matter and P carried by surface runoff into the Cox Creek wetland is driven by water flow (Figure 5.1). As water enters the wetland, particles containing phosphorus and organic materials will be deposited into the sediment through sedimentation (Lockaby *et al.* 2005; Lopez *et al.* 2009). Higher sedimentation is likely to be observed at the inlet sites due to low flow velocity from the Cox Creek to the wetland, leading to settling of suspended particles and associated nutrients. Further downstream, lower sedimentation will be observed due to less suspended particles in the water. Since most wetland sediments have a very high capacity to adsorb P (Nash and Halliwell 2000), dissolved P can be adsorbed by sediment particles and stored in the sediments. However, P sorption capacity will increase from inflow to outflow as there is often greater P deposition and P content at the inflow and so a greater degree of P saturation. P removal in constructed wetlands is generally considered to be high initially, but decline as the system "ages" (Kadlec and Bevis 1985; Mann 1990), most likely due to saturation of finite adsorption sites (Richardson 1985; Kadlec and Bevis 1997).

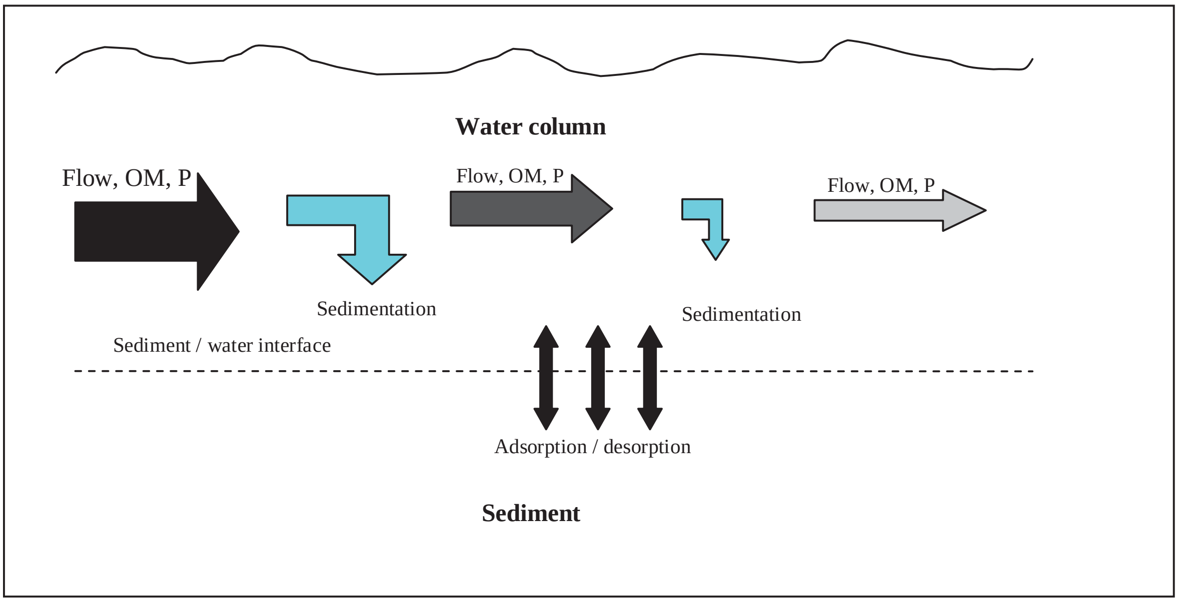

Figure 5.1: Conceptual diagram of phosphorus sedimentation and sorption process in the wetland sediment of the Cox Creek wetland. OM, organic matter; P, phosphorus.

Laboratory adsorption experiments have been used for many years to qualify and predict retention capacity of sediments (Olsen and Wanatabe 1957; Logan 1982; White 2000). In particular, the equilibrium phosphorus concentration (EPC) and P adsorbed by sediment obtained from the adsorption experiments have been calculated using standard Langmuir and Freundlich adsorption isotherms (Olsen and Wanatabe 1957; Barrow 1978; Reddy *et al.* 1995; White 2000). EPC can be defined as P concentration in which adsorption by solid phase equals to desorption, thus higher EPC indicating low P sorption capacity while lower EPC indicating high P sorption capacity. In most circumstances, phosphorus binding cations (Ca, Mg, Fe, and Al) forms complexes with phosphate ions (PO_4), leading to P retention as Fe/Al-P or Ca/Mg-P (Moore and Reddy 1994). It is believed that some forms of phosphorus in sediment are sensitive to environmental conditions, thus may be released to overlying water column under certain circumstances. For example, the P associated with ferric material is sensitive to low redox potential and may be remobilised when the sediment becomes anoxic due to bacterial respiration (Froelich 1988; Gachter and Meyer 1993). In other cases, the Ca and Al bound P is less affected by redox and sensitive to low pH value (Moore and Reddy 1994; Wen 2002). It is possible to characterise the phosphorus chemistry using the sequential extraction technique of Hieltjes and Lijklema (1980), which was modified from Williams (1971) and Kurmies (1972).

This study was conducted in order to understand P dynamics at the sediment-water interface of the Cox Creek wetland. Sediment nutrient contents, phosphorus fractionation and phosphorus sorption isotherms of Reed Bed and Pond 1 were analysed and compared between seasons. The active uptake of P by macrophytes in Reed Bed (chapter four) from sediment porewater potentially establishes concentration gradients between the water column and sediment, thus promotes the downward P flux (diffusion), and improves overall P removal. The following hypothesis was tested: Pond 1 would have higher P deposition, higher sediment nutrient content, higher EPC and more saturated bonding sites compared to Reed Bed because it receives greater flow and so greater organic matter, phosphorus deposition, and therefore has a low phosphorus retention capacity, which would be reflected by sediment P fractionation. Sediment core samples were seasonally collected and the phosphorus adsorption-desorption experiments were conducted in the laboratory.

5.2 Methods

5.2.1 Collection of sediment samples

Sediment samples were collected from Reed Bed and Pond 1 of the Cox Creek wetland system in spring 2008 (20 to 24 October 2008), summer 2009 (12 to 16 January 2009), autumn 2009 (18 to 21 May 2009) and winter 2009 (06 to 09 July 2009). The Reed Bed and Pond 1 were divided into five equal longitudinal cells, with a randomly selected transect chosen in each cell (Figure 4.1 and Figure 4.2 in chapter four). In each transect, 1 m^2 quadrats containing 25 cells (20 cm x 20 cm) were constructed at each end and in the middle of the transect line. In each quadrat, a sediment core sampler (a 30 cm length and 5.5 cm internal diameter Plexiglas cylinder tube) was used to collect sediment cores up to 10 cm in depth in order to obtain natural orientation of the cores. Polyvinyl chloride (PVC) caps were used to prevent air circulation and to preserve redox conditions, thus preventing the transformation of phosphorus and nitrogen forms. After collection, all fresh sediment cores were stored in dark at 4^oC and brought back to the laboratory in sealed plastic bags for analysis. A total of 15 samples were collected from each pond.

5.2.2 Analysis of sediment samples

In the laboratory, the sediment cores were homogenised and divided into two sub-samples (Figure 5.2). One sub-sample was used for organic matter (OM), total phosphorus (TP), total nitrogen (TN) and total carbon (TC) analysis (Figure 5.2). The sediments were dried at 60^oC for 48 hours. Sediments were then finely ground using a mortar and pestle and sieved using a standard 2 mm-mesh (Wen 2002; Kim 2009). The TP contents were measured using a Technicon Autoanalyser after nitric-perchloric acid digestion at 160^oC for 6 hours (Murphy and Riley 1962). The TN and TC were measured with a LECO CNS-2000 using high temperature combustion in an atmosphere of oxygen (Matejovic 1997). The OM contents were measured from loss of volatile solids upon ignition at 550^oC following standard method 2540E (Eaton *et al.* 1995). The second sub-sample remained fresh and was used for phosphorus adsorption-desorption experiments and phosphorus fractionation**.** The fresh sediment samples were kept in a cool room at 4^oC and brought back to room temperature condition prior to the experiments.

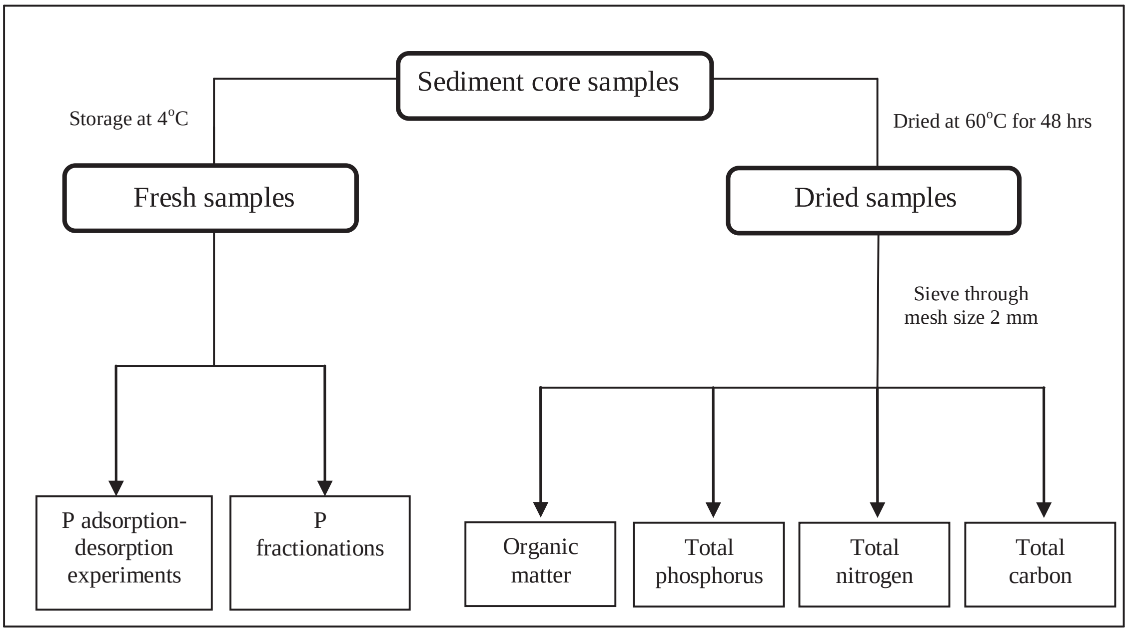

Figure 5.2: Schematic protocol for analysis of sediment core samples collected from Reed Bed and Pond 1 of the Cox Creek wetland.

5.2.3 Phosphorus fractionation

Phosphorus forms in soil sediments are characterised by their specific solubilities in various chemical extractants (Paludan and Jensen 1995; Fytianos and Kotzakioti 2005). To quantify the phosphorus forms within the sediments, sequential phosphorus fractionations were carried out following the procedure reported by Penn *et al*. (1995) and Rydin (2000). This separates phosphorus in the sediments into five pools: (1) NH_4Cl-P (loosely sorbed P), (2) HCl-P (Ca/Mg-P), (3) NaOH-iP (Fe/Al-P), (4) NaOH-oP (labile organic-P), and (5) residual phosphorus (res-P) as shown in Figure 5.3. The loosely sorbed P represents adsorbed potentially bioavailable phosphorus. The HCl-P represents P associated with calcium (Ca) and magnesium (Mg) that is relatively stable and not readily bioavailable. The NaOH-iP represents inorganic P bound with iron (Fe) and aluminium (Al) and represents P not readily bioavailable. The labile organic P is an intermediate pool between readily available and unavailable P. The res-P are the highly resistant organic P or unavailable mineral bound P which is not extracted with either alkali or acid.

The phosphorus fractionations were conducted by adding 25 mL of 1*M* NH_4Cl solution to wet sediment (0.5 g dry weight equivalent) in centrifuge tubes. Formaldehyde solution (1 mL) was added to inhibit microbial activity, followed by shaking in an over-end shaker for 2 hours. This step was repeated, resulting in loosely sorbed P (NH_4Cl-P). Following this step, 0.1*M* NaOH (25 mL) was added to the residue followed by shaking in an over-end shaker for another 17 hours, resulting in NaOH-total P (digested) and NaOH-iP (undigested). The labile organic P (NaOH-oP) was calculated from the difference of NaOH-total P and NaOH-iP. The remaining residue from 0.1*M* NaOH extractions was then added with 0.5*M* HCl acid solution (25 mL) followed by shaking for another 24 hours, resulting in HCl-P. The P remaining in the final residue (res-P) was calculated from the difference of total phosphorus (TP) and the sum of all extractable P fractions. All the extractants were filtered through 0.45-µm Milipore® membrane filter and filtrate was used for filterable reactive phosphorus (FRP) following the ascorbic acid method (APHA 2005), using a Hitachi U-2000 spectrophotometer (Hitachi Ltd. Tokyo, Japan).

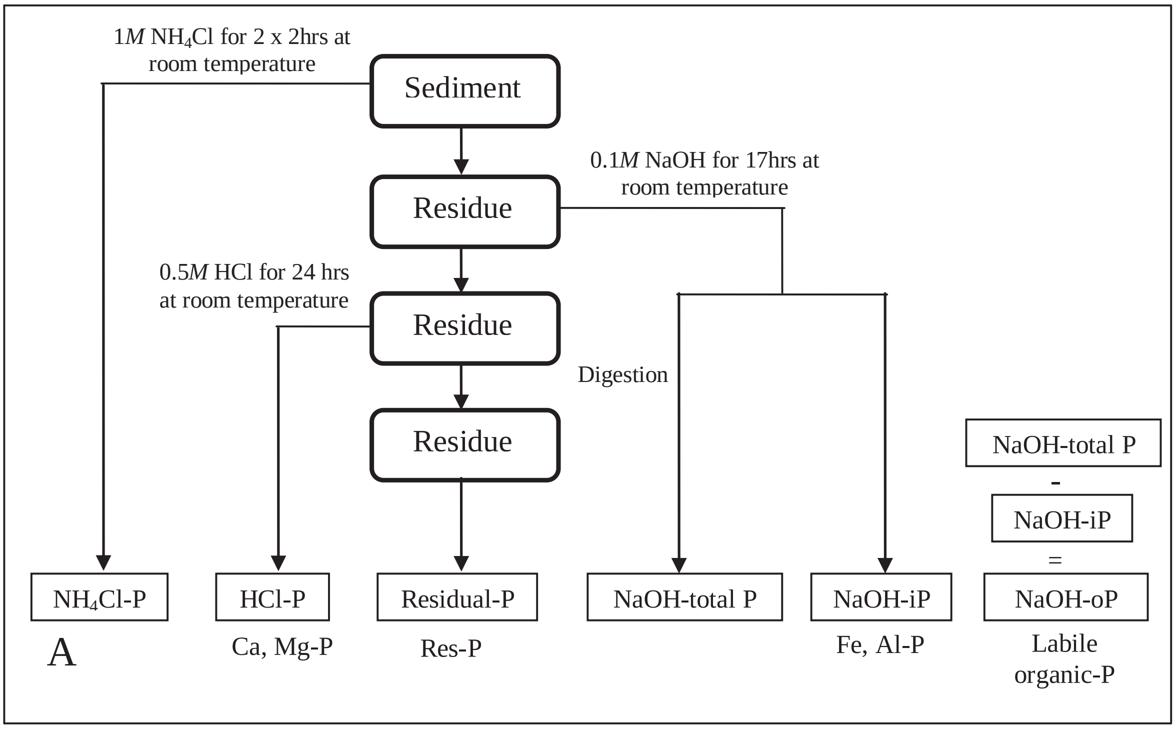

Figure 5.3: Sequential phosphorus fractionation scheme used to differentiate phosphorus forms in the sediment samples collected from the Cox Creek wetland. Abbreviations include: ammonium chloride (NH_4Cl), hydrochloric acid (HCl), sodium hydroxide (NaOH), ammonium chloride bound phosphorus (NH_4Cl-P), hydrochloric acid bound phosphorus (HCl-P), calcium, manganese bound phosphorus (Ca, Mg-P), residual phosphorus (Res-P),sodium hydroxide bound total phosphorus (NaOH-total P), sodium hydroxide bound inorganic phosphorus (NaOH-iP), iron, aluminium bound phosphorus (Fe, Al-P), and sodium hydroxide bound organic phosphorus (NaOH-oP).

5.2.4 Phosphorus adsorption-desorption experiments

Phosphorus adsorption-desorption experiments were conducted to estimate the P sorption capacity of wetland sediments. These experiments were carried out by adding a known amount of dissolved inorganic phosphorus (as KH_2PO_4) to wet sediment (0.5 g dry weight equivalent) of each sediment sample. Initial concentrations of 0, 0.2, 0.5, 1, 2, 5, 10, 50 and 80 mgP L^{-1} were used, resulting in a total volume of 25 mL. To inhibit microbial activity during the experiments, 1 mL of formaldehyde was added to each centrifuge tube. The centrifuge tubes were placed in an over-end shaker for 24 hours to reach equilibrium (Wen 2002). After 24 hours, the solutions were centrifuged for 15 minutes at 3000 rpm and filtered through 0.45-µm Milipore® membrane filters. Filtrate was analysed for FRP following the ascorbic acid method (APHA 1998) using a Hitachi U-2000 spectrophotometer (Hitachi Ltd. Tokyo, Japan). The phosphorus sorbed onto sediment (in mass, mg kg^{-1}) was calculated by multiplying the difference in initial P concentrations and P concentrations after 24 hours equilibration. The phosphorus sorbed onto sediment was regressed against initial P concentration (phosphorus sorption isotherm) to determine the equilibrium phosphorus concentration (EPC), recorded as the X-intercept (Klotz 1985; Haggard *et al*. 1999).

5.2.5 Statistical analysis

All data were tested for normality using a Shapiro-Wilk test followed by two-way analysis of variance to compare the differences between sediment nutrient (TP, TN and TC) and OM contents, P forms and EPC, with wetland pond and season as the fixed effects. When significant differences were found using two-way ANOVA, Tukey-Kramer HSD has been applied across the seasons to determine which seasons were significantly different from one another. Statistically significant differences were accepted with α of 0.05. All statistical analyses were performed using JMP-IN (Version 4.0.3, S.A.S Institute Inc. Cary, USA). Relationships between EPC and distance from inlet to outlet were analysed by regression analysis.

5.3 Results

5.3.1 Nutrient and organic matter contents

Overall, sediment TP, TN and TC contents were higher in Pond 1 than in Reed Bed (Table 5.1, Table 5.2 and Table 5.3). In Reed Bed and Pond 1, sediment TP, TN and TC contents were highest in autumn 2009 and winter 2009 and were lowest in spring 2008 and summer 2009 (Table 5.1). In Pond 1, sediment TP contents were lowest in spring 2008 than in summer 2009, autumn 2009 and winter 2009 (Table 5.2, $p < 0.001$). For TN and TC, no interactions were observed because TN and TC was greatest in winter 2009 in Pond 1, but in autumn 2009 TN and TC was greatest in Reed Bed (Table 5.2, TN: $p = 0.897$ and TC: $p = 0.079$).

The OM contents ranged between 2.5 ± 1.17 and 11.5 ± 6.16 mg kg^{-1}, and 18.2 ± 6.78 and 58.6 ± 35.41 mg kg^{-1} for Reed Bed and Pond 1, respectively (Table 5.1). The OM contents of sediments in Pond 1 were significantly higher than that in Reed Bed (Table 5.2 and Table 5.3). As for TP, TN and TC, the OM contents were highest during autumn 2009 and winter 2009 and lowest during spring 2008 and summer 2009. There was no interactions between wetland pond and season (Table 5.2, $p = 0.007$) because OM were greatest in Reed Bed and in Pond 1 during autumn 2009 and approximately equal in spring 2008 and summer 2009 (Table 5.1, Table 5.2 and Table 5.3).

Table 5.1: Sediment total phosphorus (TP), total nitrogen (TN), total carbon (TC) and organic matter (OM) contents of the reed bed and pond 1 of the Cox Creek wetland in spring 2008 (Spr 08), summer 2009 (Sum 09), autumn 2009 (Aut 09) and winter 2009 (Win 09). Mean ± standard errors, n=15.

Parameter	**Season**	**Reed bed**	**Pond 1**
TP	Spr 08	115.1± 24.85	212.3± 107.91
(mg kg^{-1})	Sum 09	112.7± 27.91	276.9 ± 118.74
	Aut 09	122.2± 47.71	449.4 ± 116.19
	Win 09	180.5± 110.73	436.1 ± 152.88
TN	Spr 08	615.5 ± 166.79	2015.9 ± 800.01
(mg kg^{-1})	Sum 09	569.6 ± 191.0	1790.6 ± 302.69
	Aut 09	1556.9 ± 138.19	2552.9 ± 485.68
	Win 09	1363 ± 156.30	2702.6 ± 540.74
TC	Spr 08	785.2 ± 183.86	3912.8 ± 901.23
(mg kg^{-1})	Sum 09	691.5 ± 164.95	2917.3 ± 586.0
	Aut 09	3590.4 ± 470.86	6810.2 ± 372.34
	Win 09	2040.5± 103.0	7280.5 ± 299.89
OM	Spr 08	2.5 ± 1.17	19.5 ± 8.68
(mg kg^{-1})	Sum 09	2.6 ± 2.41	18.2 ± 6.78
	Aut 09	11.5 ± 6.16	58.6 ± 35.41
	Win 09	8.9 ± 4.82	44.5 ± 28.81

5.3.2 Sediment phosphorus fractionation

The sediments from Pond 1 had significantly higher P content than the sediments from Reed Bed (Figure 5.4 and Table 5.2). Loosely sorbed P (NH_4Cl-P) was significantly higher in Pond 1 than in Reed Bed sediment (Figure 5.4; Table 5.2, p <0.001). This fraction was highest during summer 2009 in Reed Bed but during autumn 2009 in Pond 1 (Figure 5.4, Table 5.2 and Table 5.3). These responses were supported by the interactions of wetland and season (Table 5.2, p <0.001).

Reed Bed had a higher fraction of HCl-P (Ca/Mg-P) than Pond 1 sediments (Figure 5.4 and Table 5.2). However, these differences varied seasonally (5.15 – 45.83 mg kg^{-1}) and were highest in autumn 2009 in both Reed Bed and Pond 1 sediments, and lowest in summer 2009 in Reed Bed sediments and in spring 2009 in Pond 1 sediments, respectively (Figure 5.4, Table 5.2 and Table 5.3). An interaction was found between wetland pond and season (Table 5.2; p <0.001).

Similarly to sediment TP and loosely sorbed P, the NaOH-iP (Fe/Al-P) forms was significantly higher in Pond 1 sediment than in Reed Bed sediment (Figure 5.4; Table 5.2). In Reed Bed, the NaOH-iP form was highest during autumn 2009 and was lowest in spring 2008 (Figure 5.4 A, Table 5.2 and Table 5.3). In Pond 1, this fraction was highest in spring 2008, summer 2009 and autumn 2009 and was lowest in winter 2009 (Figure 5.4 B, Table 5.2 and Table 5.). There was an interaction between wetland and season (Table 5.2; p <0.001).

Overall, Pond 1 had a higher labile organic P (NaOH-oP) than Reed Bed sediments (Figure 5.4 and Table 5.2). However, these differences varied considerably with seasons with highest labile organic P forms in spring 2008 to autumn 2009 (Figure 5.4, Table 5.2 and Table 5.3). Residual P (res-P) forms accounted higher in Reed Bed sediments than in Pond 1 sediments with the highest in winter 2009 and was lowest in summer 2009 (Figure 5.4, Table 5.2 and Table 5.3). In Pond 1 sediments, the res-P was highest in summer 2009 and was lowest in autumn 2009 (Figure 5.4, Table 5.2 and Table 5.3). The effect of wetland was also dependent upon the effect of season (Table 5.2; p <0.001).

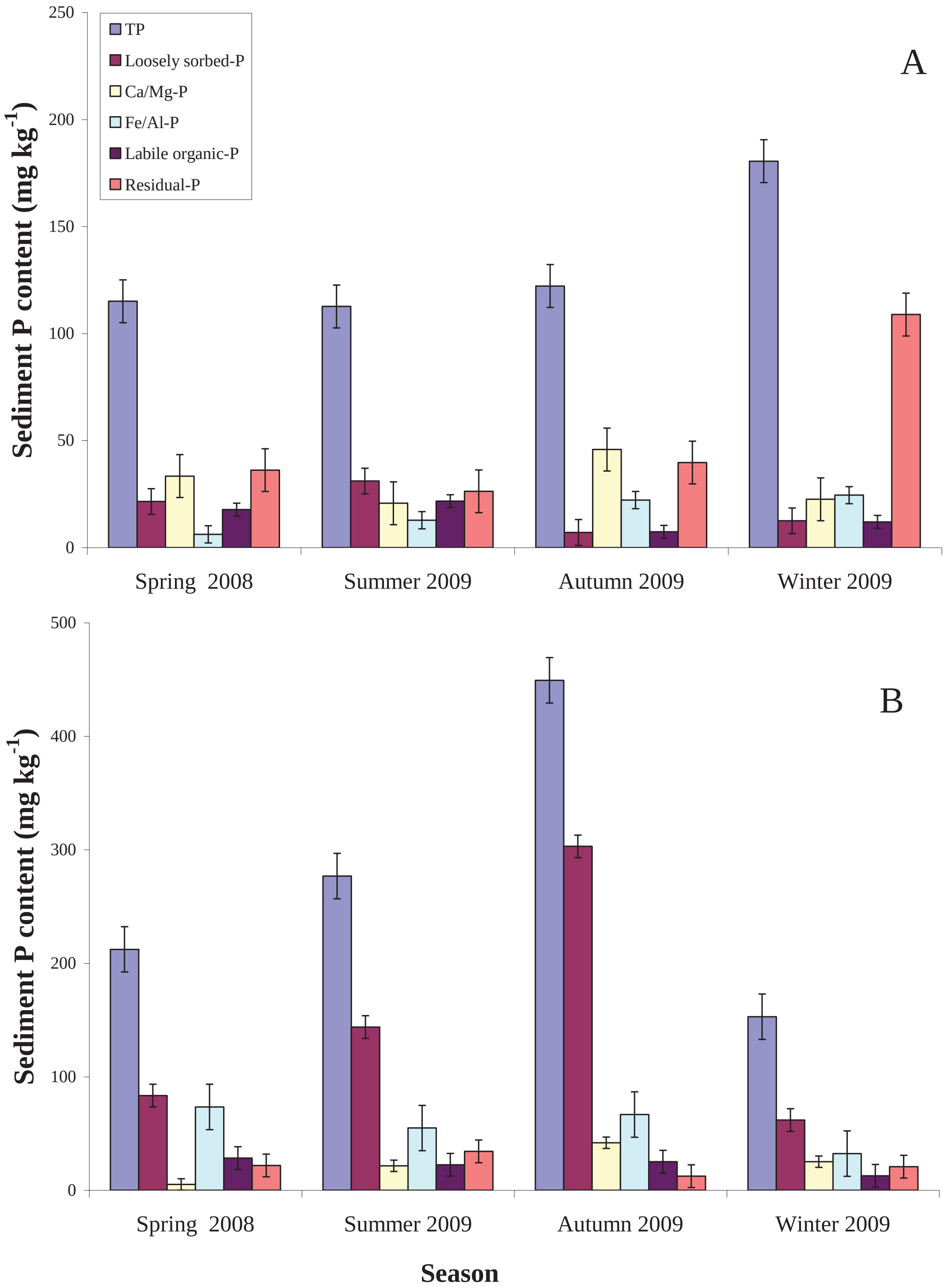

Figure 5.4: Sediment phosphorus content of different fractions for Reed Bed (A) and Pond 1 (B) of the Cox Creek wetland in spring 2008, summer 2009, autumn 2009 and winter 2009. Mean ± standard errors, n=15.

5.3.3 Phosphorus sorption

5.3.3.1 Sorption isotherms

The phosphorus sorption isotherm experiments conducted enable calculations of EPC (Figure 5.5). Figure 5.5 shows the amount of P sorbed after equilibration for 24 hours. Positive values depict adsorption of P onto sediment and negative values depict desorption of P from sediment into solution. The x-intercept of the fitted linear regression represents the equilibrium phosphorus concentration (EPC).

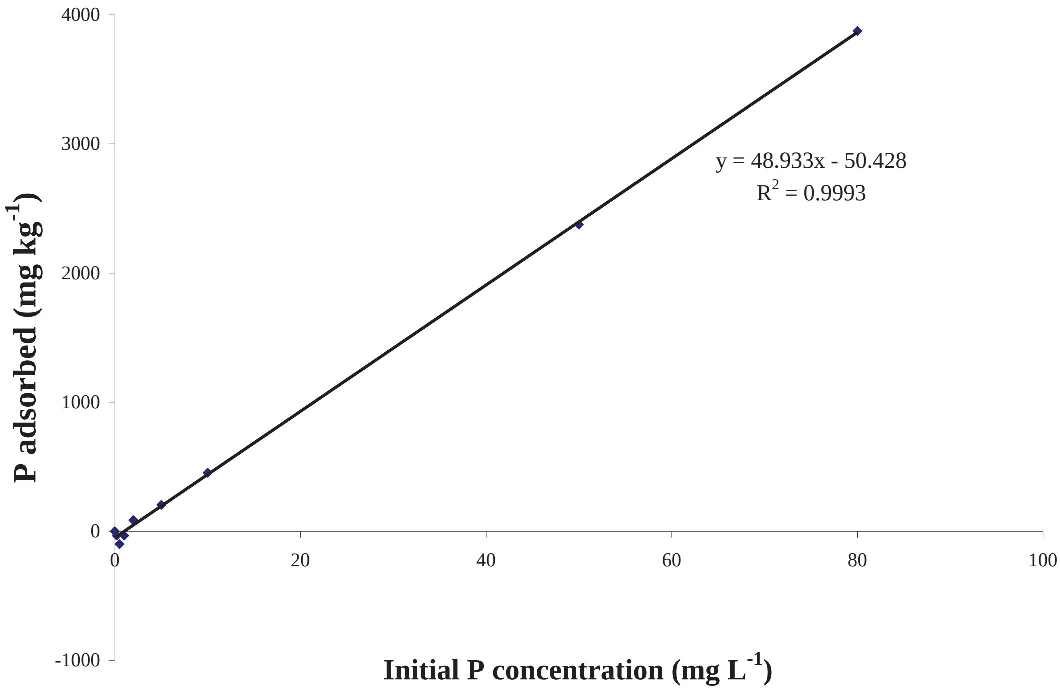

Figure 5.5: Example of fitted P adsorption isotherms for Reed Bed sediments of the Cox Creek wetland in spring 2008. The graph shows the P sediment sorbed (in mass, mg kg^{-1}) regressed against initial P concentration (mg L^{-1}). EPC was calculated as the X-intercept. Dots represent the measured data and lines are the fitted linear lines.

5.3.3.2 Phosphorus adsorption-desorption

The sediments from Reed Bed exhibited a lower equilibrium phosphorus concentration (EPC) than in Pond 1, indicating greater potential for P adsorption from the water column in Reed Bed (Figure 5.6 and Table 5.2; p <0.001). In general, the EPC was significantly lower during spring 2008 and summer 2009 than autumn 2009 and winter 2009 (Figure 5.5 and Table 5.2 and Table 5.3). The effect of wetland EPC was dependent upon the effect of season (Table 5.2; p = 0.005) because season had the same effect on both wetland ponds. The EPC was greatest in autumn 2009 and lowest in summer 2009 (Figure 5.6, Table 5.2 and Table 5.3). In addition, the EPC from both Reed Bed and Pond 1 sediments had a high correlation with distance (r^2= 0.9248, p = 0.0001 and r^2= 0.9299, p <0.001, respectively), indicating higher ability to sorb phosphorus along distance (Figure 5.7).

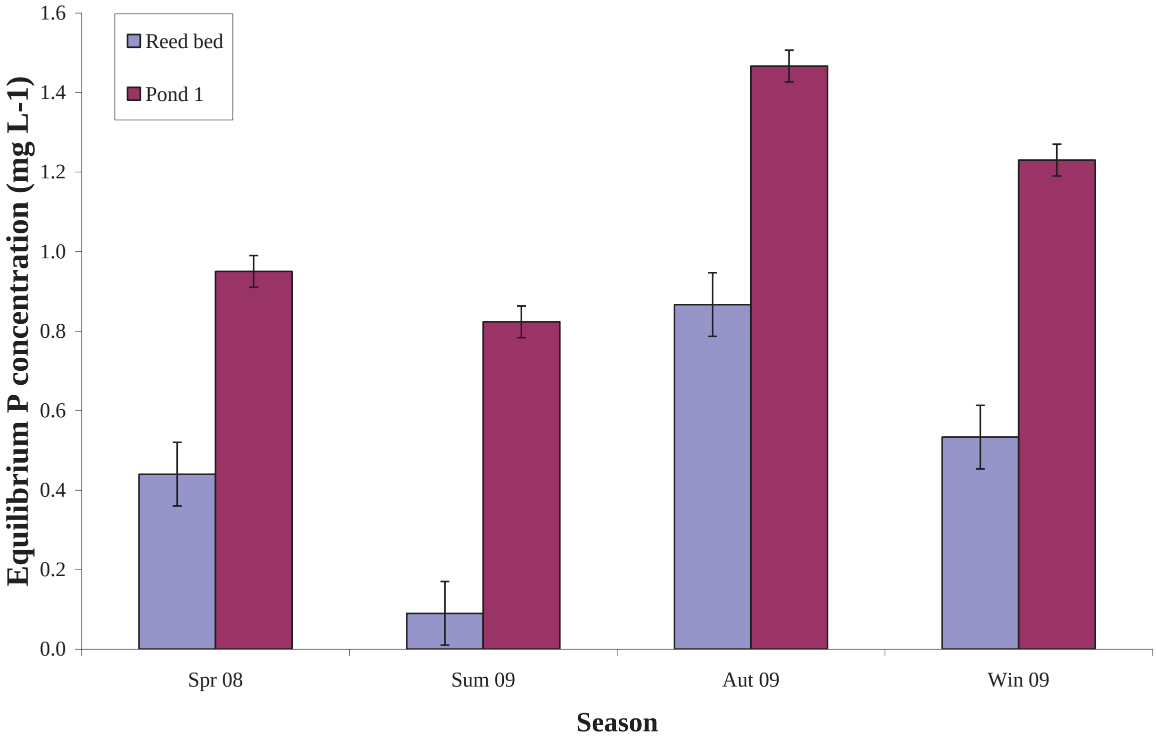

Figure 5.6: Measured equilibrium phosphorus concentration (EPC) for Reed Bed and Pond 1 of the Cox Creek wetland in spring 2008 (Spr 08), summer 2009 (Sum 09), autumn 2009 (Aut 09) and winter 2009 (Win 09). Mean ± standard error, n=15.

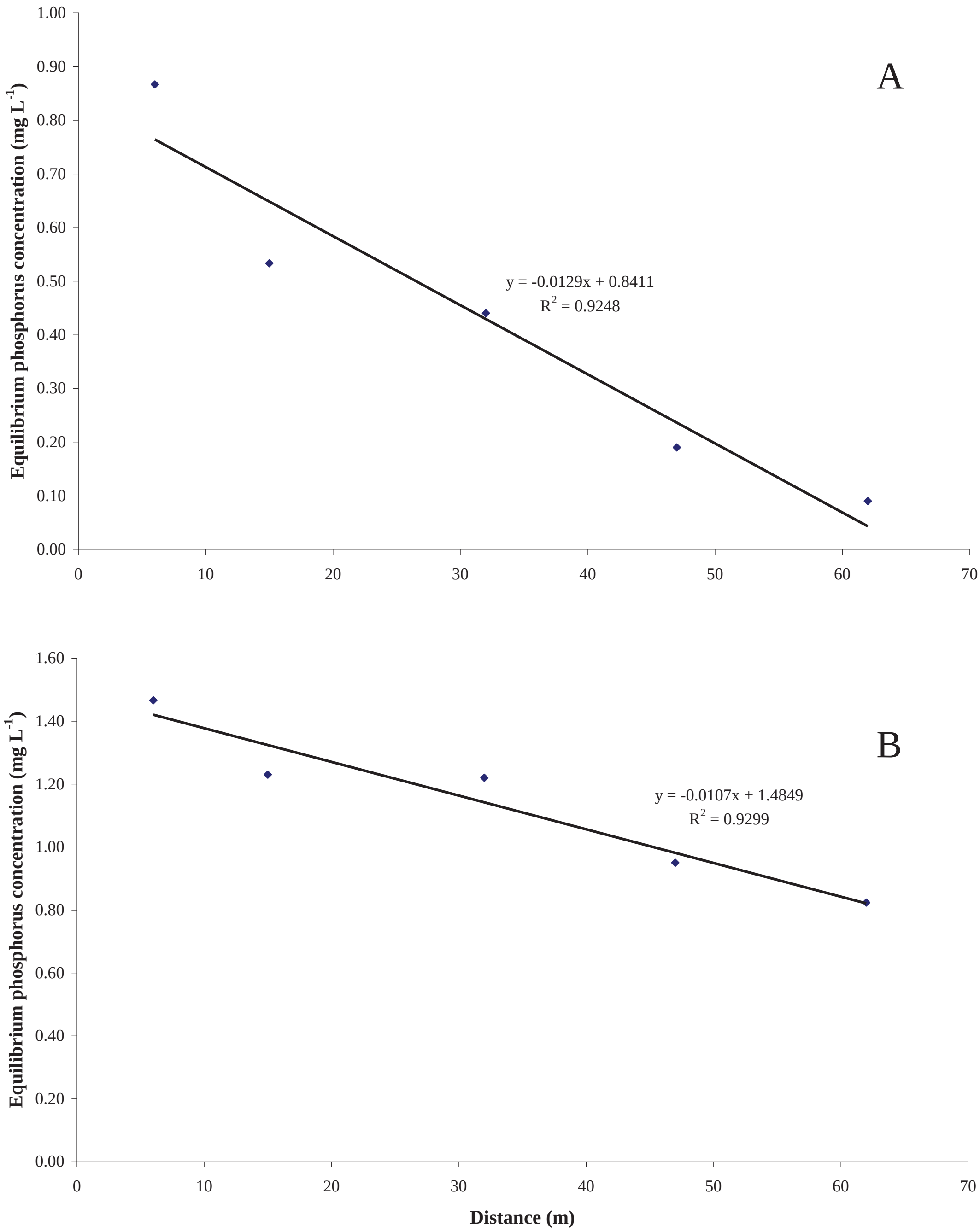

Figure 5.7: Measured equilibrium phosphorus concentration (EPC) across distance for Reed Bed (A) and Pond 1 (B) of the Cox Creek wetland system.

Table 5.2: *P*-values obtained for the effects of wetland pond and season (and interaction) on total phosphorus (TP), total nitrogen (TN), total carbon (TC), organic matter (OM), loosely sorbed P (NH_4Cl-P), hydrochloric acid bound P (HCl-P), sodium hydroxide bound inorganic P (NaOH-iP), labile organic P (NaOH-oP), residual P (res-P) and equilibrium phosphorus concentration (EPC). Interaction effects between these parameters denoted with *.

Effect	TP	TN	TC	OM	NH_4Cl-P	HCl-P	NaOH-iP	NaOH-oP	Res-P	EPC
Wetland	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Season	<0.001	0.018	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Wetland * season	<0.001	0.897	0.079	0.283	<0.001	<0.001	<0.001	<0.001	<0.001	0.005

Table 5.3: Result of post-hoc comparison (Tukey-Kramer HSD) on on total phosphorus (TP), total nitrogen (TN), total carbon (TC), organic matter (OM), loosely sorbed P (NH_4Cl-P), hydrochloric acid bound P (HCl-P), sodium hydroxide bound inorganic P NaOH-iP), labile organic P (NaOH-oP), residual P (res-P) and equilibrium phosphorus concentration (EPC).

Season-Season	TP	TN	TC	OM	NH_4Cl-P	HCl-P	NaOH-iP	NaOH-oP	Res-P	EPC
Spr 08-Sum 09	###	#	#	#	NS	#	NS	##	##	NS
Spr 08-Aut 09	#	##	##	##	#	##	##	#	#	##
Spr 08-Win 09	##	NS	NS	NS	#	###	##	NS	#	#
Sum 09-Aut 09	NS	NS	##	##	###	#	##	NS	###	###
Sum 09-Win 09	#	#	#	#	NS	NS	###	NS	NS	##
Aut 09-Win 09	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

*Note: ###, extremely significant difference (p <0.001); ##, moderately significant difference (p <0.01); #, significant difference (p <0.05); NS, not significant (p >0.05).

5.4 Discussion

The sediment in wetlands can act as a sink or temporary storage for most nutrients entering the water body, which can be released back to the water column (resolubilised) with changes in environmental conditions such as pH, redox potential and temperature (Froelich 1988; Gachter and Meyer 1993; Fishman *et al.* 1994; Mitsch and Gosselink 2000). Dissolved nutrients from the water column can be lost to the sediments by adsorption to particles with highly organic or clay soils and high cation exchange capacity for P immobilisation and subsequent sedimentation (Wen 2002; Baldwin and Williams 2007). However, due to historical applications of fertilisers for vegetable production in the Cox Creek sub-catchment, soil structure and chemical component are modified (Chittleborough 1983; Ingleton 2003; Fisher 2005), increasing levels of nutrients and organic matter. In this study, the sediment TP concentrations (Table 5.1) were found to be within the range determined for other Australian soils; 134-554 mg kg^{-1} (Perverill *et al.* 1999). In another analysis of sediments of ponds and dams in southwestern Australia, Ruan and Gilkes (2000) found that the sediment TP concentrations ranged from 29 to 1101 mg kg^{-1}. The TP concentrations of sediment observed in Pond 1 is relatively high, which might have been due to continuous flow and external P loadings from the catchment. In contrast, the lower sediment TP concentrations in Reed Bed seem to be influenced by its intermittent flow, which may result in reduced phosphorus loads.

Higher nutrient concentrations in the sediments suggests that during the non-growing season (autumn 2008 and winter 2009) the sediment may act as nutrient source to the Cox Creek wetland but act as nutrient sink during the growing season (spring 2008 and summer 2009). The higher nutrient contents in the sediment during the non-growing seasons might be attributed to leaching of nutrients during senescence of macrophytes, and no uptake of nutrients by macrophytes and external inputs from catchment runoff. In addition, the EPC was greatest in autumn 2009 (Figure 5.6), indicating low P sorption capacity. During the growing season, the emergent macrophytes utilise nutrients in the sediment for their growth (Brix 1997; Liu *et al*. 2000; Kim 2009). Unlike sediment TP contents, TN would have undergone different pathways for it to be removed from the water column (e.g. denitrification). Denitrification by the microbial community may have transformed NO^{3-} to

N_2 and N_2O under anaerobic conditions (Patrick and Tusneem 1972; Patrick 1982; Reddy and Patrick 1984; Reddy *et al*. 1989). Bowmer *et al.* (1994) showed that denitrification was the main process in removal of nitrate in subsurface wetland as the water flow through the wetland. Regarding TC content in the sediments, lower concentrations were found due to the fact that higher water temperature stimulate the utilisation of organic carbon by microorganism (Wetzel and Manny 1972 a, b; Wetzel 1984; Münster 1993; Wilcock and Croker 2004).

The roles of sediments on P cycles in wetlands are closely related to the P forms in the systems (Pettersson *et al.* 1988; Jauregui and Garcia Sanchez 1993). The differences of P forms in the sediments can be used to predict sediment-water interactions and its impact on water quality (Søndergaard *et al.* 2001; Wen 2002). Among the inorganic forms of P (loosely sorbed-P, Ca/Mg-P and Fe/Al-P), the relatively higher level of loosely sorbed P was identified, suggesting that this P forms may be readily bioavailable and can be readily mobilised to enter sediment porewater. In addition, the loosely sorbed-P is considered as labile and important for plant growth and controlling the P balance between sediment particle and porewater (Ann *et al.* 1999). As the loosely sorbed-P was consistently higher in Pond 1 than in Reed Bed, the value of EPC, which is the indicator of sediment P adsorption capacity was also correspondingly higher (Figure 5.6). Borovec and Hejzlar (2001) found that there was no correlation between P fractions and P sorption characteristics of freshwater sediment, but Wen (2002) found a positive relationship between EPC and loosely sorbed-P or exchangeable-P in wetland sediment. Søndergaard *et al.* (1993) found that the inorganic forms of P were positively correlated with the external P loadings, sediment organic contents and phytoplankton in 32 shallow lakes in Denmark, but not correlated to TP and Fe, suggesting its role on governing the balance between sediment and water. Also, many studies recommended that the effect of inorganic forms of P on sediment P adsorption is difficult to explain due to its rapid turnover rates (Gale *et al.* 1994; Richardson 1999; Rydin 2000; Wang *et al.* 2005).

The ability of sediments to retain P regulates the productivity of many aquatic systems through adsorption and desorption of P from and to the water column (Caraco *et al.*

1991; Phillips *et al*. 1994; Gonsiorczyk *et al*. 2001; Maberly *et al*. 2003). Thus, improved understanding is needed about the interaction between P in overlying water column and wetland sediment, which is governed by the P sorption capacity of sediment. This study indicated that the Fe/Al-P dominated the forms of P in Pond 1 (Figure 5.4), which showed fast response to inundation and can be mobilised and dissolved under anaerobic conditions (Welch and Cook 1995; Søndergaard *et al*. 2001; Kisand and Nõges 2003). The Fe/Al-P decreased dramatically as the wetland was flooded in winter 2009. Furthermore, the EPC value showed the decreasing sorption potential of P from the water column onto Pond 1 sediment, suggesting that the sediment P adsorption capacity in Pond 1 is likely less efficient. In contrast, the sediment in Reed Bed were dominated by Ca/Mg-P and res-P, which are less sensitive to redox potential (Froelich 1988). It is expected that anaerobic conditions caused by flooding would not release a large amount of P from the sediment to the water column, indicated by lower EPC value than in Pond 1. On the other hand, the process of photosynthesis of emergent macrophytes in Reed Bed also contributed to increased DO concentration and pH which could have increased the potential for co-precipitation of P with Ca (Ann *et al.* 1999; Wen 2002). House *et al.*(1995) suggested that the co-precipitation of P with Ca would take place when pH in water was higher than 8.5. Since pH was not measured in this study, there was no evidence of the transformation of Fe/Al-P to Ca/Mg-P at higher pH value.

The P retention capacity of the Cox Creek wetland system sediments varied considerably seasonally as indicated by the EPC values. The different P adsorption capacity during growing season and the non-growing seasons corresponded to the available sorption sites (Reddy *et al*. 1999), suggesting that during the growing season the sediment have higher available sorption sites. The P sorption isotherms showed Reed Bed have a greater potential to rapidly adsorb large amount of P compared to Pond 1 from the water column. The greater P-binding capacity in Reed Bed is shown by the lower EPC, indicating macrophytes may promote P retention into the sediments. This potential is intimately linked to lower P saturation longitudinally and maybe tied to downstream P transport, causing a P in water to follow a spiral pathway as it is successively taken up, deposited and transported downstream. This study also revealed that the average rate of 0.04 hr^{-1} of P adsorption was recorded from P sorption isotherms, resulting in a maximum of 43.5 kg P yr^{-1} of P adsorption by the wetland sediment (Figure 7.1 in chapter seven), when correlated with the FRP concentration (as PO_4^{3-}) in the water column.

Chapter six

6 Influence of sedimentation rates in reducing P loads from the Cox Creek wetland system under different flows

6.1 Introduction

Constructed wetlands play a vital role for improving water quality due to their ability to transform and store nutrients in the sediment (Johnston 1991; Gilliam 1994; Mitsch and Gosselink 2000; Craft and Casey 2000). The primary processes of wetlands that lead to water quality improvements include the uptake and storage of nutrients by macrophytes (chapter four) and other organisms, adsorption of nutrients to sediment (chapter five) and chemical transformation, and sedimentation of TP-bearing particles (Lloyd 1997; Reddy *et al*. 1999; Bartley *et al*. 2004). The focus of this study was to determine the rate of particle sedimentation in the Cox Creek wetlands and the role of particle sedimentation in reducing the TP load to downstream ecosystems. The rate of particle and TP sedimentation was measured using sediment traps to determine particle settling during different flow regimes. Understanding sedimentation processes can give insight into the complexity of particle size distribution, organic matter content and nutrient sedimentation rate (phosphorus in particular) to improve predictions for the functional lifetime of the wetland.

Sedimentation has long been recognised as the most important physical process in the removal and retention of nutrients in freshwater wetlands (Fennesy *et al*. 1994; Gleason and Euliss Jr. 1998; Hupp and Bazemore 1993; Zajackzkowski 2000). This process occurs in wetlands where deposition of suspended sediment from water leads to settling of nutrient bound particles sorbed into wetland sediment (Phillips 1989; Craft and Casey 2000; Lockaby *et al.* 2005). As most suspended matter and nutrients input enters the wetland by stream flow (Kadlec and Robbin 1984), thus it is considered that slow water velocities in wetlands can create the most suitable depositional environment for sedimentation.

Nutrient accumulation and storage are important in regulating wetland productivity and water quality (Craft and Casey 2000; Hopkinson 1992; Craft and Richardson 1993). In Flint River, Georgia, USA, Craft and Casey (2000) found that freshwater wetlands trapped sediments and accumulated nutrients 1.5 to three times greater than in depressional wetlands (e.g. marsh, savanna and forest), resulting in reduced turbidity in stream and better downstream water quality. They also suggested that vegetation type can influence the removal of suspended matter from the flowing water. On the other hand, the ability of wetland sediment function as nutrient storage and nutrient transformation for solubilisation, there is high potential for burial and reduction in the release of bound nutrient (Neely and Baker 1989; Hammer 1992; Mitsh and Gooselink 1993). The aerated zones at the sediment-water interface and aerobic zones surrounding the roots of vascular plants are essential for sorption of inorganic nutrients (Hammer 1992; Mitsh and Gooselink 1993).

This study was designed to obtain information on the sedimentation and composition of particles entering and leaving the Cox Creek wetlands. The aim of this study was to measure rates of sedimentation of phosphorus in the Cox Creek wetlands, allowing analysis of the contribution of sedimentation to the phosphorus budget. The key question was how sedimentation contributes to the sediment bound phosphorus settling into the wetland under different flow regimes. This study tested the hypothesis that the vegetated wetland (Reed Bed) has greater sedimentation and P accumulation rates than the unvegetated wetland (Pond 1). In addition, high flow events transport more particles and therefore increase sedimentation rates compared to low flow events. This experiment was carried out in the Cox Creek wetland ponds where three sediment traps were deployed at the inlet and outlet of Reed Bed and Pond 1.

6.2 Methods

6.2.1 Hydrograph and the flow events

Daily hydrograph and flow rates during the sampling periods were provided by Water Data Service through SA Water Corporation, Australia. The flow conditions were continuously monitored at the gauge station throughout the year. Daily flows were then divided into six different flow rate classes: (1) 0 to 1 ML day^{-1}, (2) 2 to 5 ML day^{-1}, (3) 6 to 15 ML day^{-1}, (4) 16 to 30 ML day^{-1}, (5) 31 to 45 ML day^{-1} and (6) 46 to 300 ML day^{-1}. The sedimentation rates were then classified according to the corresponding flow class, which fell within the range of 46 to 300 ML day^{-1}, 31 to 45 ML day^{-1} and 16 to 30 ML day^{-1} flow rate classes (Figure 6.1).

6.2.2 Design of sediment traps

The sediment traps were constructed according to the design of others (Bloesch and Burns 1980; Gardner 1980 a, b; Håkanson *et al*. 1989 and Fennessy *et al*. 1994). They suggested that cylinders with aspect ratios (height/diameter) between 10:1 and 20:1 will adequately represent the sedimentation rate without collecting particles from the reverse process, resuspension. However, due to low water depth in the Cox Creek wetland, an aspect ratio of 10:1 was selected as the most suitable design because the opening of the cylinder (trap mouth) would be in the water column consistently (Figure 6.2 and Figure 6.3).

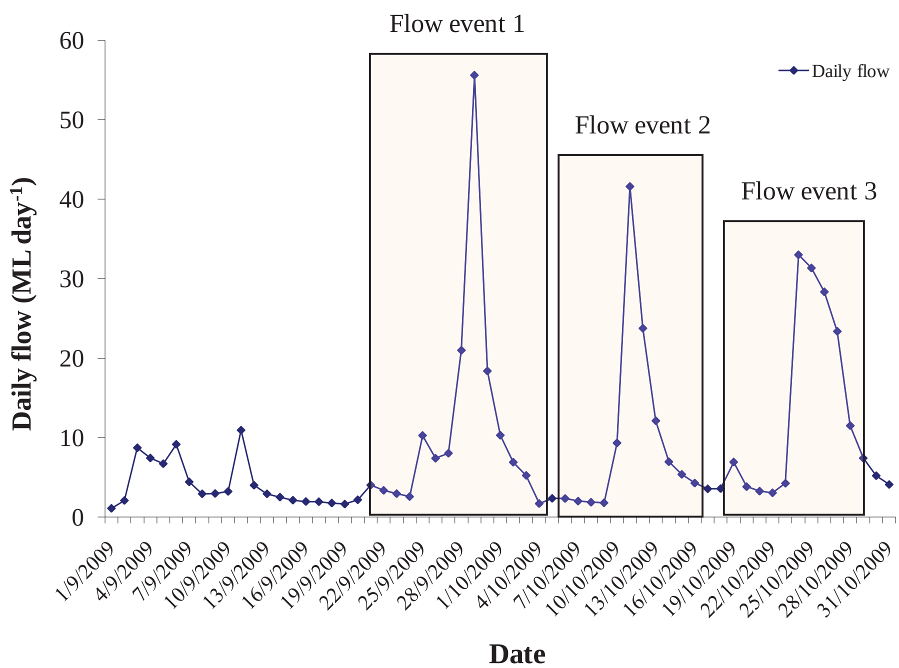

Figure 6.1: Hydrograph showing three flow events at the Cox Creek wetland during study period (September 2009 to October 2009). Shaded area showing sediment traps deployments on 24 September 2009 to 5 October 2009 (flow event 1), 7 October 2009 to 16 October 2009 (flow event 2), and 19 October 2009 to 28 October 2009 (flow event 3).

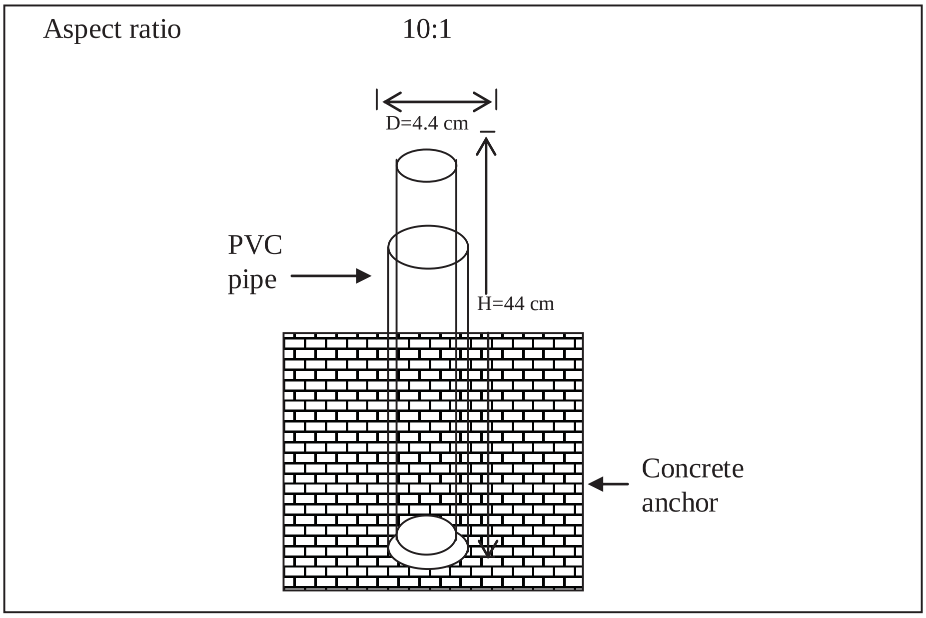

Figure 6.2: Illustration of sediment trap design constructed for the experimental study of sedimentation process within the Cox Creek wetland. The traps were deployed at 10 cm above the sediment/water interface.

Figure 6.3: Photo of the sediment trap used for the experimental study of sedimentation process within Cox Creek wetland. Note that each cylinder was placed at the inlet and outlet of both Reed Bed and Pond 1.

6.2.3 Sediment traps deployment at different flow regimes

The inlet and outlet of Reed Bed and Pond 1 were chosen for sediment traps deployment to investigate rates of sedimentation (Figure 2.5 in chapter two). Sediment traps were deployed during three flow events which occurred on: 24 September 2009 to 5 October 2009 (flow event 1), 7 October 2009 to 16 October 2009 (flow event 2), and 19 October 2009 to 28 October 2009 (flow event 3) as shown in Figure 6.1. Triplicate traps were deployed at the inlet and outlet of Reed Bed and Pond 1 to allow sufficient quantities of sediments to be collected. The bottom of the traps were placed 10 cm above the sediment/water interface in order to capture new sediments and to minimise the collection of resuspended sediments. To avoid any sediment entering the cylinders whilst lowering into position, the cylinders were filled with frozen distilled water prior to field deployment. To retrieve the samples, the trap assemblies were raised slowly and the cylinders were sealed immediately. Retrieved samples were stored on ice and transported to a cool room (4°C) within 24 hours.

6.2.4 Laboratory analysis

Captured sediment samples were analysed for dry weight, nutrient concentrations (TP, TN and TC), particle size and organic matter (OM) within three days of collection. The measurement of sediment dry weight was performed after filtration through Whatman International GF-C filters. The filtrate was then weighed, followed by drying in an oven at 80^{o}C for 48 hours and weighed again. The sediment dry weight was calculated as the difference between before drying weighted and after drying weighted. TP concentrations were measured by the nitric-perchloric acid digestion method following Murphy and Riley (1962) using the ascorbic acid reduction method. TN and TC were determined by high temperature combustion in an atmosphere of oxygen using a LECO CNS-2000 (Matejovic 1997). A Laser *In-Situ* Scattering and Transmissometry (LISST) particle size profiler was used to determine particle size distribution between 2 µm and 500 µm. Material greater than 1000 µm was removed by sieving prior to the particle size distribution analysis. The quantity of OM present in the samples were determined from loss of volatile solids upon ignition at 550^{o}C following standard method 2540E (Eaton *et al*. 1995).

The number of moles of TP, TN and TC were calculated by dividing the mass of each molecule within the sample by the atomic weight of the molecule. The TP, TN and TC molar ratios were then calculated to determine the relative availability of these nutrients.

6.2.5 Calculation of sedimentation rates

The rates of sedimentation should be considered as an estimation of net sedimentation process that has taken place, since no evaluation of resuspension was performed (Håkanson *et al*. 1989; Fennesy *et al*. 1994; Fernandes *et al*. 2008). The rates of sedimentation (g m^{-2} day^{-1}) were calculated based on the duration of the collection period and the surface area of the cylinders (height x diameter), following this equations:

$$SR = (DW / A / D) \qquad \textbf{(Equation 6-1)}$$

where SR is the sedimentation rate (g m^{-2} day^{-1}), DW is the dry weight of sediment in each trap (g), A is the surface area of sediment trap (m^2) and D is the period of sediment trap deployment (days).

The annual sediment accumulation rate (SR_{accum}, g m^{-2} yr^{-1}) of the Cox Creek wetland was estimated by the following equation:

$$SR_{accum} = (D \times SR_{Reed\ Bed} \times A_{Reed\ Bed}) + (D \times SR_{Pond\ 1} \times A_{Pond\ 1}) \qquad \textbf{(Equation 6-2)}$$

where SR_{accum} is the sediment accumulation rate (g m^{-2} yr^{-1}), D is the number of days of each flow rate class, $SR_{Reed\ Bed}$ is the sedimentation rate in Reed Bed (g m^{-2} day^{-1}), $SR_{Pond\ 1}$ is the sedimentation rate in Pond 1 (g m^{-2} day^{-1}), $A_{Reed\ Bed}$ is the area of Reed Bed (m^2) and $A_{Pond\ 1}$ is the area of Pond 1 (m^2).

The mean annual sediment accumulation rates of the Cox Creek wetland system was calculated based on an assumption that the sedimentation rates of the lowest three flow events (0-1 ML day^{-1}, 2-5 ML day^{-1} and 6-15 ML day^{-1}) was half of the 16-30 ML day^{-1} flow rate class (flow event 3) recorded from this study. This assumption was made since lower flow class was not recorded during the periods of hydrograph obtained.

The P accumulation rate (PAR, g P m^{-2} day^{-1}) associated with sedimentation were calculated by the following equation:

$$PAR = TP_{content} \times SR \qquad \textbf{(Equation 6-3)}$$

where $TP_{content}$ is the total phosphorus content of deposited sediment (g P g^{-1} DW) and SR is the sedimentation rate (g m^{-2} day^{-1}).

The annual P accumulation rate (P_{accum}, g P m^{-2} yr^{-1}) of the Cox Creek wetland was estimated by the following equation:

$$P_{accum} = (D \times PAR_{Reed\ Bed} \times A_{Reed\ Bed}) + (D \times PAR_{Pond\ 1} \times A_{Pond\ 1}) \qquad \textbf{(Equation 6-4)}$$

where P_{accum} is the P accumulation rate (g P m^{-2} yr^{-1}), D is the number of days of each flow class, $PAR_{Reed\ Bed}$ is the P accumulation rate in Reed Bed, (g P m^{-2} day^{-1}), $PAR_{Pond\ 1}$ is the P accumulation rate in Pond 1 (g P m^{-2} day^{-1}), $A_{Reed\ Bed}$ is the area of Reed Bed (m^2) and $A_{Pond\ 1}$ is the area of Pond 1 (m^2).

As for the mean annual sedimentation rates, a similar assumption was made for the calculation of the mean annual P accumulation rates (g P m^{-2} yr^{-1}), where the P accumulation rates of the lowest three flow events (0-1 ML day^{-1}, 2-5 ML day^{-1} and 6-15 ML day^{-1}) was half of the 16-30 ML day^{-1} flow rate class (flow event 3) recorded from this study. This assumption was also made since lower flow class was not recorded during the periods of hydrograph obtained.

6.2.6 Statistical analysis

All data were tested for normality using a Shapiro-Wilk test. Differences between sedimentation rates, phosphorus accumulation rates, nutrients and OM concentrations and particle size were compared by two-way analysis of variance, with flow event and wetland pond as the fixed effects. Statistically significant difference were accepted with α of 0.05. All statistical analyses were performed using JMP-IN (Version 4.0.3, S.A.S Institute Inc., Cary, USA).

6.3 Results

6.3.1 Hydrograph and the flow events

Three elevated flow events were observed fell within the range of 46–300 ML day^{-1}, 31–45 ML day^{-1} and 16–30 ML day^{-1} flow rate classifications, represented flow event 1, flow event 2 and flow event 3, respectively (Figure 6.1).

6.3.2 Sedimentation rates of the Cox Creek wetland

Measured sedimentation rates (SR) in Reed Bed and Pond 1 ranged between 25.7 ± 4.71 - 75.5 ± 21.62 g m^{-2} day^{-1} and 23.3 ± 5.71 - 87.3 ± 12.08 g m^{-2} day^{-1}, respectively (Figure 6.4). In general, the SR were higher in Reed Bed than in Pond 1for all deployment periods (Table 6.2; p = 0.0071). In Pond 1, the highest SR were found at the inlet (87.3 ± 12.08 g m^{-2} day^{-1}) within the 46–300 ML day^{-1} flow rate class (flow event 1) and lowest at the outlet (26.4 ± 11.09 g m^{-2} day^{-1}) within the 16–30 ML day^{-1} flow rate class (flow event 3). Similar patterns of SR were found for Reed Bed, which were highest at the inlet (75.5 ± 21.62 g m^{-2} day^{-1}) during flow event 1 and lowest at the outlet (25.7 ± 4.71 g m^{-2} day^{-1}) during flow event 3 (Figure 6.4). By comparing all sites, the decreasing patterns of SR between the inlet and the outlet sites have been observed during three different flow events (Table 6.2). This study also revealed that the sedimentation rates was dependent upon the flow events, since there was an effect of site * flow event (Table 6.2, p = 0.0283).

The annual sediment accumulation rates (SR_{accum}) measured from the year 2004 to 2009 ranged between 1.9 ± 0.08 and 2.3 ± 0.31 kg m^{-2} yr^{-1}, but was not different between years (Figure 6.5 and Table 6.3). Assuming average rates of sediment accumulation of 2.2 kg m^{-2} yr^{-1} and a density of 175.9 g m^{-3} of trapped sediment determined from measured volume of the water-sediment mixture, the calculated mass of sediment accumulation for the entire wetland was 7.9 cm yr^{-1}.

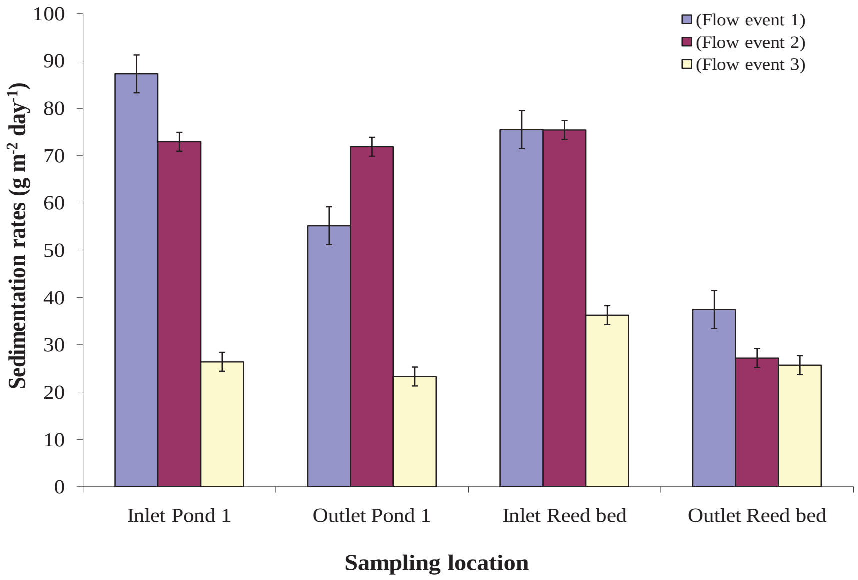

Figure 6.4: Sedimentation rates (SR, g m^{-2} day^{-1}) at the inlet and outlet of Reed Bed and Pond 1. Flow event 1: 24 September 2009 to 5 October 2009; flow event 2: 7 October 2009 to 16 October 2009; and flow event 3: 19 October 2009 to 28 October 2009. Error bars represent standard errors.

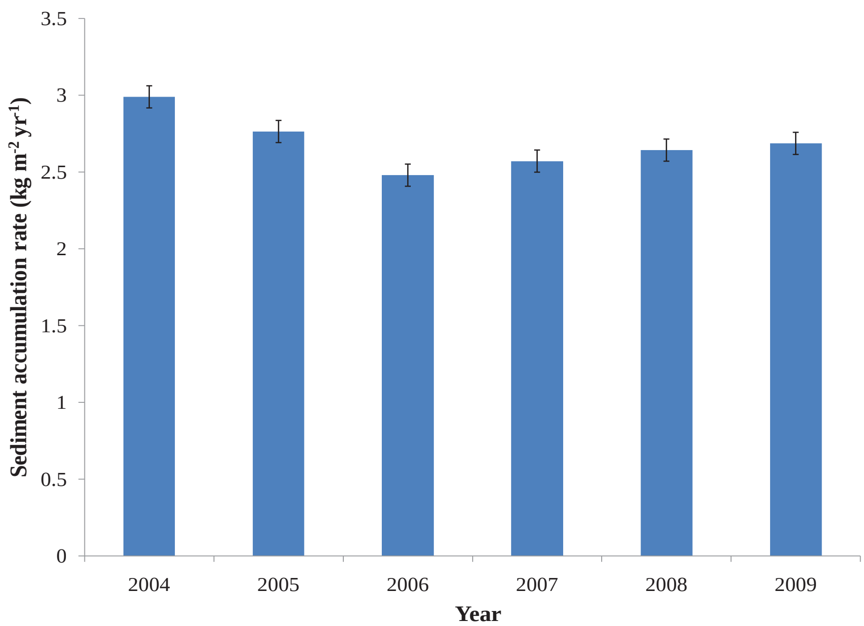

Figure 6.5: Sediment accumulation rate (SR_{accum}, kg m^{-2} yr^{-1}) of the Cox Creek wetland from the year 2004 to 2009. Error bars represent standard errors.

6.3.3 Characteristics of deposited sediments

A decreasing trend of TP, TN and TC concentrations in Reed Bed and Pond 1 was observed over the sampling period (Table 6.1). In addition, the TP concentration at the outlet of Pond 1 showed significantly lower levels than the inlet sites (Table 6.2; $p = 0.0028$). In Pond 1, the deposited sediment TC to TN molar ratio increased during the study period and was highest at the outlet sites during flow event 3. In Reed Bed, the deposited sediment TC to TP and TN to TP molar ratios were higher at the outlet sites during flow event 3. Similarly to the deposited sediment TC to TN molar ratio in Pond 1, the molar ratio of TC to TN in Reed Bed were highest at the outlet sites during flow event 3 and were lowest at the inlet sites during flow event 2 (Table 6.1).

The OM contents varied between 0.4 ± 0.06 and 3.1 ± 1.1 g m^{-2} (Table 6.1), but were not significantly different between Reed Bed and Pond 1 (Table 6.2; $p > 0.05$). In general, the OM content in the deposited sediments was highest in flow event 1.

Overall, particle size distributions of trapped sediments were larger in Pond 1 than in Reed Bed (Table 6.1 and Table 6.2). In Pond 1, particle size was largest at the inlet in flow event 3 and was smallest at the outlet in flow event 1. Preferential settling of the larger particles led to an enrichment of fine material from inlet to outlet. For instance, in Reed bed, the effect of sedimentation rates (see also Figure 6.4) on the particle size distribution showed the decreasing average particle size from inlet to outlet, with the dominance of material finer than 30 µm at the outlet area (Table 6.1).

Table 6.1: Mean total phosphorus (TP), total nitrogen (TN), total carbon (TC), ratios by molar, organic matter (OM) concentrations and particle size distributions of deposited sediment samples collected using sediment traps during three flow events. Flow event 1: 24 September 2009 to 5 October 2009; flow event 2: 7 October 2009 to 16 October 2009; and flow event 3: 19 October 2009 to 28 October 2009. Error bars represent standard errors. Mean ± standard errors, n = 3.

Parameters	**Flow event**	**Pond 1**		**Reed Bed**	
		Inlet	Outlet	Inlet	Outlet
TP	Flow event 1	53 ± 9.1	42 ± 8.3	27 ± 16.5	18 ± 5.2
(mg m^{-2})	Flow event 2	41 ± 11.4	39 ± 16.4	26 ± 13.1	20 ± 6.6
	Flow event 3	24 ± 7.2	17 ± 5.3	10 ± 7.9	12 ± 3.9
TN	Flow event 1	515 ± 108.4	499 ± 73.9	314 ± 57.3	128 ± 31.1
(mg m^{-2})	Flow event 2	560 ± 193.3	352 ± 94.7	294 ± 63.2	219 ± 41.8
	Flow event 3	303 ± 84.9	211 ± 87.3	114 ± 39.7	104 ± 38.2
TC	Flow event 1	1894 ± 201	1790 ± 292	1807 ± 302	460 ± 105
(mg m^{-2})	Flow event 2	1809 ± 392	845 ± 101	1616 ± 591	1095 ± 328
	Flow event 3	1779 ± 442	780 ± 116	1619 ± 445	1071 ± 119
TC to TP ratio	Flow event 1	92.8 ± 21	106.4 ± 13	187.5 ± 33	188.3 ± 38
(molar)	Flow event 2	115.8 ± 15	99.2 ± 11	167.5 ± 11	213.3 ± 63
	Flow event 3	164.4 ± 29	268 ± 23	270 ± 41	410 ± 58
TC to TN ratio	Flow event 1	4.3 ± 1.5	5.2 ± 1.1	6.7 ± 2.0	12.4 ± 1.2
(molar)	Flow event 2	3.8 ± 1.3	5.1 ± 1.2	6.4 ± 1.4	8.2 ± 2.7
	Flow event 3	6.9 ± 2.9	8.8 ± 1.6	14.7 ± 2.5	16.6 ± 2.9
TN to TP ratio	Flow event 1	21.6 ± 3.9	25.5 ± 2.4	28 ± 3.1	17.2 ± 3.9
(molar)	Flow event 2	20.7 ± 2.3	19.3 ± 3.1	26.3 ± 2.1	26 ± 2.3
	Flow event 3	24.0 ± 4.8	30.1 ± 4.9	16.2 ± 3.3	32.7 ± 2.5
Organic matter	Flow event 1	3.11 ± 1.1	2.19 ± 1.2	1.75 ± 0.2	1.08 ± 0.7
(g m^{-2})	Flow event 2	2.03 ± 0.3	2.84 ± 1.8	1.19 ± 0.4	0.39 ± 0.06
	Flow event 3	2.28 ± 1.2	1.13 ± 0.7	1.02 ± 0.2	0.63 ± 0.1
Particle size	Flow event 1	88 ± 29.4	45 ± 19.3	44 ± 22.0	21 ± 13.4
(µm)	Flow event 2	189 ± 62.4	50 ± 12.8	52± 16.1	28 ± 9.7
	Flow event 3	75 ± 21.7	67 ± 29.1	61 ± 11.9	23 ± 11.0

6.3.4 Phosphorus accumulation rates of the Cox Creek wetland

The phosphorus accumulation rates (PAR) in the deposited sediments were highest at the inlet sites of Pond 1 (Figure 6.6 and Table 6.2) due to the highest sedimentation rate (see Figure 6.4) and the highest TP concentration (see Table 6.1). Although there was a 50% reduction of the PAR in flow event 1 from inlet to outlet, the outlet showed higher PAR in flow event 2 than in flow event 1 (Figure 6.6). There was only a 6.7% reduction of the PAR in flow event 2 from inlet to outlet due to equal sedimentation rates (see Figure 6.4). The lowest PAR (0.4 ± 0.06 g P m^{-2} day^{-1}) was found at the outlet of Pond 1 during flow event 3 (Figure 6.6), which was driven by the sediment being deplete of TP (Table 6.1). In Reed Bed, the levels of PAR also revealed significant changes between the inlet and the outlet sites (Figure 6.6 and Table 6.2). It was found that PAR in flow event 1, flow event 2 and flow event 3 decreased 60%, 75% and 50%, respectively from inlet to outlet. There were siginificant differences between site and flow event (Table 6.2, $p < 0.0001$), with PAR dependent upon the flow event (Table 6.2; $p < 0.0001$).

The annual phosphorus accumulation rate (PR_{accum}) was highest in 2004 and was lowest in 2006 (Figure 6.7 and Table 6.3). There was decreasing trends of PR_{accum} from 2004 to 2006, but PR_{accum} showed increasing trends from 2007 to 2009, corresponding with the flow volume (Figure 3.5 in chapter three) within the Cox Creek wetland system.

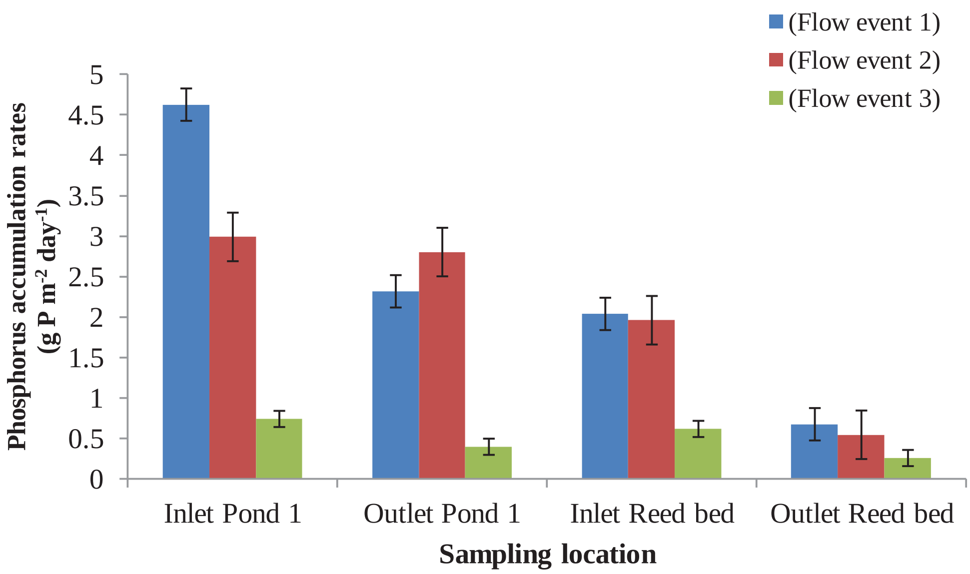

Figure 6.6: Total phosphorus accumulation rate (PAR, g P m^{-2} day^{-1}) at the inlet and outlet of Reed Bed and Pond 1. Flow event 1: 24 September 2009 to 5 October 2009; flow event 2: 7 October 2009 to 16 October 2009; and flow event 3: 19 October 2009 to 28 October 2009. Error bars represent standard errors.

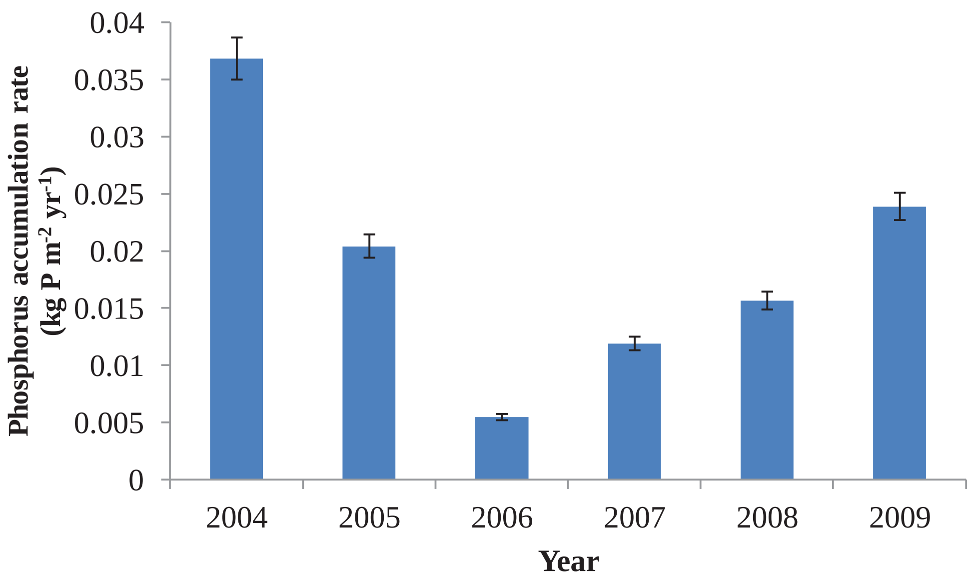

Figure 6.7: Total phosphorus accumulation rates (PR_{accum}, kg P m^{-2} yr^{-1}) of the Cox Creek wetland from the year 2004 to 2009. Error bars represent standard errors.

Table 6.2: *P*-values obtained for the effects of sampling site and flow event (and interaction) on sedimentation rate (SR), P accumulation rate (PAR), total phosphorus (TP), total nitrogen (TN), total carbon (TC), organic matter (OM) and particle size. Interaction effects between these parameters denoted with *. Significant difference are recorded when *p*-value less than 0.05.

Effect	**SR**	**PAR**	**TP**	**TN**	**TC**	**OM**	**Particle size**
Site	0.0071	<0.001	0.0028	0.0030	<0.0001	0.0715	<0.0001
Flow event	0.0062	<0.001	<0.0001	<0.0001	<0.0001	0.2081	<0.0001
Site * flow event	0.0283	<0.001	<0.0001	<0.0001	<0.0001	0.6291	0.0060

Table 6.3: P-values obtained for the effects of years on the annual sedimentation accumulation rate (SR_{accum}) and P accumulation rate (PR_{accum}). Significant differences are recorded when *p*-value less than 0.05.

Parameters	**Years (2004 to 2009)**
SR_{accum}, (kg m^{-2} yr^{-1})	0.0518
PR_{accum}, (kg P m^{-2} yr^{-1})	0.0024

6.4 Discussion

Sedimentation describes a number of processes that affect nutrient retention capacity in wetlands, including settling of organic and inorganic suspended particles and accumulation of heterotrophic and autotrophic organic materials (Gleason and Euliss Jr. 1998; Reddy *et al*. 1999; Harter and Mitsch 2003). The sedimentation rates measured in this study during all the three flow events (Figure 6.4) were within the range of those observed by Fennesy *et al*. (1994) which were between 1.0 and 102.7 g m^{-2} day^{-1} in a constructed wetland in northeastern Illinois, USA and Fernandes *et al*. (2008) which were between 3.3 and 218.5 g m^{-2} day^{-1} in Adelaide's Coastal Reefs, South Australia. The annual sedimentation rates of the Cox Creek wetland system ranged between 1.9 and 2.3 kg m^{-2} yr^{-1} (Figure 6.5) and were lower than demonstrated by Fennesy *et al*. (1994) which ranged between 5.9 and 12.8 kg m^{-2} yr^{-1}.

The inlet of Pond 1 had significantly higher sedimentation rates during flow event 1 (46–300 ML day^{-1}) compared to flow event 2 (31–45 ML day^{-1}) and flow event 3 (16–30 ML day^{-1}) (Figure 6.4). This corresponds to high suspended sediment loads being carried in the water into the wetlands during high flow class (Table 3.2, chapter three). This study suggests that high flow events entering the stream have higher stream competence and can carry greater amounts of suspended particles (e.g. resuspension and redeposition) than low flow events. On the other hand, the sediment accumulation rate calculation based on measuring the inlet and outlet of both ponds showed that 12 to 41 percent of sediment mass flowing into the wetlands was trapped within the wetlands. Higher sedimentation rates were observed at the inlets suggesting that more sedimentation as the water first enters the wetlands resulting from low flow velocity from the creek to the wetland and a higher particle concentration that decrease by sedimentation as water travels through the wetland. The outlets of both ponds were characterised by the deposition of fewer larger sediment particles and had the lowest rates of sedimentation (Figure 6.4) possibly due to less suspended particles in the water leading to decrease deposition of nutrients.

The chemical characteristics of the Cox Creek wetland system sediments are influenced by previous agricultural activities which originated primarily from fertiliser applications (Ingleton 2003; Fisher 2005; Bradley *et al*. 2007). When flooded, the majority of nutrients in soils can be released as soluble forms and soil loss from market gardening, thus affecting the nutrient dynamics within the wetlands. The ratios of TC to TN are commonly used as a measure of the degree of decomposition, with lower ratios value indicating greater decomposition (Moore and Ramamoorthy 1984; Krull and Skjemstad 2003). Microbial residues with lower TC to TN ratios tend to accumulate during decomposition, further decreasing overall TC to TN ratios (Wetzel 1984; Baldock *et al.* 1992; Elser and Foster 1998). In this study, a comparison of TC to TN ratios of both wetland sediments revealed that those sediments at the inlets were lower than those of the outlet (Table 6.1). In addition, this study suggests that sediment particle size is probably more important than decomposition, which might have different TC to TN ratios, and so this could shape the sediment characteristics.

In general, the ratios of TN to TP were well above the Redfield ratio of 16 (Reynolds 1997). As for the ratios of TC to TN, the ratios of TN to TP in both wetland ponds were lower at the inlet than those at the outlet, suggesting a decrease of TN throughout the wetland (Table 6.1). It is possibly due to microbial-driven denitrification under anaerobic conditions, resulting in loss of N through the wetland (Patrick 1982; Reddy *et al*. 1989; Pardue and Williams 1995; Kadlec and Knight 1996). On the other hand, the ratios of TN to TP were considerably lower in Reed Bed than in Pond 1 (Table 6.1) possibly due to uptake of soluble P by macrophytes and subsequent trapped or incorporated into vegetation (Hupp and Bazemore 1993; Reynolds 1997; Craft and Casey 2000; Braskerud 2001).

Higher P accumulation rates in Pond 1 are likely to be the result of greater sediment depositions and nutrient loadings than in Reed Bed (Figure 6.6). These findings suggest that the presence of vegetation (Reed Bed) did not enhance sedimentation rates, as expected as vegetation can reduce flow velocity and turbulence as well as increase particle sedimentation (Harlin *et al.* 1982; Carpenter and Lodge 1986; Stevenson *et al.* 1988; Braskerud 2001). Even though vegetation may increase particle sedimentation, macrophytes may also have adverse impact on P removal where vegetation patterns can lead to preferential flow patterns in constructed wetlands (Johnston 1991; Bowmer *et al.* 1994), resulting in reduction of sedimentation capacity. In addition, the retention rates would also change as the depth decreased (Bartsch *et al.* 1996; Braskerud 2001). The ability of P bound to fine textured sediments (e.g. clay) may also facilitate P accumulation in Pond 1 by the adsorption of inorganic compounds (Søndergaard *et al*. 2001; Kisand and Nõges 2003).

In summary, sedimentation traps were successfully used to determine the rates of sedimentation and phosphorus accumulation associated with deposited sediments during three different flow events. Although materials captured in this study reflected only three major flow events, it can give an approximate estimation for the assessment of the contribution of sedimentation processes to the nutrient budget. Based on measurement of suspended sediment loads collected from monitoring data over six years (Table 3.2, chapter three), an average sedimentation accumulation rate of 2.2 kg m^{-2} yr^{-1} was recorded in the Cox Creek wetland system. Therefore, the sediment accumulation of 7.9 cm per year was estimated in the wetlands for sediment deposition, and was higher than that found by Fennesy *et al*. (1994) which were between 0.5 and 1.0 cm per year. The high sediment accumulation might be due to internal autochthonous production of organic matter and resuspension. Estimated amount of sediment accumulation of 7.9 cm per year suggested the Cox Creek wetland system would retain sediment for another 19 years, based on the average water depth of 1.5 m (Fisher 2005).

Chapter seven

7 General discussion

7.1 Partitioning phosphorus removal

Wetlands are considered amongst the most biologically productive ecosystems in the world (Kadlec and Knight 1996; Mitsch and Gosselink 2000) and host a range of biotic components (e.g. plants, animals and microorganisms) that interact with, and are influenced by abiotic components (e.g. water, soil and air). Anthropogenic landuse modification has modified hydrology and accelerated the transport of contaminants from catchment to the receiving water bodies. Furthermore the application of fertilisers has increased nutrient concentrations in aquatic systems that can lead to problems with eutrophication and excessive algal growth. Constructed wetlands are viewed as a mechanism to slow the flow and arrest the transport of nutrients, thereby improving water quality (Mitsch and Gosselink 2000; Tao *et al*. 2006; Ghosh and Gopal 2010; Huang *et al.* 2010).

Cox Creek wetland was constructed to provide storage, transformation, decomposition and reconstitution of nutrient and organic matter through the activities of aquatic plants, animals and other organisms as illustred in the conceptual model of Reddy *et al*. (1999) (Figure 1.1, modified). Given that constructed wetlands provide abundant colonisable substrata, particularly macrophytes and sediments, they have the ability to host biofilms and act as nutrient sinks (Mistch and Gooselink 2000; Sharpley and Tunney 2000; Moreno-Mateos *et al.* 2009; Zhang *et al.* 2010).

The aim of this work was to determine how well the Cox Creek wetland functioned as a system for phosphorus removal. This was addresssed by determining the phosphorus budget for the wetland and conducting targeted experiments to attribute phosphorus loss (or gain) to the various processes. The nutrient budget and candidate processes are summarised in Figure 7.1. During the period 2007-2009 the annual load of nutrients to Cox Creek wetland was 450.8 kg yr^{-1} and the annual load exiting the system was 169.2 kg yr^{-1}. From the nutrient mass balance it is evident that the wetland is retaining phosphorus at a rate of 281.6 kg yr^{-1}. Sedimentation, P adsorption on sediment and P uptake and storage in plants were measured to be 90.1, 43.5 and 36 kg yr^{-1}, respectively. There is a further loss of phosphorus of approximately 112 kg yr^{-1}, that is as yet unaccounted but several candidate processes are proposed in the next section.

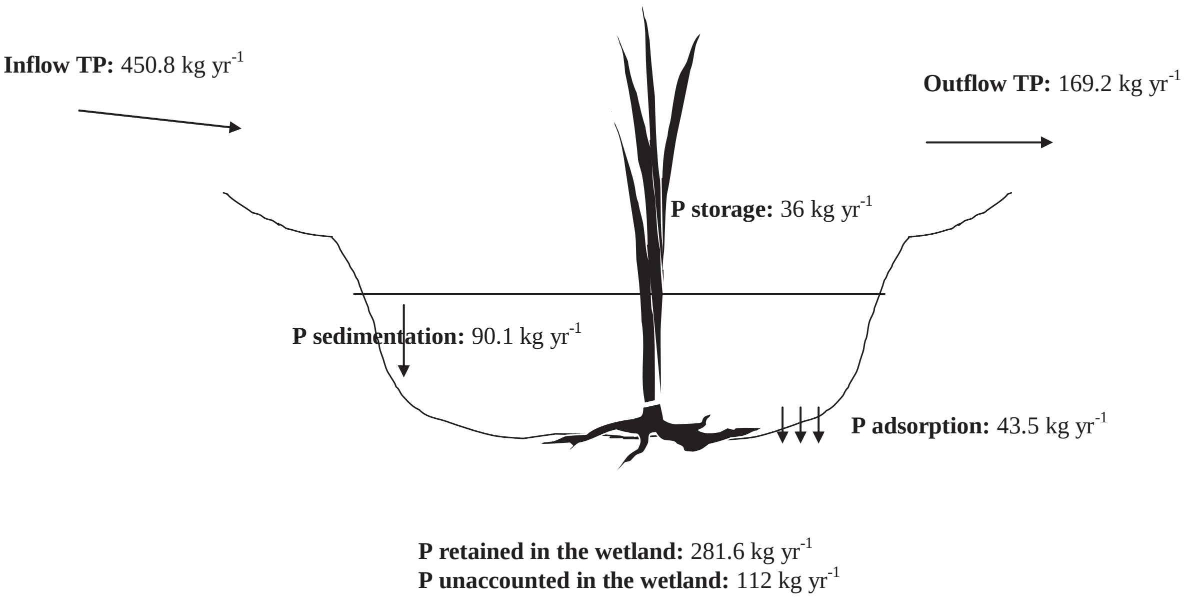

Figure 7.1: Conceptual model of phosphorus mass balances in the Cox Creek wetland system. Results were determined using the average of P inflow-outflow from 2007 to 2009.

7.1.1 Nutrient loading and hydrology

The greatest P inputs to the wetland derived from the upper Cox Creek sub-catchment occured during high flow events (46-300 ML day^{-1}) (Table 3.2). In the low flow periods (0-1 ML day^{-1}, 2-5 ML day^{-1} and 6-15 ML day^{-1}) between the year 2007 and 2009, these inputs were estimated to deliver lower nutrient loads to the wetland. It was found that the Cox Creek wetland acts as an effective P sink under variable flow conditions (Table 3.4). Between the year 2007 and 2009, an average of 281.6 kg yr^{-1} of P inputs were retained (Figure 7.1). High flows also correspond to the highest loads of SS and highlight the importance of particulate removal/sedimentation as part of a phosphorus removal in wetlands. As high flows contribute the highest loads this highlights that effective removal of nutrients relies upon sufficient residence time in the wetland, in which an average of 122 ML of water were retained during high flow events (chapter three).

7.1.2 Contribution of macrophytes

Nutrient uptake and storage by macrophytes may be a dominant removal mechanism in constructed wetlands (Breen1990; Rogers *et al.* 1991; Wigand *et al*. 1997; Karjalainen *et al*. 2001). In chapter four, it was demonstrated that macrophytes contributed significantly to phosphorus and nitrogen storage. Furthermore the basin containing macrophytes (Reed Bed) stored more nutrients than the basin without macrophytes (Pond 1) (Table 4.4). Nutrient concentration in above ground and below ground biomass of *S. validus* and *P. australis* showed distinct seasonal patterns, which indicated that the nutrient uptake by these emergent macrophytes occurs mainly during the growing season. In fact, vegetation nutrient concentrations tend to be highest in the early growing stage and decrease as the plant matures and senesces (Boyd 1970; Bernard and Solsky 1977; Kadlec and Knights 1996). Therefore nutrient uptake generally had a positive impact on the removal of nutrients in the Cox Creek wetland system, however, vegetation removal may be considered in the future to remove nutrients before plants senesce. The seasonal biomass and nutrient storage by the two dominant species (*S. validus* and *P. australis*) suggests that the best timing for harvesting is in mid summer (chapter four). Plant harvesting will prevent nutrient recycling after the growing season in autumn and winter when macrophytes senesce (Suzuki *et al.* 1989; Haberl and Perfler 1990).

7.1.3 Contribution of sediments

Sediments are key components of wetlands for P retention (chapter five). Strong interactions between P and wetland sediments determine the fate and mobility of P in the wetlands (White *et al*. 2000; Walling *et al*. 2003; Lopez *et al*. 2009). The nature and type of sediment, the chemical composition and the cation exchange capacity of the soil play important roles in the retention and conversion of phosphorus and other pollutants (Baldwin *et al*. 2000; Webster *et al.* 2001). The results from the laboratory batch experiments revealed that sediments of Pond 1 had higher P contents but had less capability to adsorb P from the water column than sediments of Reed Bed (chapter five). Therefore, it can be concluded that Reed Bed sediments have a higher P adsorption capacity than Pond 1. Implications of this are that sediment characteristics may vary depending upon the position of the basin in the wetland complex and the vegetation that it contains. When wetland sediments exceed their capacity to adsorb additional phosphorus, the wetland becomes less effective as a barrier to phosphorus transport. Continual renewal of sediment from inflows may increase the P-binding capacity but removal of sediment may be necessary to increase the longevity of the wetland as a P-removal system (Fisher *et al.* 2008).

7.1.4 Contribution of sedimentation

Little research has been conducted on sedimentation processes in constructed wetlands (Brueske and Barrett 1994; Fennessy *et al*. 1994; Braskerud *et al*. 2000; Braskerud 2001). Some studies in lakes and coastal estuaries concluded that sedimentation promotes nutrient retention (Craft and Richardson 1993; Douglas *et al.* 2000; Lopez *et al.* 2009). For instance, low water flow can cause wetlands to retain suspended sediments and adsorb nutrients and other chemicals to sediments (Phillips *et al.* 1994). This study has shown that P sedimentation in the Cox Creek wetland reduced the amount of phosphorus flowing downstream by 90.1 kg P yr^{-1}, which is almost twenty percent of the total P load entering the Cox Creek wetland from the catchment (Figure 7.1). The lower capacity of sediments around the inlet to take up P may be due to higher sedimentation of P at the inlet, and greater uptake of dissolved phosphorus thus decreasing the availability of sorption sites.

7.1.5 Conceptual model of phosphorus mass balance

The conceptual model of phosphorus mass balance provides a basis for management of the Cox Creek wetland system (Figure 7.1). With the current configuration of the Cox Creek wetland system approximately 65 percent of influent P was retained in the wetland. To enhance the P-retention performance of this wetland a number of individual processes could be expanded or optimised.

The design of the Cox Creek wetlands has considered the flow paths, surface area and aquatic vegetation to facilitate sedimentation, nutrient uptake by plants and adsorption to sediments (Fisher *et al.* 2008). Slowing down the flow has dual benefits of allowing fine suspended sediment to settle out (Stubbs *et al.* 2004; Fisher *et al.* 2008), and allowing time for dissolved nutrients to adsorb to sediments. Accumulation of organic clay in sediments is the characteristic of many wetlands that is ultimately responsible for P adsorption (Wen 2002). While this adsorption is temporary and influenced by pH and redox potential, sediments act as sink for P which leads to P burial. On the other hand, P uptake and accumulation in plant material can also lead to P removal.

Dissolved forms of phosphorus are typically more difficult to remove from the water column than particulate forms. To further improve water quality within this wetland, future management initiatives may directly target the transport of dissolved P. One possible option may be to extend the reed bed area in order to increase macrophytes and algal uptake. To maintain good sediment P adsorption, sediment replacement or modification might be possible to increase the adsorption of P and to rejuvenate the wetland system.

Providing a rigorous quantitative description of the inputs, outputs and internal cycling of P in the wetland system enables evaluation of where P removal occurs and where there is opportunity for improvement. Even though this thesis examined what were considered to be the main processes of P retention in the Cox Creek wetland system, there is a phosphorus removal that is not explained by these processes (Figure 7.1). The understanding of P transfer to biofilms and microbial consumption in the conceptual model of this project is limited.

7.1.6 Reconciling the nutrient budget

P uptake by macrophytes, sediment adsorption and sedimentation have been quantified for the Cox Creek wetland. However, a phosphorus loss of 112 kg P yr^{-1} remains unaccounted (Figure 7.1). This could be because a major process was not examined or there were errors or invalid assumptions in the calculation of the mass balance. Several possibilities to explain the unaccounted phosphorus loss are postulated below:

i The contribution of biofilms for P uptake was ignored in the mass balances calculations. Nutrient uptake by biofilms in two selected streams of the Torrens River Catchment, South Australia (Aldridge *et al.* 2010) which have similar environment (e.g. climate, soil, topography) may be applicable to estimate the lost of P in this wetland. Using the same biotic uptake rate (K_B) of 0.03 hr^{-1} found by Aldridge *et al.* (2010), an estimation of 32.6 kg P yr^{-1} of P uptake by biofilms could be possible in Cox Creek wetland when correlated with the FRP concentration (as PO_4^{3-}) in the water column. This suggests that P uptake by biofilms may also be important for P retention in the wetland due to their high nutrient affinity and rapid response to nutrient inputs (Scinto and Reddy 2003; Aldridge *et al.* 2010).

ii Limited coverage of deployed sediment traps: Due to shallow water depth (an average of 1.5 m), relative to the orifice of the sediment trap (0.5 m above sediment), the overall quantity of uncaptured particles in each sediment trap was approximately 33% of the total sediment depositions. If the loss of these particles was included in the mass balances, sedimentation could attribute another 44.4 kg P yr^{-1} for the entire wetland.

iii The assumption made for the sedimentation rates and phosphorus accumulation rates in the lower flow rate class may be incorrect (chapter six). Since this study only measured three major flow events, rates of sedimentation in the lower flow class was assumed to be half of the flow event 3, resulting in lower total amount of mean annual sedimentation rates. Improvements to the estimation of sediment deposition could be made with a more highly resolved temporal and spatial sampling of sedimentation.

7.2 Implications for water quality control and management strategy

There is a strong interest in the control of P pollution in agricultural watersheds (Behrendt and Opitz 2000; Ekholm *et al*. 2000; Arnscheidt *et al*. 2007; Billen *et al*. 2007; Whiters and Jarvie 2008). Constructed wetlands are considered as effective option to control non-point sources of phosphorus (Kadlec 1997; Richardson 1999). This study had been a contribution to improve knowledge on nutrient retention processes (particularly phosphorus) in the Cox Creek wetland system in which macrophytes uptake, sediment adsorption and sedimentation were emphasised.

Phosphorus in runoff from agricultural land area is an important component of non-point source of pollution and can accelerate eutrophication processes in downstream lakes and rivers. As for the Cox Creek sub-catchment, P inputs to the stream depend on land use and P management within the catchment. The large agricultural land use causes high P supply to the wetland. Therefore management of P loads in this catchment needs to address the sustainable use of P fertilisers.

The ability of the Cox Creek wetland system to reduce P loads can provide long term retention of P before the stream enters the downstream reservoir, Mount Bold. This study quantified the water quality improvement that can be expected from the wetland as a whole (chapter three), the P storage by wetland plant (chapter four), the sediment P sorption capacity (chapter five) and the sediment accumulation rates (chapter six). Approximately 65 percent of phosphorus entering the wetland is retained within the wetland, contributing significantly to improving downstream water quality. Further examination of phosphorus uptake by biolfilms would be beneficial to wetland management and help reconcile the nutrient budget.

7.3 Future research recommendations

The basis of future planning and management of the Cox Creek wetland system should take into consideration long-term responses to P retention capacity so that it remains viable and productive. In particular, information on factors that determine the P retention and transport still needs to be determined. Further work is required to follow up the observations and hypotheses made in this study following these suggestions for future research. This includes but is not necessarily limited to:

i. Ongoing monitoring of the nutrient concentrations in the water column, sediment and macrophytes to better understand how nutrient transformation may change as the wetland matures and inform management such as macrophyte harvesting.
ii. Determination of the relative contribution of biological processes on P utilisation and chemical transformation, particularly by biofilms that may be comprised of microorganisms, periphyton and phytoplankton.
iii. Assessment of how sediment loading and sedimentation rates may vary seasonally to better understand the contributions of sediment P transport and deposition for better control of P movement within the wetland.

7.4 Conclusion

This study aimed to quantify important processes contributing to P retention in the Cox Creek wetland system (Figure 1.1) to guide management and assess wetlands as a mechanism for controlling phosphorus from non-point sources in agricultural catchments. The relative contributions of important processes were quantified (Figure 7.1), and although there is still unaccounted P in the mass balance, it is evident that sedimentation, uptake by macrophytes and sediment adsorption are all important in P removal. Wetland design should include a variety of pond structures that promote these processes to maximise opportunity for P removal.

Although the Cox Creek wetland system retains approximately 65 percent of incoming P, the need for future remediation strategies should incorporate catchment management to target diffuse source pollution. Therefore any potential management option that could minimise P availability at the source should be considered. Such strategies include balancing fertiliser application to crop requirement, maintenance of riparian zones in water courses and soil ameliorants to retain P on catchments (House *et al.* 1999; Wen 2002; Stubbs *et al.* 2004; Fisher *et al.* 2008).

In conclusion, it is clear that the Cox Creek wetland system plays an important role in reducing phosphorus loads to downstream water bodies including Mount Bold reservoir and investment in similar systems elsewhere will pay dividends with careful design and process optimisation.

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